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Review (Special Column on Progress in Catalysis in China during 1982–2012)

Progress in catalysis in China during 1982–2012: Theory and technological innovations

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ABSTRACT

The development of catalytic science and technology in China dates from the early 20th century. In the beginning, the efforts of our predecessors gave an initial period of steady development. Then in the 1960s, there were serious obstacles by human factors during which the development of catalysis was stagnant and we lost more than ten years of development opportunity. In the 1980s, catalysis in China entered a period of rapid expansion. During this period, three main research sectors, namely, Chinese Academy of Sciences (CAS), universities, and industries, were rapidly established and development recovered. Researchers carried out research using reaction kinetics as the main method and means. In basic research, the discovery of novel catalytic materials, characterization methods, and novel catalytic reactions were the main research directions. The introduction of surface science and nanoscience has greatly promoted and deepened the basic exploration of catalysis. Catalysis is now changing from an art to a science. In different historical periods, researches in applied catalysis were determined by national needs and these have made notable contributions to many fields, such as the optimal utilization of coal, petroleum and natural gas, advanced materials, and protection of environment as well as human health. Currently, China has begun contributing to important progress in catalysis and is moving towards becoming a regular contributor.

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1. Introduction

Since the People's Republic of China was founded, its catalytic research teams have been positioned in three main sectors, namely, Chinese Academy of Sciences (CAS), universities, and the research institutes of the industry. The older generation of scientists, such as Zhang Dayu, Cai Liusheng, Cai Qirui, Yu Zuxi, and Min Enze et al., are the representative figures of these sectors. During the Cultural Revolution, research teams suffered from severe damage to facilities, incomplete and obsolete instruments, temporary shortage of young scientists, and lack of research funding [1–3]. Since the reform and opening-up policy was introduced in the 1980s, CAS, Commission of Education, and Science & Technology Commission have orga-

nized and established many high level catalytic research teams, such as State Key Laboratory of Catalysis led by Guo Xiexian, Xin Qin, Xu Yide, Xiong Guoxing et al. and Dalian Institute of Chemical Physics (DICP), CAS led by Lin Liwu, Li Wenzhao, Wang Hongli, Zheng Lubing et al., State Key Laboratory of Physical Chemistry of Solid Surfaces, Xiamen University led by Cai Qirui, Wan Huilin, Zhang Hongbing et al., State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, CAS led by Peng Shaoyi, Zhong Bing, Chen Songying et al., State Key Laboratory for Oxo Synthesis and Selective Oxidation, Lanzhou Institute of Chemical Physics, CAS led by Li Shuben, Yin Yuanqi, Wang Hongli, Chen Yingwu, Shen Shikong, Kou Yuan et al., Changchun Institute of Applied Chemistry, CAS led by Wu Yue, Xie Xiaofan, Zhang Manzheng et al., teams at Fudan University

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led by Deng Jingfa, Gao Zi, Zheng Sheng'an, Li Quanzhi et al., teams at Perking University led by Pang Li, Li Xuanwen, Xie Youchang, Lin Bingxiong et al., teams at Nanjing University led by Chen Yi, Xu Qinhua, Yan Qijie et al., teams at Jilin University led by Cai Liusheng, Zheng Zuoguang, Ding Yingru, Zhen Kaiji, Wu Tonghao et al., teams at Zhejiang University led by Jin Songshou, Zheng Xiaoming, Shen Zhiquan et al., teams at Tsinghua University led by Zhu Qiming et al., teams at Tianjing University led by Zhang Liu, Zhao Jiusheng, Qin Yongning, Zhong Shunhe et al., teams at Nankai University led by Li Hexuan, Xiang Shouhe, Tao Keyi et al., teams at Dalian University of Technology led by Wang Xiangsheng, Cai Tianxi, He Ren, Jin Zilin et al., teams at Zhejiang University of Technology led by Liu Huazhang et al., teams at South China University of Technology and Sun Yat-Sen University led by Huang Zhongtao, Zeng Shaokui et al., teams at East China of Science and Technology led by Wang Ren, Li Chenglie et al., teams at Fuzhou University led by Wei Kemei, Fu Xianzhi et al., SINOPEC Corp Research Institute of Petroleum Processing led by Min Enze, Li Dadong, He Mingyuan, Wang Xiqing, Shu Xingtian et al., Shanghai Research Institute of Petrochemical Technology led by Zhang Shi, Guan Xingya, Chen Qingling et al., SINOPEC Fushun Institute of Petroleum and Petrochemicals led by Hu Yongkang, Han Chongren et al., SINOPEC Beijing Research Institute of Chemical Industry led by Mao Bingquan, Liu Xinxiang, Yang Yuanyi et al.

The establishment of SINOPEC Corp and National Foundation of China further promoted the development of catalytic science and technology in China. The reestablished postgraduate education policy gave personnel training that cultivated many elite scientists in the catalytic field. With the meticulous planning and efforts of these academic leaders, Chinese catalytic research teams have collaborated widely with international research groups. Many researchers were sent abroad to study advanced technologies. Among them, a considerable number have become the elites in developed countries all over the world.

In order to participate in the international academic arena of catalysis, Chinese scientists in catalysis have actively participated in and host international meetings. China has hosted the China-Japan-America Congresses of Catalysis (that developed into the Asia Pacific Congress of Catalysis), International Conference of Spillover, and International Conference on Catalysis in Membrane Reactors. In addition, many bilateral and multi-lateral cooperation projects in science and technology have been signed with Japan, countries in Europe, USA, and Russia.

Since petroleum resources were becoming increasingly scarce, Li Wenzhao et al. proposed the project entitled "Conversion of Natural Gas", which was included in the 8th Five Year Plan. In order to get more research fundings, attract academic proposals and develop talents, Guo Xiexian, Cai Qirui, Peng Shaoyi, Min Enze, Chen Yi et al. proposed the national "summit climbing" project entitled "Optimal Conversion of Natural Gas and Refinery Gases", which was sponsored by the National Science Foundation of China and SINOPEC. At that time, this project was the biggest State key project in catalytic research. Its research topic was also the theme for a quite long

period of time in China. After that, the development of catalytic science and technology was well supported in the 9th Five Year Plan, the National Key R&D Programs, 973 and 863 programs, etc. During this period, many mainstream journals of catalysis were launched (or resumed publishing), including *Chinese Journal of Catalysis*, *Journal of Molecular Catalysis (China)*, *Journal of Fuel Chemistry and Technology*, *Natural Gas Chemistry*, *Acta Petrolei Sinica*, *Petroleum Refining and Petrochemicals*, *Industrial Catalysis*, *Petrochemicals (China)*, and so on. The Catalysis Society of China and its Standing Secretariat were established. The National Catalysis Award and National Catalysis Prize for Young Scientists were set up. In 2010, an additional award for scientists below 35 years old, the National Catalysis Award for Excellent Young Scientists, was also established. In addition, the Chinese National Conferences on Catalysis were held biannually. Until now, there have been 14 conferences. The number of participants has increased from the previous hundreds to more than 1500 now. This conference promotes the exchanges of academic works and technology. At present, we have set up substantial international cooperation with the major catalytic powers and powerful countries. Chinese catalytic scientists serve as editorial members and international advisors in almost all the international mainstream journals of catalysis. The Secretariat of the Asia-Pacific Association of Catalysis Societies is located in China. As the representatives of Chinese Catalysis Society, Cai Qirui, Guo Xiexian, Chen Yi, He Mingyuan and Li Can have been members of the International Association of Catalysis Societies Council. In 2004, Li Can was appointed as the vice president of the International Association of Catalysis Societies, and as president in 2008. This was the first time that a Chinese catalytic scientist was appointed to be the president of the International Association of Catalysis Societies. It indicated that catalytic research in China is receiving more attention from international catalytic scientists. The above measures as well as the efforts in pursuing excellence and the dedication of the older generation of catalytic elites laid the foundation for the current state of Chinese catalysis.

2. Basic research in catalysis

2.1. Exploration of catalytic theory

In the 1980s, a benefit from the reform and opening-up policy was that through the national and international exchanges and cooperation, Chinese scientists in the catalytic field were exposed to the novel ideas of catalytic theory in the world, and the attention paid to the development of new materials, reactions and characterization methods. Dr. Zhang Dayu [4,5] proposed the concept of surface bonding. Based on many years of industrial catalyst research experience, he proposed "Catalysts Library" and elaborated on the role of catalyst transplant in the R&D of industrial catalysts. Next, Chen Rong and Guo Xiexian et al. [6] published the relationship between the coverage in chemisorption and kinetics. They considered that empty active centers also played an important role in activating reactant molecules. Later on, Guo Xiexian et al. [7] investigated a concerted exchange mechanism of adsorption and desorption,

namely, the AAD mechanism, which included the interactions between adsorbed molecules and active centers. Cai Qirui, Wan Huilin et al. [8,9] systematically studied the intermediates and mechanism of the conversion of synthesis gas to ethanol, as well as the active oxygen centers in the oxidation of lower alkanes. Peng Shaoyi et al. [10] proposed that ultrafine particles of catalyst played an important role in explaining the product distribution of carbon monoxide hydrogenation and in preparing a deoxidizer for inert gas. Min Enze [11,12] directed oriented basic research of new catalytic materials, reactions and reaction engineering, including amorphous alloys and nano molecule sieves, which laid the foundation for the technologies of oil refining and petrochemical catalyst preparation. At the same time, he also guided the development of a set of green technology for the synthesis of caprolactam, the monomer of chemical fibers. For his many contributions to oil refining and petrochemistry in China, Min Enze was awarded the National Catalysis Award and 2007 State Science and Technology Top Awards. He was acknowledged as the leading authority in the catalytic field of China. Following Min Enze, Lin Liwu was awarded the National Catalysis Award in recognition of his contributions with the successful industrial applications of his research on the catalyst active phase and its modifications in the processes of hydrocarbon reforming, hydrocracking and long-chain alkane dehydrogenation. Wu Yue et al. [13–15] systematically and thoroughly investigated the structures of active centers in oxides and composite oxide catalysts and developed the interaction models. Zhou Wangyue, Yin Yuangen and Li Shuben et al. studied oxidative dehydrogenation reaction of butylene to butadiene in order to meet the current needs of the country. The W-Mn-SiO₂ series of catalysts, developed by Li Shuben et al. [16,17] for methane oxidative coupling to alkene, were among the best catalysts in the world and received attention from other scientists at that time.

Cai Qirui, Zhang Hongbing et al. [18] investigated the formation of amine by nitrogen fixation catalyzed by nitrogenase and a Fe catalyst, as well as the preparation of carbon nanotubes. Wu Hua, Yuan Quan, and Zhu Baolin et al. [19] developed the engineering design basis of catalyst particles, and the non-uniform activity distribution of catalyst pellets. Tang Youqi and Xie Youchang et al. [20] first discovered and systematically studied monolayer dispersion phenomenon on the surface. Chen Yi et al. [21] proposed the embedding model of oxide catalysts and systematically studied the preparation of oxide catalysts. Liang Juan, Li Hexuan, Xu Qinhua, Gao Zi, Lin Bingxiong, and Pang Wenqin et al. investigated the structure, surface acidity, catalytic activity, and preparation of nanoporous zeolites. Deng Jingfa et al. [22] intensively studied the surface oxygen species of amorphous Ag catalysts. Liu Hanfan investigated the synthesis and catalytic activity of polymer-stabilized metal nano-clusters. Shen Zhiquan et al. [23–26] applied rare earth catalysts to the synthesis of polymers. They investigated oriented polymerization by rare earth catalysts and proposed rare earth compounds as the components of the catalysts for the oriented polymerization of dienes. They also developed a series of Ni ternary alloy catalysts used in the Z-N reaction to synthesize butadiene rubber. This is the basis of the polymerization

technology for the synthesis of millions of tons of butadiene rubber in China. They expanded the application of rare earth coordination catalysts to other research areas, including the polymerization of alkynes, epoxy alkanes, epithio alkanes, lactide and lactone, and polar monomer, as well as the preparation of polycarbonate by the fixing carbon dioxide method. Xin Qin and Sun Gongquan et al. [27–33] first applied multiwalled carbon nanotubes as the support of cathode catalysts for direct methanol fuel cells. They developed the EG method to prepare multi-metallic catalysts with high loadings. By using high resolution transmission electron microscopy, they further investigated the effect of particle size, loading and morphology on the performance of cathode catalysts. These innovative achievements were from the combination of catalytic technology and fuel cells cathode technology. The publications have been cited numerous times by national and international scientists. By comparing multi-walled carbon nanotubes and carbon black, Xu Boqing et al. [34,35] found that single-walled carbon nanotubes as the support of Pt electrocatalysts significantly improved the stability and activity of the catalysts, which provided new ideas to develop nano-noble metal catalysts with low loadings. Using nano-synthesis technologies (such as tailoring of carbon nanotube, assembly of metal catalysts in carbon nanotubes, and the preparation of Pt/FeO catalysts and modification technologies) and high resolution transmission electron microscopy, Bao Xinhe, Pan Xiulian, Fu Qiang et al. [36,37] investigated the effects of nano-particle size, morphology, composition and microenvironment on the activity of catalysts. In addition, in combination with DFT computations, they proposed the concept of the confinement effect, which explained well the experimental results. Shen Wenjie et al. [38] synthesized nanorod-shaped Ce₃O₄ and developed the morphological control technology of oxide catalysts. Zhao Tao and his group [39] first prepared a single atom Pt catalyst on Fe₂O₃. Using the oxidation of carbon monoxide as the probe reaction, they found that the activity of the single atom Pt catalyst was higher than that of a nano-Pt catalyst under the same conditions. In collaboration with Liu Jingyue and Li Jun, they investigated the structure of single atom supported catalysts by high resolution transmission electron microscopy and DFT computation, and proposed the new concept of single atom catalysis.

2.2. Establishment and application of characterization method for catalysts

The depth of catalytic theory is closely related to modern characterization technologies, computational chemistry, and material science, especially nano-science, developed in the 1990s. In China, catalytic scientists have attached great importance to the development of novel characterization techniques. Using in situ infrared spectroscopic method with double probe molecules, Xin Qin et al. [40–45] investigated sulfided Co-Mo/Al₂O₃ catalyst and discovered H spillover between the Co-Mo active sites. This method can be efficiently used to study the interaction of active centers and the reaction mechanism. It was honored as one of the most important progress in catalysis at the 9th International Congress on Catalysis. They developed

a series of in situ molecular spectroscopic methods, which have been successively applied in hundreds of national and international labs. They have also published six monographs and promoted the popularization of in situ catalytic characterization methods at home and abroad. Li Can et al. developed the UV Raman spectroscopic technique applied in the characterization of catalytic materials. They found that UV-Raman spectroscopy is a very sensitive method to probe the surface phase of a metal oxide. They set up a novel UV-Raman spectroscopic characterization method to identify the active centers on a metallosilicate. They were the earliest group to apply UV-Raman spectroscopy to catalytic research in the world and have made great progress. From their use of UV-Raman spectroscopy, the direct evidence of the titanium framework species on TS-1 zeolite was first reported. They also established an internationally recognized method to identify transition metal atoms in the framework of microporous and mesoporous zeolites by UV-Raman spectroscopy. For the first time, they tracked the synthesis process of a zeolite by in situ UV-Raman spectroscopy. They determined the most important conversion process and active intermediates during zeolite synthesis, and proposed the mechanism of catalytic material synthesis. In addition, they discovered the structural difference between the surface and phases of oxides, especially the photocatalyst, TiO_2 . Based on their UV-Raman spectroscopic study, they proposed the new concept of a photocatalytic activity enhanced by a surface-phase junction. They have contributed to the commercialization of the UV-Raman spectrometer and made the catalytic characterization method by UV-Raman spectroscopy a cutting edge technology in the world. Bao Xinhe and his group [46] and He Heyong and his group [47] have made great progress in applying the in situ NMR technique to investigate catalysts and catalytic reactions (acidity of microporous materials, identification of intermediates, etc.). Ding Yingru, Lin Liwu, Zhang Su, and Shen Jianyi et al. have developed in situ Mossbauer spectroscopy and applied it to the characterization of catalysts [48]. Photoemission Electron Microscopy (PEEM) is a widely used emission microscopy. UV light or X-ray excites the electrons on the solid surface and magnetic electron lenses record the photoelectron emission to generate the image contrast. It is a new technology for in situ and dynamic studies of physical and chemical properties of surfaces, such as surface structure, electronic states, and chemical reactions. This technology has been extensively applied in chemistry, physics and materials. Right now, the space resolution of PEEM is around 20–50 nm. However, most physical and chemical processes on surfaces are carried out at very small space scales, at less than 10 nm. Therefore, the current space resolution of PEEM limits its extensive application. Bao Xinhe and Fu Qiang et al. [49] at DICP first applied and independently developed a deep ultraviolet (DUV) light source in PEEM. Taking advantage of the high energy and high power from DUV, the space resolution of PEEM reached 3.9 nm, which is the best in the world. In addition, the energy resolution also reached 0.102 eV. This system has been successfully used in in situ and dynamic studies of catalysis, materials, and energy fields. The investigation of surface process can be carried out with various temperature and atmos-

phere conditions. In some areas, it has an irreplaceable role. Compared with regular Raman spectroscopy, UV-Raman has the advantages of high sensitivity and it avoids fluorescence interference. In addition, by making use of the UV absorption of many compounds, the resonance Raman spectroscopic characterization technique has also been used in catalysis, materials and life science. Thus, UV-Raman spectroscopy has received more and more attention. Right now, most laser sources are ultraviolet laser light sources with wavelengths above 200 nm. Scientists have pursued the developing of Raman spectroscopy with a short wavelength laser. Sanford Asher et al. developed deep UV-Raman spectroscopy with the wavelength reaching 193 nm, which was used to investigate the secondary structure of proteins [2]. DICP is among the earliest groups in the world to apply UV-Raman spectroscopy in catalysis and material science. By using UV-Raman spectroscopy, many important scientific projects on zeolite materials have been completed. With the support of National Major Scientific Instruments Development Project, scientists at Technical Institute of Physics and Chemistry and DICP developed a 177.3 nm light through the sixth harmonic of 1064 nm in KBBF. By using the 177.3 nm deep ultraviolet (DUV) laser source independently developed by our scientists, DUV collecting mirror through an external optical path and ellipse reflector, as well as a triple-grating monochromator with the spectral response at the DUV of 170–400 nm, they developed the first 177.3 nm deep ultraviolet Raman spectrometer and continuous wave (193–240 nm) resonance Raman spectrometer in the world. The preliminary results of deep ultraviolet spectroscopy applied to semiconductor and catalytic materials have already showed its special advantages. It is expected to play an important role in observing the active centers of wide band-gap semiconductors and zeolites containing Al and Ga atoms. Thus, the deep ultraviolet Raman spectroscopy developed by Li Can and Feng Zhaochi [50] provides a novel tool for the characterization of catalysts. By combining DFT computation and experiments, Fu Qiang, Li Weixue, and Bao Xinhe et al. [36,51,52] investigated the catalytic mechanism of nano oxide-metal systems. They found a strong interaction at the interface between Pt and FeO nano-islands, in which a coordinately unsaturated Fe species showed a high activity and stability in CO oxidation at low temperature. After the paper was published, C&E news, Chemistry World, and Science Foundation in China published a topic report entitled “The Dream of Catalyst Design may arrive”. This achievement has important heuristic value in optimizing catalyst design and developing catalytic basic theory. The selectivity in syngas conversion is one of the most challenging projects in heterogeneous catalysis. The major problems include the activity of carbon monoxide, growth of the carbon chain, formation of oxide and catalyst deactivation, and so on. Using DFT computation method and Rh and Co catalysts, Li Weixue et al. investigated the formyl radical as the most important intermediate in syngas conversion reaction. They found that the formyl radical is an important intermediate not only for the formation of oxides, but also for the growth of the carbon chain. This result amended and supplemented the mechanism of syngas conversion, which was accepted as occurring by oxide for-

mation through the insertion of carbon monoxide, and the carbon chain growth through alkyl coupling.

With a new transition state search method, Li Zhipan et al. [53] developed a theoretical method to calculate the selectivity of the complex reactions in direct ethanol fuel cell applications. Chemical reactions of ethanol on three different Pt surface were explored, including C–C and C–O bond breaking, the breaking order of O–H or C–H bonds on the catalytic surface, as well as the stability of different intermediates. The theoretical results for the first time gave the dynamic priority of ethanol C–H and O–H bond breaking on Pt surface. This explained the selectivity of ethanol oxidation. They also proposed the surface coverage effects of ethanol oxidation and pointed out that Pt(100) is the best facet to fully oxidize ethanol. Parts of the results have been confirmed by experimental results and other theoretical calculations. This discovery changed some basic knowledge obtained from traditional surface science.

At present, characterization techniques, including in situ X-ray, energy dispersive spectroscopy, molecular spectroscopy, NMR and high resolution transmission electron microscopy have been mastered at a high level by domestic mainstream catalytic laboratories. Computational chemistry is also widely used in catalytic studies and there has been a substantial increase in the research level.

2.3. Development of novel catalytic reactions

During the interest in developing the oxidative coupling of methane to alkenes at home and abroad, Wang Linsheng, Xie Maosong, and Xu Yide et al. [54] found for the first time that methane can be directly transformed into arenes and hydrogen over zeolite-supported catalysts in the absence of oxygen. This has received much attention from catalytic scientists. Using further collaborations with Bao Xinhe and Lin Liwu et al., they confirmed that the active centers are the exchanged molybdenum species and proposed the mechanism of the methane dehydroaromatization reaction. Kou Yuan et al. [55] introduced a new concept of the immobilization of heterogeneous catalysts in the liquid phase. The nano-particles are immobilized in an ionic liquid rather than on a surface, which can create three-dimensional heterogeneous catalysts. Fischer-Tropsch synthesis is the key process for the conversion of coal to liquid fuel. With the traditional catalysts, the catalytic efficiency is low. By using nano-metal particles fixed in an ionic liquid as the catalyst, the catalytic efficiency was enhanced ten times in the water phase although the temperature was lower by 100 °C. This achievement has been transferred to industry. Xu Jie et al. [56–59] investigated the catalytic active site of hydrocarbon selective oxidation, organic modification on the catalyst surface and the design of a nitrogenous metal-free catalytic system. Based on these research results, they successfully developed the industrial application of sorbitol conversion to ethylene glycol, cyclohexane oxidization to cyclohexanone and paraxylene oxidization to terephthalic acid. Among these, a non-metal catalytic system was established, composed of *N*-hydroxyphthalimide (NHPI) and quinone derivative, which acts as electron-transfer additives. This is the first organic catalytic system

for hydrocarbon oxidation under mild conditions without a reducing agent and radical initiator. With the use of NHPI (or trace NaBr or Br₂) and a nitrogen-containing cation of 1,10-phenanthroline, acridine yellow, methyl violet and methyl blue, the redox cycle of hydrocarbon oxidation was carried out. The major technical development of a non-metal catalytic system applied to cyclohexane oxidation to cyclohexanone has made great progress. This has successfully passed the industrial application test with a capacity of 70 kt/yr. In 2001, Xi Zuwei group [60] discovered reaction-controlled phase-transfer catalysis for propylene epoxidation with hydrogen peroxide. They developed a tungsten-containing catalyst with both homogeneous and heterogeneous advantages, which provides a novel approach for the difficult problem of the separation of the homogeneous catalysts. The related industrial technique is under development. Li Xianjun et al. [61–64] studied a water-soluble organic metal complex catalytic system. They proposed the metastable micelle-ion pair interaction mechanism in the hydroformylation of alkene under a two-phase condition and theoretically explained the relationship between self-assembly on the surface of the two phases and the highly regioselective hydroformylation of alkene. Ethylene hydroformylation to propionaldehyde and *n*-propanol was also industrialized. Yang Weishen, Xiong Guoxing, and Lin Liwu et al. [65–69] are among the earlier scientists in the world who studied catalysis and separation integration with an inorganic membrane. They synthesized an oxygen permeable membrane, Ba_{0.5}Sr_{0.5}Co_{0.8}Fe_{0.2}O_{3-δ} which had the highest international permeability. Many chemical reactions, such as the selective oxidation of hydrocarbon to syngas and hydrogen, oxidative coupling of methane to ethylene, oxidative dehydrogenation of ethane to ethylene, have been carried out in membrane reactors. Yang Weishen and his group first applied the microwave technique to successfully synthesize defect-free zeolite membranes, which has been used in the dehydration of ethanol and higher alcohols in industry. A novel pervaporation membrane based on a mixed matrix of zeolite nanoparticles is under exploration. It is expected to be applied in the efficient recovery of second generation biofuels (butanol). Yin Yuanqi et al. [70] studied the synthesis, characterization, and catalytic activity of multinuclear metal clusters, which have been applied in asymmetric carbonylation and hydroformylation of olefins in industry. In the world, the first industrial test of formaldehyde conversion to trioxymethylene catalyzed by an ionic liquid was achieved by Xia Chungu and Chen Jing [71,72]. They also applied an ionic liquid to catalyze the cycloaddition of epoxide and carbon dioxide to cyclic carbonate in industry of China. Li Can et al. [73–76] began to investigate solar photocatalytic H₂ production and CO₂ conversion and have made big progress in basic research. They proposed and led the Chinese Academy of Sciences Action Plan for solar energy. In 2008, Zhang Tao and his group [77] first discovered a highly selective catalytic conversion of cellulose to ethylene glycol using a nickel-promoted tungsten carbide catalyst. The cellulose conversion was nearly 100% and ethylene glycol yield was above 61%. The related industrial technique is under development.

2.4. Application and development of novel catalytic materials

The innovation and commercialized integration of an amorphous alloy catalyst and the magnetically stabilized bed reaction technology that included an amorphous alloy catalyst and a magnetically stabilized bed reaction technique was developed by Min Enze and Zong Baoning et al. By converting the crystalline catalyst into an amorphous alloy catalyst, there was an increase in the quality of the hydrogenation properties of Raney Ni. The limitation of the low thermal stability and small specific surface area of the amorphous alloy catalyst was overcome by adding a rare earth element in it to enhance the crystallization potential energy barrier and using the alkaline extraction of Al to synthesize a porous catalyst. After developing the production unit and optimizing the technology, they set up a unit for producing hundreds of tons of the amorphous Ni alloy. The control and amplification of a uniform magnetic field were achieved. In addition, they proposed different production technologies for various reactions. The amorphous Ni alloy has been applied in the process of the purification of caprolactam in place of an imported Raney Ni. With this catalyst, they modified the foreign refining technology of caprolactam oxidation to hydrogenation refining. A Pd/C catalyst is partially replaced by the amorphous Ni alloy in the hydrogenation of benzoic acid. A number of industrial enterprises have used this catalyst to produce pharmaceutical intermediates and for glucose hydrogenation.

Ding Quiling et al. [78–81] developed a novel chiral catalyst prepared through a combinatorial approach and assembly strategy. By systematically combining the concepts of asymmetric activation, chiral poisoning and asymmetric amplification with combinatorial chemistry, they designed and evaluated a chiral catalyst library, and developed several series of novel catalysts with high efficiency and selectivity. They discovered and clarified the effect of asymmetric amplification in the catalytic system, as well as the mechanism and activity of the additive. Based on the theory of molecular assembly, they first proposed the self-supporting concept of chiral catalysts. Several heterogeneous catalytic reactions including carbonyl-ene, oxidation and hydrogenation reactions achieved high selectivity and activity. This approach suggests a new idea for supported chiral catalysts and also provides an efficient way to synthesize the key intermediates of some chiral drugs. Li Can and Yang Qihua et al. [82] studied heterogeneous chiral catalysis quite early in China. They have made important progress in chiral catalytic reactions on a nano-particle surface, the emulsion catalytic systems and the nano-reactor. In particular, by using the space threshold effect of a nano-channel and the modification of the channel microenvironment, chiral catalysts in the nano-channels gave higher enantioselectivity and activity than the homogeneous catalysts. Chiral catalysis on a nano-reactor was realized, which has important impact in international catalytic academia.

The spontaneous monolayer dispersion theory explored by Xie Youchang et al. [83] was widely used in studies of catalysts, adsorbents and nano-materials. A highly efficient adsorbent of CO was produced by dispersing a CuCl monolayer on a zeolite

surface. This achievement made our pressure-swing adsorption separation of CO technology the leader in the world. In addition, they developed a highly efficient adsorbent for the separation of oxygen from air, which was applied in large scale pressure-swing adsorption separation. Our pressure-swing adsorption separation technology has reached an internationally advanced level. Shu Xingtian and He Mingyuan et al. successfully explored the ZRP-1 zeolite. By using a REY zeolite as seed crystal, a ZRP-1 zeolite with the Pentasil structure was directly oriented synthesized from different crystalline sources, containing rare earth and phosphorus. The rare earth stabilizes the framework of the zeolite and maintains the integrity of the lattice structure under hydrothermal conditions, which inhibits or slows the zeolite inactivation process due to dealumination. Introduction of the rare earth element into the ZRP-1 zeolite causes the channel to be much narrower than that of HZSM-5 and creates a secondary mesopore of 4 nm. The secondary mesopores with a larger pore size provide the cracking space for large hydrocarbons in cracking feedstocks, which enhances the conversion of heavy oil. The study of the CHZ (SRNY) zeolite was awarded the second prize of national invention. The discovery of the β molecular sieve and its novel synthesis method were honored with the third prize of national invention in 1999.

The aerospace series of catalysts for the decomposition of hydrazine were developed by Yang Baoshan, Zhou Yeshen, and Zhang Tao et al. over forty years, which solved the problems of spacecraft attitude and orbit control. This is a great leap in space technology [84]. Using composite oxides instead of a metal catalyst, Zhang Tao and his group [85] explored a highly efficient catalyst for the decomposition of hydrogen peroxide of high concentration. Their research expanded the new area of the application of aerospace catalytic technology. Using the catalytic decomposition of hydrogen peroxide as the ejector gas of a chemical laser, they developed composite oxide catalysts that resist oxidization at high temperatures and a cyclic thin-layer reactor for catalytic decomposition. This solves the bed reactant even distribution in the bed and thermal control problems in the large scale engineering applications, and achieved the first engineering application of a nontoxic catalytic decomposition technology. They have made an important contribution to the development of the chemical laser in China. Li Hexuan et al. [86] discovered a novel approach to synthesize NKF zeolite (ZSM-5) without an organic amine template, which greatly reduced the cost of the raw materials as well as solving the environmental pollution problems caused by organic amines. A number of industrial catalysts derived from the zeolites produced by this approach have been applied in industry. Xu Longya and Wang Qingxia et al. explored new methods for the synthesis of multipore materials, including composition template assembly, control of crystallization rate, and so on. They successfully synthesized a series of ultrafine and co-crystallized molecular sieve materials, such as MCM-22, MCM-49, ZSM-35, MCM-22/ZSM-35, and ZSM-5/ZSM-11. They solved the major technical problems of zeolite controlled synthesis, functionalization and industrialization. In addition, they developed novel and highly efficient catalysts and a set of

technology for the conversion of dry gas to ethylbenzene, condensation of aldehyde and ammonia to pyridine, and aromatization of liquefied petroleum gas to BTX aromatics or high-octane gasoline, which have been popularized and applied in large areas. They provided important technical support for the sustainable development of the petroleum and chemical industries [87]. Using the structure unit of a zeolite and assembly of a surfactant, Xiao Fenshou et al. [88–89] synthesized composite catalytic materials with disordered micropores and ordered mesopores, which gave excellent catalytic activity in the conversion of large molecules. In addition, they successfully synthesized β zeolite without templates, which greatly reduced the cost of the catalytic materials and pollutant emissions during β zeolite synthesis. Wang Xiangsheng et al. [92] studied the synthesis of a high silica shape selective zeolite and its application in the conversion of hydrocarbons. They found a ZSM-5 zeolite synthesized from an ammonia system with a proper acid strength and pore curvature. It is suitable as the catalyst matrix for the selective alkylation reaction. Mixed rare earths can regulate the shape selectivity and lower the combustion temperature of the carbonaceous deposit. The intercrystalline pores of the ZSM-5 zeolite with ultrafine particles are the sites that produce coke. They illustrated the key role of the tetrapropylammonium cation in the oriented synthesis of titanium silicalite at the molecular level. Working mainly with mixed rare earths, they first applied a combined modification approach in the modification of ZSM-5 produced by ammonia synthesis to synthesize a catalyst for high purity (98%) *o*-diethylbenzene. The technology for the synthesis of *o*-diethylbenzene from ethylbenzene-ethylene has also been successfully set up. Zhao Dongyuan and Tang Yi et al. studied the assembly synthesis and functionalization of ordered nano-multiporous materials. Based on nano- and molecular assembly chemistry, template-directed chemistry, and surfactant chemistry, they set up the synthesis method for microporous, mesoporous, and multi-ordered zeolite materials. By considering material morphology, pore structure and active sites in the channel, they developed the acid-base pairs and electrostatic compatibility theory, and discovered a pore engineering approach that is suitable for micro- and mesoporous materials. They proposed the ordered arrangement and assembly concept of low dimension nanomaterials and developed a number of nano-zeolite assembly technologies, such as stacked layer, electrophoretic deposition, micro and nano-pouring and regrowth. In addition, they have synthesized dozens of novel mesoporous, microporous, metal-organic complexed nanomaterials, macroporous-microporous zeolites, biomimetic materials and nanotubes with controllable mesoscopic structure. Xie Zaiku and Yang Weimin et al. [87] systematically studied multi-ordered composite catalytic materials, zeolites with hydrothermal stability, shape-selective catalytic materials with small crystal grain and zeolite morphology control, which have been applied in the shape-selective disproportionation of toluene, cracking of C_4 olefin and alkylation of benzene and propylene to cumene in industry. Wang Ren and Lu Guanzhong et al. [93,94] investigated the oxygen storage capacity of rare earth composite oxides and its mechanism.

They found that the Ce cation causes the transition metal cations to be stabilized as a high valence state and reduced at low temperature. In addition, they developed integral rare earth composite oxides catalysts used in industrial VOCs purification and vehicle exhaust purification. Lu Guanzhong et al. also synthesized a series of SAPO-5, MCM-41, MCM-48, and SBA-15 zeolites containing rare earth elements. They found that doping with rare earth played a large role in the regulation of redox properties and surface acidity of the mesoporous materials, as well as giving excellent activity in selective oxidation of olefin, oxidation of alkanes and purification of chlorinated VOCs. The reactions using rare earths as the main catalysts were explored. In the studies of layered and interlayered catalytic materials, Duan Xue and his group [95–98] took advantage of the regulation and designable properties of layered and pillared structures to develop novel layered solid esterification catalysts, layered mesoporous solid alkali catalysts, pillared enzyme catalytic materials, interlayered chiral catalysts and supported metal catalysts with high dispersion. The layered solid esterification catalysts have been widely applied in industrial production. Deng Youquan et al. [99–104] first started the investigation of ionic liquid synthesis at room temperature and its application as well as Au catalysts. Using an ionothermal synthesis method, Tian Zhijian et al. [105–110] successfully synthesized a series of zeolite and zeolite membrane in ionic liquid.

In the past thirty years, catalytic basic research in China has experienced laid the foundation stage for moving towards the international academic arena now. During this period, the number of scientists and engineers in catalytic academia and industry have expanded from several thousands to more than twenty thousand. More than 13000 scientific articles have been published in Chinese mainstream catalytic journals. 3000 articles have been published in international mainstream catalytic journals (about 5% of the total papers published in international journals). About 60 papers have been referenced more than 100 times. Chinese scholars have published 6 papers on catalysis in Science, and one paper in Nature. More than 100 catalytic monographs have been published, of which over 10 monographs were published abroad. From 1982 to 2010, 914 national nature science awards were issued, in which 19 were issued to catalysis groups. 2762 national invention prizes were issued, of which catalysis groups won 64 prizes. Catalysis groups also won 121 awards of 10139 of science and technology progress awards.

3. Significant achievements in industrialization during the last three decades

3.1. Catalytic technology for refining

In China, the development of catalyst in the refining industry originated from the 1960s. In the 1980s, oil refining gradually moved away from the introduction and imitation stages. The refining industry has undergone very fast development. The refining capacity, product variety, product quality have been greatly improved. This period is the transition period of our catalytic technology for refining from imitation to inde-

pendent innovation. We have to mention the contributions of Hou Xianglin in the petrochemical field. He was responsible for organizing and leading scientific research in the petroleum industry for a long time. He presided over the project to solve the key problems of self-sufficiency in the supply of aviation kerosene in China. With the technology of heavy oil hydrocracking to aviation kerosene with a low freezing point developed by DICP, they solved problems in the production and application of the national urgently needed jet fuel. He sponsored and organized the related institutes to co-develop the new petroleum refining technologies, known as “Five Golden Flowers” with great success, such as catalytic cracking and platinum reforming. He was also engaged in the research and development of dozens of special lubrication materials, which met our defense industry needs in time. In addition, he proposed and promoted the suggestion of “make good use of 1 billion tons of oil”. He made outstanding contributions to petroleum refining and petrochemical industry in China.

In the 1990s, the developing of a complete set of technology instead of a single technology can not only meet most domestic needs, but also lead to the developed petroleum refining technology entering into the international market. A number of technologies and catalysts have been exported to Southeast Asia, Middle East and America and European markets. This achieved the export of a complete set of refining technology, which shows the international competitiveness of our petrochemical technology.

Entering into the 21st century, the import of crude oil has increased dramatically in China. The quality of the world crude oil tends to be inferior, containing more and more sulfur and metals, which results in difficulties in the refining process. The development tendency of the refining industry includes heavy oil deep processing and the highly efficient conversion to light oil, cleaner products and production process, integration of refining and chemical engineering, as well as the production of alternative fuels. The refining capacity in China is the second largest in the world and exceeds 500 million tons. At present, the refining technology in China has formed a complete system. Based on self-developed technology, a modern refinery with a 10-million-ton scale can be built. The catalysts and the key technologies of the refining process, such as catalytic cracking, hydrogenation and continuous reforming, have achieved advanced levels in the world. New processes, new catalysts and new technologies have emerged, and part of the prominent achievements are described in the following.

3.1.1. Catalytic cracking and hydrocracking

Research Institute of Petroleum Processing developed Maximizing Iso-paraffins technology, which is applied in catalytic cracking for producing clean gasoline. Based on the chemical mechanism of catalytic cracking, a new concept of two reaction zones, cracking and conversion (isomerization, hydrogen transfer and alkylation), was proposed in the MIP technology. A novel reactor of a two-staged riser in series was developed and the related engineering technology was also established. From theory to practice, based on heavy oil cracking, they applied technical means to effectively reduce the olefin

content in fluid catalytic cracking gasoline, enhance the content of iso-paraffins and decrease the sulfur content in gasoline. In addition, the MIP technology has several advantages, including improving the conversion of heavy oil, increasing the production of gasoline and enhancing the total liquid yield. Over 100 patents on this technology have been applied for in China, from which 80 patents have been issued. A number of patents have also been applied and transferred to other countries, such as USA and Japan. A complete set of technology comprising our own intellectual proprietary rights has been set up to produce clean gasoline, and gradually has become the platform for the development of catalytic cracking technology. The MIP technology is at a leading international level, and has been applied in over 30 sets of process technologies and been transferred to the oil company in Cuba.

Deep catalytic cracking (DCC) technology to produce low carbon olefin developed by Research Institute of Petroleum Processing: Using a heavy distillate oil as the raw material reacting in a riser-fluidized bed reactor, they explored a novel technique, technological conditions, reactor type and special catalyst (CHP-1) for maximum propylene production. The new technological route has been achieved to mainly produce light olefins using a heavy distillate oil as the raw material, which connects the refining and chemical industry. Right now, the technology has been transferred at home and abroad. Several sets of production unit have been built up.

Series of hydrocracking catalysts discovered by Fushun Research Institute of Petroleum and Petrochemicals: Over 30 series of hydrocracking catalysts have been developed, including (1) the catalysts for light oil, which have been used to produce the maximum amount of chemical naphtha, (2) flexible catalysts, by which the production of chemical naphtha and middle distillates can be controlled flexibly, (3) mid-barrel catalysts, producing maximum middle distillates, as well as (4) amorphous and molecular sieve catalysts used in the processing of single-stage hydrocracking. Among these catalysts, 22 series of hydrocracking catalysts have been used in over 60 sets of industrial units and gave good performance. Nine series of hydrocracking pre-refining catalysts also have achieved good results in over 40 sets of industrial units. The successful development and application of these catalysts are adapted to the industrial enterprise needs, and also improve our hydrocracking technology.

Mild hydrocracking catalyst (3882) developed by Fushun Research Institute of Petroleum Petrochemicals: Treating vacuum gas oil by a two series process can produce a high quality feedstock for the production of ethylene from steam cracking, as well as some diesel and naphtha. By using the mild hydrocracking technology to treat vacuum gas oil, from which the tail oil acts as the feedstock in steam cracking to produce ethylene, the yields of ethylene and triene are enhanced significantly. Hydro-conversion of diesel catalyzed by MIC is a diesel hydrotreating technology, which can greatly improve the cetane number of the diesel. The main feature of this technology is to control the reaction in the stage of polycyclic aromatic hydrocarbons saturation, ring opening without breaking the chain by selecting a special combination of technological condi-

tions. Therefore, it can be used to significantly improve the cetane number of the diesel, lower the density, and also control the sulfur content to meet the European V standards. This is the first technology in the world.

Tail oil hydro-isomerization dewaxing technology developed by Fushun Research Institute of Petroleum Petrochemicals: On the demand of API two or three grade lube base oil and industrial or food grade white oil, they developed a hydro-isomerization dewaxing technology, which sets up two reactors in series. The first one is filled with a hydro-isomerization dewaxing noble metal catalyst with a special shape-selective zeolite as the acidic component, which decreases the freezing point of the feed tail oil in hydrocracking. The second is filled with a noble metal hydrofinishing catalyst with high hydrogenation and dearomatization activities, which is used for the deep hydrogenation and dearomatization of isomerization dewaxing products. This process has the advantages of a high adaptability of raw materials, high flexibility of production, high activity of catalysts, good stability, high product selectivity and high quality. In 2005, a unit for 100000 tons/year production was industrialized.

Catalysts and a complete set of process technology for first and second stage hydrogenation of pyrolysis gasoline developed by Shanghai Research Institute of Petrochemical Technology and SINOPEC Engineering Incorporation: After first and second stage hydrogenation of pyrolysis gasoline, the byproduct from the production of ethylene is converted to the raw materials of aromatic extraction. By considering the complexity and severity of the raw materials, they developed a specific composite macroporous alumina support, modified hydrophobic property, as well as controlled and refined noble metal particle size, to much improve the water-tolerant/colloid properties of first stage selective hydrogenation catalysts and prolong catalyst service life. The second-stage hydrogenation catalyst used in Dual-bed with a high proportion of active phase was explored, which has solved the problems of rapid coking, high aromatic loss, and easy deactivation under periodical low-sulfur conditions. The first and second stage catalysts and a complete set of process technology have been successfully applied in ethylene production unit with the capacity of a million tons in China. This technology has the leading position in the world.

3.1.2. Hydrotreating

RN-1 hydrotreating catalyst developed by Research Institute of Petroleum Processing: Ni-W as the active component has high activity for hydrodenitrogenation, hydrodesulfurization, hydrogenation dearomatization, excellent stability and wide adaptability for various raw materials. The RN-1 catalyst is suitable for the hydrotreating of straight-run distillates and the secondary processing of oil distilled from high nitrogen and high sulfur crude oil. It is also suitable for the hydrodenitrogenation and aromatic saturation of refined raw materials in mid-pressure and high pressure hydrocracking, or middle pressure hydrotreating processing. A RS-2000 ultra-deep desulfurization of diesel catalyst has been developed by the MAS preparation platform. It can be used in current diesel hy-

drogenation units for national III diesel to obtain V diesel oil products. They also developed the RHT series catalysts for the hydrotreating of residual oil. The support of these catalysts has unique channels, which resulted in high efficiency of metal removal and a high capacity for metal. Therefore, they can run for longer period than other catalysts at home and abroad. Later on, the RN-10, RN-10B, RN-32V, and RS-1000 catalysts maintained the advantages in the performance of distillate hydrotreating, and have been introduced into domestic and international hydrogenation units. This achieved a great-leap-forward development of this technology in China.

SRH technology for residual oil hydrotreating and the supporting catalysts developed by Fushun Research Institute of Petroleum Petrochemicals: By using the treated residual oil from the SRH technology as the feedstock of catalytic cracking, the quality and yield of catalytic cracking products are much improved. The FZC series of catalysts have reached the level of similar foreign catalysts. The process technology of the sulfur crude oil is a breakthrough. In the hydrotreating catalyst, Mo-Co and W-Ni active phase of W-Mo-Ni-Co are formed, and introducing nano SiO₂ improves the dispersion of the active metal in the catalyst and increases the number of active centers. They prepared the FH-DS catalyst for diesel distillate hydrotreating, FF-16 catalyst for hydrocracking pretreatment, and a distillate hydrodewaxing catalyst. Hydrodewaxing is a refining technology to lower the freezing point of jet fuel, solidifying point of diesel oil, and pour point of lubricants.

A hydrotreating catalyst for low-grade heavy oils developed by Research Institute of Petroleum Processing: In view of crude oils becoming heavier and lower in quality, the explored series of residual oil hydrotreating catalysts need to have strong abilities of metal removal and asphaltene conversion. The proprietary technology of catalyst grading has much improved the running cycle and economic benefits of fixed bed unit for residue hydrotreating. The products have entered the overseas market.

Catalytic cracking catalysts and technology for gasoline selective hydrodesulfurization developed by Research Institute of Petroleum Petrochemicals: The complete set of RSDS technology for gasoline selective hydrodesulfurization is composed of light FCC gasoline extraction desulfurization process, selective hydrodesulfurization of heavy distillates and a highly selective hydrodesulfurization catalyst. Over ten sets of industrial production units have been built. The sulfur content in gasoline can be controlled to below $(50-60) \times 10^{-6}$. It is one of the important technologies to produce national four and national five gasoline in China.

Hydrodewaxing (FDW), hydrofining-hydrodewaxing (HFDW), and hydrotreating-hydrodewaxing (FHUG-DW) technologies developed by Fushun Research Institute of Petroleum and Petrochemicals: By taking advantages of the unique channel and proper acidic centers in special zeolite catalysts, the components with a high pour point in raw materials, such as *n*-alkanes, isoparaffins with short side chain and cyclic hydrocarbon with long side chain, are selectively cracked into small molecules, in the presence of hydrogen, at a specific temperature and low pressure. Therefore, the FDW technology can

decrease the pour point of oil and is suitable for processing low sulfur and low nitrogen straight-run diesel oil. The pour point can be lowered by up to 50 °C. At medium pressure, the hydro-refining or pretreatment of raw materials by MCI in FHDW and FHUG-DW technologies not only enhance the adaptability of the unit to high sulfur, high nitrogen straight-run diesel oil and/or secondary processing raw oil, improve the feedstock quality in the following hydrowaxing process, give milder operating conditions, prolong the equipment lifetime and operation cycle, and also improve the product quality of diesel oil with low pour point, which meets the diesel quality upgrade requirements. The above technologies have been applied in several sets of industrial units.

SRH liquid phase recycling hydrogenation technology developed by Fushun Research Institute of Petroleum and Petrochemicals: The SRH technology takes advantages of dissolved hydrogen, which is carried into the reaction system during the cycle of liquid products, to provide the hydrogen for the hydrogenation of fresh raw materials. With the SRH technology, since there is no hydrogen circulation system, a recycle hydrogen compressor is not needed, which significantly reduces the equipment investment and operating cost. In addition, the influence of the catalyst-wetting factor is eliminated. The large specific heat capacity of the circulating oil results in greatly reducing the reactor temperature rise. Thus, it improves the catalyst efficiency and reduces side reactions, such as cracking. This technology has passed the test in industrial demonstration unit with a capacity of 200000 tons/year, and has produced diesel with the sulfur content less than the Euro V diesel standard in an industrial unit with a capacity of 600000 tons/year. In 2009, the industrialization test was started and it has achieved good results.

DICP and Research Institute of Petroleum Processing jointly developed the catalyst for hydrogenated isodewaxing of lubricant base (PIC802). The catalyst and its processing have been applied in a high pressure hydrogenation unit with a capacity of 200000 tons/year in Daqing Refinery, PetroChina Company Limited. The novel isodewaxing catalyst, PIC802 has the advantages of high activity and high yield of heavy base oil. By using the PIC802 catalyst in Daqing Refinery, the yield of lubricant, product quality and catalyst life time were much better than with previous imported catalysts.

3.1.3. Catalytic reforming

Platinum-Rhenium-Titanium (CB-5) reforming catalyst developed by Fushun Research Institute of Petroleum Petrochemicals: In order to improve China's reforming technology, CB-5 was developed as the semi-regenerated Pt-Re-Ti reforming catalyst. The introduction of the third metal, titanium, further enhanced the selectivity and stability of the bimetallic catalyst. The activity of this catalyst is similar to that of foreign catalysts, while, the selectivity of this catalyst is much better. This results in the development of our Pt-Re series catalysts to a new level. Research Institute of Petroleum Processing has developed a complete set of naphtha catalytic continuous reforming technology. The purpose of continuous reforming is to provide high-octane gasoline blending components and aro-

matics and hydrogen, which directly influences the technological progress and competitiveness of our petroleum refining and petrochemical industry. They discovered a series of continuous reforming catalysts with low coking and high yield, named as PS-VI and PS-VII. Combining with a number of core technologies, including catalyst, processing, control system and special equipment, they developed a domestic continuous catalytic reforming complete set of technology.

Semi-regenerated reforming catalyst and processing technology developed by Research Institute of Petroleum Processing: They developed CB-6/CB-7, CB-60/CB-70, and PRT-C/PRT-D, three generations of semi-regenerated reforming catalysts, as well as the application of the processing of catalyst split-packed and two-stage hydrogen mixing. Since the 1980s, these catalysts have over 85% of the domestic market. By introducing new metal catalytic components, optimizing the surface and channel structure of the support, and discovering a multi-metal impregnation preparation method, they developed the PRT series of catalysts, which maintained the high activity of bimetallic catalysts, and achieve better selectivity and obviously reduced the coking rate. In addition, on the basis of high yield of target products, semi-regenerated reforming can steadily operate for long periods.

Continuous reforming catalysts and technology developed by Research Institute of Petroleum and Processing: They have developed three generations of the PS series catalysts. During the development of the third generation PS-VI/VII catalysts, they designed and regulated metal-acidic centers to solve several problems, such as the decrease of surface area causing short catalyst life time and loss of chlorine, and the enhancement of Pt content resulting in the increase of coking. This is good technological progress in this field. The domestic catalyst market share remains 80%. Industrial enterprises have obtained great economic benefits. They have made an important contribution to the quality upgrading of our clean gasoline and progress in the technology of producing aromatics. The catalysts have been exported to other countries and received great attention in the international market.

Complete set of technology for naphtha catalytic reforming developed by Luoyang Petrochemical Engineering Corporation and Research Institute of Petroleum and Processing: The purpose of naphtha catalytic reforming is to provide high-octane gasoline blending components or aromatics and hydrogen, which reflects the technological progress and competitiveness of our petroleum refining and petrochemical industry. Through the investigation of the reaction process, they first proposed a new concept of aromatic and gasoline type unit design based on aromatics and octane barrel. They successfully developed the technology for solid dechlorination of the recycle gas, which solved chlorine corrosion problem. They have a patent of sulfide-desulfurization technology, which solved the problem of unit without sulfur coking and catalyst with sulfur poisoning. Independent innovation has been achieved in the reaction, catalyst delivery and regeneration processing, engineering technology, special unit and operating technology. They integrated several core technologies, including catalyst, processing, control system and special units, and developed a complete set

of technology for naphtha catalytic reforming with independent intellectual proprietary rights. China is the third country in the world to own this technology. It has been applied in four domestic industrial enterprises and given enormous economic benefits.

3.1.4. Comprehensive utilization of refinery gas

In order to comprehensively utilize refinery gas and dry gas resources, and produce national urgently needed ethylbenzene-styrene, DICP and Fushun Research Institute of Petroleum and Petrochemicals developed a series of technologies for the catalytic cracking of dry gas to ethylbenzene. Among these, the first and second generation technologies were applied in Fushun Petroleum Plant (30000 tons/year) and Dalian Petrochemical Company (100000 tons/year) in 1993 and 1999, respectively, which were included in the innovation achievements of the Third World Academy. In order to further reduce the energy consumption and cost of ethylbenzene production, improve the product quality, prolong catalyst life time, DICP explored a high performance low temperature vapor-phase alkylation catalyst (ZSM-5/ZSM-11 eutectic zeolite), and a liquid phase transalkylation catalyst (ultrafine beta zeolite). They successfully developed the third generation technology of catalytic cracking of dry gas to ethylbenzene. This technology solves the major technological problem for the direct utilization of dry gas to produce high quality ethylbenzene, effectively improves the utilization rate of petroleum resource, as well as reduces the energy consumption and cost of ethylbenzene production. Compared with the pure ethylene method, the cost of raw materials is reduced about 15%–20%. At present, over 20 industrial enterprises have successfully applied this technology, with annual output of more than 150 tons of ethylbenzene. In addition, in order to optimize and utilize large amounts of liquid gas resource from petrochemical byproducts, DICP first proposed the technology of liquid gas aromatization at low temperature, and developed an efficient multiporous zeolite as the aromatization catalyst, which has been successfully applied in industrial units with a capacity of 200000 tons/year.

Complete set of light hydrocarbon aromatization fixed bed technology developed by Dalian University of Technology (Nano-reforming processing): Taking advantage of a nano-ZSM-5 zeolite, they discovered an aromatization catalyst with good resistance of coking and deactivation. This effectively solved the problems of the fast deactivation of the catalyst and high frequency changing in the fixed-bed reactor. In 2006, the first set of liquid gas aromatization to BTX unit with a capacity of 100000 tons/year was set up in China. At present, this technology has been developed into two types of processing, high temperature aromatization to benzene-rich mixed aromatics and low temperature aromatization to mixed aromatics with a low content of benzene. A number of units have been built up in China. The suitable raw materials include *n*-butane, isobutene, mixed butane, FCC liquidized petroleum gas (MTBE raffinate material) and light naphtha feedstock (such as reforming raffinate oil, topped oil). This technology has great significance in the optimal application of light hydrocarbons such as liquefied

petroleum gas.

Complete set of light hydrocarbon aromatization technology developed by Research Institute of Petroleum Processing: They explored a specially formed spherical aromatization catalyst. Combined with the corresponding technologies of catalyst feeding on moving bed and regeneration, a complete set of light hydrocarbon aromatization technology has been successfully developed. By using liquefied petroleum gas with four carbon and other light hydrocarbons as raw materials, they mainly produce the aromatic products of benzene, methylbenzene and dimethylbenzene. Hydrogen is a byproduct. This technology has achieved continuous and stable operation of aromatization units. Until now, a number of complete set of units have been built in industry. Benzene, methylbenzene and dimethylbenzene are very important organic raw materials, mainly used in the production of chemical products such as PX, PTA, and polyester.

Alumina-based catalyst for sulfur recovery developed by Qilu Research Institute of Petroleum Processing: The LS series of catalysts for sulfur recovery and tail gas hydrogenation have been successfully applied in over 100 sulfur recovery units in SINOPEC Qilu and Yanshan companies. These LS catalysts include the LS-971 catalyst with protection of oxygen leakage, LS-981 catalyst with multifunction sulfur recovery, LS-951, LS-951T, and LS-951Q catalysts for Claus tail gas hydrogenation, LSH-02 catalyst for low temperature Claus tail gas hydrogenation, LSH-03 catalyst with high oxygen resistance for low temperature Claus tail gas hydrogenation.

3.2. Petrochemical and fine chemicals [111,112]

Petrochemical and fine chemicals are closely related to the basic necessities of human life. During the last three decades, we mainly focused on the development of the production of organic materials, such as ethylene, propylene, methanol benzene, ethylbenzene and xylene, to be independent of imports, fill the gap of key products and intermediates, improve catalytic efficiency and reduce pollution.

3.2.1. Preparation of synthetic fiber monomer and raw materials

MB-86 acrylonitrile catalyst developed by Shanghai Research Institute of Petrochemical Technology: They completed the component design and industrial scale preparation of the MB series catalysts. They developed the MB-86 catalyst suitable for operating under high pressure and high load conditions, which has a successful application in industry. The catalyst and complete set of technology for toluene and heavy aromatics disproportionation and alkyl transfer were explored, in which mordenite was the main catalyst, raw materials, including toluene, C₉ arene, C₁₀ arene and above C₁₀ arene, achieve disproportionation and alkyl transfer to produce benzene and xylene. During toluene disproportionation and alkyl transfer process, C₁₀ arenes and other heavy aromatics are simultaneously converted to light aromatics in the same reactor. The HAT series catalysts have been successfully applied in Shanghai Petrochemical Company Limited and other seven domestic compa-

nies. The total amount of throughput is around 3800000 tons/year, which is 90% of the total processing capacity in China.

Complete technology of acrylonitrile preparation developed by Shanghai Research Institute of Petrochemical Technology and SINOPEC Qilu Petrochemicals Company: With research efforts on each individual key technology in acrylonitrile production, they own independent intellectual proprietary rights patents or proprietary technology. They have integrated individual key technologies, including the MB-98 acrylonitrile catalyst, novel air distribution plate, propylene-ammonia distributor, new high efficiency cyclone separator, composite extraction separation, decyanation tower with negative pressure, novel gas-liquid separator and oriented float-valve, which have been successfully used in different units.

Technology for benzene and ethylene liquid phase alkylation to ethylbenzene developed by Research Institute of Petroleum Processing: They developed the circulation technology for benzene and ethylene liquid phase alkylation, the catalyst for benzene and ethylbenzene liquid phase alkylation, and catalyst for multi ethylbenzene alkyl transfer in liquid phase. They established a complete set of technology for benzene and ethylene liquid phase alkylation to ethylbenzene, and built several sets of units to produce ethylbenzene, which achieved the domestication of ethylbenzene production technology in China. Ethylbenzene is one of the most important organic chemical materials used to produce styrene and propylene oxide.

Complete set of technology for butane hydration dehydrogenation to methyl ethyl ketone developed by Fushun Research Institute of Petroleum Petrochemicals: They developed a complete set of technology and catalyst for butane hydration dehydrogenation to methyl ethyl ketone. Styrene-divinylbenzene as main raw materials has five steps, including polymerization, stabilization of physical structure, halogenation, sulfonation and stabilization of active groups, to prepare a high temperature cation exchange resin catalyst for butane hydration to produce 2-butanol. The copper catalyst used in 2-butanol dehydrogenation to methyl ethyl acetone is modified by potassium oxide to reduce the catalyst acidity. This catalyst has been applied in over 10 industrial units of CPNC and SINOPEC companies. The market occupancy in China is more than 90%.

Polyethylene catalysts developed by Beijing Research Institute of Chemical Industry: BCS-02 is a suitable Z-N catalyst for the gas phase polymerization process of ethylene. It can be used to prepare high density polyethylene resin, and has several advantages, such as high activity, excellent performance of copolymerization, good grain shape of resin powder, high bulk density, capability used in the condensing and non-condensing status. In addition, the powder is not sticky and feeds smoothly. The BCE catalyst is a new generation catalyst for the slurry polymerization of ethylene developed by Beijing Research Institute of Chemical Industry. It is used in the slurry polymerization of ethylene to produce medium or high density polyethylene resin and is suitable for the slurry polymerization processing of CX, Hostalen, Innovene S and Philips Loop. In 1980s, Beijing Research Institute of Chemical Industry developed the BCH catalyst for slurry polymerization of ethylene, which is

suitable for CX processing and is used in the production of extrusion molding, injection molding and blow molding. At present, a large number of this catalyst is exported to Southeast Asian countries. The study of the metallocene polyethylene catalyst dated from the 1990s. In 2002, a supported metallocene catalyst was developed and prepared on a large scale. In 2011, it achieved industrialization in Qilu Petroleum Company. It has the advantages of high activity, strong copolymerization ability and uniform distribution of comonomer in polymer.

Technology and catalyst for terephthalic acid hydrorefining developed by Shanghai Research Institute of Petrochemical Technology and SINOPEC Shanghai Petrochemical Company Limited: Purified terephthalic acid (PTA) is an important basic organic chemical raw material, which is mainly used in the production of polyester (PET) and the follow-up products. By applying a pioneering international emulsification impregnated method to control metal dispersion, as well as a technology of catalyst crystallite structure stability, they explored a novel PTA hydrorefining catalyst with a particularly excellent performance, and developed a hydrotreatment process suitable for high load, long period and stable operation. They solved the previous technical problems with the heat-resistance, anti-poison, and anti-jamming of catalysts. In addition, they broke through the technical bottleneck of stable operation in PTA unit and capacity expansion, and achieved the domestication of core technologies. The catalysts have been successfully used in over 60% PTA units in China. The comprehensive performance is in at the leading position in the world.

Technology for high yield xylene series aromatics productions developed by Shanghai Research Institute of Petrochemical Technology: By using a macroporous zeolite as major catalyst, toluene, C₉ hydrocarbons and other heavy aromatics as raw materials, the disproportionation and alkyl transfer of toluene as well as the conversion of other heavy aromatics to light olefin and their alkyl transfer reaction can be achieved in the same reactor. These catalysts have been successfully used in over 20 units at home and abroad. The domestic market share is around 90%. Based on these technologies, a disproportionation unit with the total processing capacity of 15 million tons/year was built in China. ZSM-5 zeolite as the major catalytic active component was modified on the surface and orifice. It can catalyze the selective disproportionation of purity toluene to produce *p*-xylene with high selectivity. Through crystallization separation, *p*-xylene can be obtained with high efficiency and low cost. This technology has passed the industrial verification, which can combine with alkyl transfer technology of benzene/heavy aromatics. Benzene produced in selective disproportionation unit reacts with heavy aromatics by alkyl transfer to produce xylene and toluene. Then, Toluene acts as the raw material of selective disproportionation. In this combination process, the concentration of *p*-xylene can be over 60%. It greatly reduces the *p*-xylene production load and improves the *p*-xylene production capacity of the unit.

Complete set of technology and catalyst for catalytic cracking of olefins to propylene developed by Shanghai Research Institute of Petrochemical Technology: They took advantage of the byproducts C₄, C₅ hydrocarbons from refinery and ethylene

plant to increase the production of propylene, synthesized binderless composite mesoporous zeolite materials, and developed the processing technologies, including a reactor with ultra-low resistance, reaction-regeneration switch technology at high temperature, efficient heat exchanger and product separation process. They own the independent intellectual property rights of complete set of technology for olefin catalytic cracking. An industrial unit with capacity of 60000 tons/year was built up in Zhongyuan Petroleum & Chemical Corporation. It is the first time to achieve the industrial application of binderless zeolite technology in the world. Through the innovation of catalytic materials, the catalysts perform significantly advancement in space velocity and stability, which is in the leading position in the world.

Novel titanium-based polyester catalysts developed by Shanghai Research Institute of Petrochemical Technology: By using these titanium-based catalysts, the reaction temperature of esterification can be reduced in polyester production process, which lowers energy consumption. In China, they were the first to produce polyester products without heavy metal in an industry environmentally friendly way. In collaboration with Shanghai Petrochemical Company Limited, they produced NEP polyester chips, which have been exported to European Union. These titanium-based catalysts can be used for light, semidull, full dull fiber grade polyester chip and film grade polyester chip.

Catalysts for C₃ hydrogenation developed by Beijing Research Institute of Chemical Industry: Cracking fractions of C₃ hydrocarbons contain 1%–5% of the propyne and propadiene (MAPD). Selective hydrogenation method is usually used in ethylene unit to convert MAPD to propyne. Beijing Research Institute of Chemical Industry developed the catalyst BC-H-33 for gas phase hydrogenation of C₃ hydrocarbons, as well as catalysts BC-L-83 and BC-L-30A for liquid phase hydrogenation of C₃. The above catalysts have the advantages of high space velocity, high selectivity of propene, low production of polymer, long regeneration cycle and long service life, wide range of applicable working conditions, strong ability of anti-fluctuation and excellent comprehensive performance. At present, the BC-H-33 catalyst is being used in the only two sets of domestic C₃ gas phase hydrogenation unit. The catalysts for selective liquid phase hydrogenation of C₃ hydrocarbons have been applied in 22 sets of domestic units (including Taiwan), as well as in 10 sets of units on abroad, such as Mideast, Southeast Asia, Japan, and Korea.

Catalysts for C₂ hydrogenation developed by Beijing Research Institute of Chemical Industry: Selective hydrogenation of C₂ fractions to get rid of acetylene is one of the most important processes in the steam cracking of petroleum hydrocarbon to ethylene processing. Beijing Research Institute of Chemical Industry have developed the BC-H-20 series C₂ hydrogenation catalysts suitable for the sequential separation procedure and the BC-H-21B C₂ hydrogenation catalysts suitable for the front-end depropanization and acetylene front-end hydrogenation process. The above catalysts have the advantages of a wide range of operation condition, good stability, high space velocity, good selectivity of ethylene, low production

of anthracene oil and long operation period. The catalysts for C₂ hydrogenation have been used in 17 sets of ethylene units in Yanshan, Shanghai, Qilu, Guangzhou, Zhongyuan, Yangzi, Daqing, Liaoning, Dushanzi, Tianjin, and Dongfang chemical companies, which perform very well. In 2008, these catalysts were exported to BIPC Company in Iran. Until now, they have been running well, and received a good reputation from the user. In 2010, they were exported to SABIC in United Kingdom. It is the first time for domestic catalysts to be promoted to western developed countries.

3.2.2. Hydrogenation and dehydrogenation

NDC-2 type of Pt-Sn-Li/Al₂O₃ catalyst for dehydrogenation of long chain *n*-alkanes (*n*C_{10–13}) collaboratively developed by DICP, Institute of Daily-Used Chemical Industry and Nanjing Alkyl Benzene Plant: There is a M2 active center with a Pt-SnO₂-Al₂O₃ sandwich structure on the surface of this catalyst. It has strong adsorption of hydrogen at high temperature and can suppress coking. Thus, it significantly proved the catalyst stability. The NDC type of catalyst has been exported to India, which gave enormous economic benefits.

Complete set of technology and catalyst for maleic anhydride esterification/hydrogenation for the production of 1,4-butanediol developed by Fushun Research Institute of Petroleum and Petrochemicals: After using twenty batches in 1,4-butanediol industrial unit with capacity of 10000 tons/year, the catalyst was continuously applied in 55000 tons/year unit in 2011. Compared with other similar catalysts at home and abroad, the service life of this catalyst was prolonged more than 50%.

Catalyst for carbonylation of methanol to acetic acid developed by Beijing Research Institute of Chemical Industry: Beijing Research Institute of Chemical Industry developed the synthesis method for a triiodinated rhodium catalyst, in which rhodium powder is ionized by melting in sodium bisulfate, and followed by hydrolysis conversion. In 2003, they finished the regeneration method test of deactivated catalysts in industrial unit. Therefore, a complete set of catalyst processing and regeneration system was established. Industrial application showed that the catalyst solubility properties, impurity content and physicochemical index, as well as all kinds of control indexes in industrial unit reach the same level as those of the imported catalysts. This technology breaks the long-term monopoly of foreign companies, and decreases the price of imported catalysts, which is beneficial for domestic enterprises.

3.2.3. Selective hydrocracking

Novel catalytic materials and industrial application technologies for the conversion of glucose-sorbitol to lower alcohols developed by DICP and Changchun Dacheng Industrial Group Company Ltd: They invented a new method with independent intellectual proprietary rights to prepare ethylene glycol and propylene glycol through a non-oil route. It has been applied in industrial unit with a capacity of 200000 tons/year for many years. Right now, the production has been increased to 100 million tons/year, which is the only industrial production line to produce polyols from biomass. Dehydrogenation of

ethylbenzene: Shanghai Research Institute of Petrochemical Technology and East China University of Science and Technology developed the key technologies of styrene preparation, which include novel axial-radial flow reactor, dehydrogenation catalyst and its industrial application. Through combining overall technologies, a complete set of technology for vacuum dehydrogenation of ethylbenzene to styrene was formed. The complete set of unit achieved localization.

3.2.4. Catalytic oxidation

Novel method and technology for the oxidation of *p*-xylene to terephthalic acid developed by DICP: The stable operation of this novel technology has been achieved for more than 30 months in an industrial unit with a capacity of 100000 tons/year. Catalytic efficiency was obviously improved. The amount of bromine was reduced substantially. Corrosion and environment pollution were also reduced. The industrial application with the scale of 1650000 tons/year is being tested in Xiameng. Shanghai Research Institute of Petrochemical Technology and Shanghai Petrochemical Company Limited developed the catalyst and processing technology for terephthalic acid hydrotreating. This was the first time to discover a novel crude terephthalic acid (TA) refining catalyst with particularly excellent performance as well as the hydrogenation technology with high load and long-term stable operation in the world. They dissolved the technical bottleneck in PTA production and capacity expansion revamping. The PTA core technologies achieved domestication.

Catalyst for the oxidation of benzene to maleic anhydride developed by Beijing Research Institute of Chemical Industry: The BC-118 series catalysts are novel rare earth V_2O_5 - MoO_3 catalysts used in the selective oxidation of benzene to maleic anhydride in fixed bed reactors. These catalysts can be activated during production process and directly loaded for use, which solved the problem of the low production efficiency in industrial enterprises. At present, this technology has been used by more than 10 domestic maleic anhydride manufacturers. The market share is above 70%.

Catalyst and technology for ammonia oxidation to produce aromatic nitrile developed by Shanghai Research Institute of Petrochemical Technology: Benzonitrile, phthalonitrile, and halogenated benzonitrile are fine chemical products with high added value. They developed the process technology of a turbulent fluidized bed reactor and the catalyst, which significantly improved the production yield and reduced waste emissions. The developed vanadium catalysts have the advantages of strong wear resistance and excellent selectivity. The overall technology has achieved the advanced level in the world and been widely applied in domestic aromatic nitrile production plants. It provides strong technical support for pesticides, pharmaceuticals, dyes and other industries in China.

Catalyst for ethylene trimerization to 1-hexene developed by Beijing Research Institute of Chemical Industry: 1-hexene, a derivative of ethylene, is an important comonomer to produce various polyethylene products, as well as a raw material for some fine chemicals. The technology of ethylene trimerization to 1-hexene is the process of ethylene conversion to 1-hexene,

which is catalyzed by a coordination catalyst composed of a center metallic chromium. Due to the high selectivity of target product and excellent product quality, a complete set of industrial unit with a capacity of 50000 tons/year has been built and put into operation in SINOPEC Yanshan Company, which promotes technical progress and product upgrading in domestic polyethylene industry.

Catalyst for ethylene oligomerization to produce advanced α -olefin developed by Beijing Research Institute of Chemical Industry: Ethylene oligomerization to α -olefin is a technology for ethylene derivatives preparation. α -Olefin has wide applications in the fields of ethylene comonomer, synthesis intermediates of surfactant, plasticizer alcohol, synthetic lubricating oil and oil additives. In cooperation with Institute of Chemistry, they developed an iron-based ethylene oligomerization technology. After continuous improvement and innovation, the activity is around $0.81.0 \times 10^7$ (g·mol)/h. The specific distribution is C_4 : 19%–24%, C_6 – C_{18} : 69%–72%, C_{20+} : 7%–11%. The average content of the linear α -olefin products with carbon below 18 is more than 98%, and the polymer content is less than 1%. With significantly reducing of the catalyst cost, the performance indexes of activity and α -olefin selectivity achieved advanced international level.

Catalyst for MTBE cracking to isobutylene developed by Beijing Research Institute of Chemical Industry: The technology of MTBE cracking to isobutylene is a comprehensive utilization project of C_4 cracking and C_4 refining. In 1981, Beijing Research Institute of Chemical Industry started to investigate the catalyst for methyl *tert*-butyl ether (MTBE) cracking to isobutylene. Subsequently, they developed a complete set of technology for MTBE cracking to produce polymer grade isobutylene. This technology has been used in an isobutylene production unit with a capacity of 35000 tons/year in SINOPEC Yanshan Company, which produces over 40000 tons of high pure isobutylene every year and creates more than 500 million Yuan output value. In addition, it provides the main raw material for butyl rubber plant, breaks the long-term dependence on imports of butyl rubber, as well as create good economic and social benefits.

Catalyst for rare earth isoprene rubber developed by Beijing Research Institute of Chemical Industry: They independently developed novel homogeneous rare earth catalysts with high activity for isoprene rubber. In addition, they successfully carried out a complete flowsheet trial of isoprene rubber synthesis. All the performance indexes of synthetic isoprene rubber in pilot-scale experiment achieved the same level of foreign products. The evaluation by domestic research institutes and tire manufactures showed the isoprene rubber meets all the requirements for industrial products. The rare earth catalyst is prepared by the aging reaction of carboxylic neodymium, the main catalyst, with aluminum alkyl and halogen compounds. This catalyst has the advantages of high activity and excellent stability, and can remain homogeneous for a long time.

3.2.5. The synthesis of pyridine from aldehyde and ammonia

Complete set of technology and novel high performance catalysts for the synthesis of pyridine from aldehyde and ammonia

developed by DICP: They have overcome the key technical problem of the zeolite catalyst by preventing alkali poisoning and broken the monopoly of foreign technology. Several pyridine production units have been put into operation, including the largest unit with a capacity of 25000 tons/year in the world. Thus, China has become the world's largest pyridine production base. It achieved scale, and the continuous and clean production of pyridine compounds, which are the critical bulk intermediates in many industries, such as pesticides and pharmaceuticals. In addition, it also provides the critical scientific and technical support for the development of many downstream industries. This application in industrial production improves our innovation abilities and competitiveness with international competition in pesticides, pharmaceuticals and other chemical industries, as well as accelerates the industrialization and technology development of critical bulk chemical intermediates and leading pesticides.

3.2.6. Hydroammoniation

DICP developed the technology of ethanolamine hydroammoniation to produce ethylenediamine, in which ethanolamine and ammonia are raw materials for the production of ethylenediamine. High product selectivity can be achieved under mild processing conditions. In addition, diethylenetriamine and piperazine, domestic scarce products, are produced with ethylenediamine. It is suitable for general use in the country. The use of a non-benzene reagent as dehydrating agent in this complete set of technology makes it more environmentally friendly.

3.2.7. Reppe synthesis

Hydrogenation catalyst for 1,4-butanediol synthesis through Reppe method developed by Shanxi University: Based on the imported core technology in the 1,4-butanediol production process through Reppe synthesis method, they developed hydrogenation catalysts with the suitable pore structure, surface properties, high hydrothermal stability and dual functions of hydrolysis and hydrogenation. Due to the achievement of this technology, China has become one of the few countries to have mastered the critical technology to produce this type of catalysts.

3.2.8. Olefin esterification

Direct addition reaction of carboxylic acid and olefin to esters studied by South China University of Technology: In their studies, the catalysts include resins, heteropolyacid and molecular sieves. The reactions include the synthesis of isopropyl acetate from acetic acid and propylene, 2-butyl acetate from acetic acid and butane, ethyl acetate from acetate and acetic acid, as well as synthesis of isopropyl salicylate from salicylic acid and propylene ethylene. They have been successfully applied in industry and achieved great economic benefits.

3.3. Ammonia synthesis catalyst [111,112]

The chemical fertilizer industry in China was begun in the 1930s. In 1980, the total amount of fertilizer produced (pure nutrients) was 12.319 million tons. In 2010, it reached 66.198

million tons, which was an increase of 4.37 times in 30 years. Both the total amount of fertilizers and nitrogen fertilizer production are listed in the first position in the world. In the chemical fertilizer industry, the catalysts are mainly applied in ammonia synthesis, which is the basic raw material for nitrogen fertilizers. Based on the feedstock in ammonia synthesis, such as coal, naphtha, heavy oil, residual oil and nature gas, different types of catalysts are selected. There are eight types of catalysts, including catalysts for hydro-conversion of organic sulfur, adsorption of inorganic sulfur, primary and secondary reforming of natural gas or naphtha, high temperature and low temperature shift, methanation and ammonia synthesis.

The activity and stability of the A201 and A202 ammonia synthesis catalysts developed by Fuzhou University are suitable for small and medium-sized plants. They also successfully developed the B116 type low chromium CO mild temperature shift catalyst, as well as the B121 type non-chromium CO high temperature shift catalyst.

After 70 years after Fritz Haber invented the fused iron catalyst for ammonia synthesis, in the early twentieth century, Zhejiang University of Technology made a breakthrough in the classic Fe_3O_4 system, and discovered a new generation of Fe_{1-x}O -based catalyst for ammonia synthesis. In addition, they established an original Fe_{1-x}O catalyst theory, in which the single phase theory is the core theory.

South China University of Technology successfully developed the HG-1 rare earth ammonia synthesis catalyst, which has improved catalyst activity at low temperature, heat resistance and poison resistance.

Shanghai Research Institute of Chemical Industry developed the B301 sulfur-resistant CO shift catalyst, which was the first successfully developed and widely used sulfur-resistant shift catalyst in China.

Qilu Petroleum & Chemical Corporation Research Institute of Petroleum Processing successfully developed a series of catalyst and the corresponding application technology suitable for the conversion of natural gas, refinery gas, naphtha and other gaseous, liquid hydrocarbon vapor into hydrogen and synthesis gas. They developed the QCS-01 and QCS-04 sulfur-resistant shift catalysts, which achieved the localization of sulfur resistance shift catalyst in large fertilizer plant.

3.4. Catalysis for environmental purification

Developments of catalytic science and technology bring us great material benefits. At the same time, these also result in tremendous impact on human activities in nature and the environment. Therefore, environmental catalysis has emerged. The mission of environmental catalysis is to use the means of catalysis to solve the chemical pollution problems facing the mankind, which is a new challenge for catalytic science and technology [113].

3.4.1. Catalytic elimination of pollutants from non-moving sources

Catalytic desulfurization and denitrification of flue gases: The emission of SO_2 and NO_x with coal-fired flue gases is the

major air pollution source in China. How to effectively eliminate SO_2 and NO_x is a heavily researched topic in environmental catalysis. In order to eliminate SO_2 , catalytic oxidation can be used to oxidize SO_2 to SO_3 so as to obtain sulfuric acid. Thus a resource can be produced from the waste. Alternatively, SO_2 can be reduced to elemental sulfur and recycled for further use by catalytic reduction. For the catalytic elimination of NO_x , selective catalytic reduction of NO_x to N_2 (NH_3 -SCR technology) can be performed by adding a reducing agent (NH_3). In China, research on catalytic desulfurization and denitrification of flue gas started a little late. In the early stage (before 2000), the technology of flue gas treatment usually used the “import-use and learn-innovate” mode, and there existed some intellectual property barriers. Southeast University presided over the project, “Development and application of complete flue gas desulfurization and denitrification key technologies in large thermal power plants”, which has made rapid progress in SCR denitrification. DICP has developed a technology of desulfurization and denitrification in power plants, which has completed an industrial test. The catalysts for flue gas desulfurization and denitrification developed by Fushun Research Institute of Petroleum and Petrochemicals have passed the industrial sidestream experiment. In 2012, they completed industrial experiments of flue gas denitrification by fluid catalytic cracking and flue gas denitrification in power plants. Fushun Research Institute of Petroleum and Petrochemicals have also developed technology for the catalytic oxidation of volatile organic compounds (VOCs) [114]. They explored a series of catalysts for VOC catalytic oxidation, and showed that the WSH-1 type of catalyst is suitable for the treatment of exhaust gas from a petrochemical sewage farm. This has been widely applied in more than a dozen petrochemical companies. The WSH-1 and WSH-2 catalysts developed by SINOPEC Beijing Yanshan Company have been used in industrial units for rubber exhaust gas and PO/SM tail gas treatment, respectively. A complete set of catalytic oxidation technology including process, design, equipment production and catalyst development is available.

3.4.2. Catalytic purification of motor vehicle exhaust

In 2010, with the production of around 17 million cars, China became the world's largest car producer. The production of motorcycles reached more than 25 million, which was more than 40% of the world production. With 80 million vehicles and 110 million motorcycles being used, vehicle pollutants contribute 50%–80% of the pollutants in the cities of China. These are the main sources of air pollution. In the field of environmental catalysis, CO, hydrocarbons (HC), NO_x and particulate matter (PM) from automobile tail gas are eliminated by a combination of catalysis and particulate matter filtering. The technologies include three-way catalysis (TWC), Diesel Particulate Filter (DPF), NO_x selective catalytic reduction (SCR), NO_x storage-reduction (NSR) technology, as well as a combined purification and four-way catalytic technology that was developed based on the above technologies.

The FD automobile catalytic converter of exhaust gas developed by Fuzhou University has satisfied the Euro IV and Euro V emission limits. It has been industrialized. It has com-

peted with United States, Japan, Germany, and other foreign countries, which used to monopolize the Euro IV emission limits converter market in China, and the FD catalytic converter of exhaust has been widely used by automobile manufacturers, such as First Automobile Works and Changfeng Motor Co., Ltd. Sichuan University has achieved a significant breakthrough in the science and technology of catalyst preparation for the purification of tail gas from gasoline cars, motorcycles, compressed natural gas vehicles and diesel vehicles. They made a series of important scientific innovations in the field of catalytic materials and catalysts for vehicle exhaust gas purification [115–119]. On the basis of these investigations, Sichuan University and Sichuan Zhongzi Technology Co., Ltd collaborated to set up production lines of rare earth oxygen storage materials with high performance, materials with good heat resistance and high surface area, as well as the catalysts for the purification of vehicle exhaust gases. They supply catalysts for the purification of exhaust gas from gasoline cars, motorcycles, compressed natural gas vehicles and diesel vehicles. They are the major catalyst supplier for CNG vehicles from the domestic original equipment manufacturer (OEM). Their catalysts for motorcycles have been widely used in Suzuki and Yamaha motorcycles.

Tsinghua University, East China University of Science and Technology and Tianjin University investigated the key reactions, major catalyst materials, interaction between rare earth and non-noble metal components, design of active component and preparation techniques for catalysts for the purification of vehicle exhaust gases. On the basis of these investigations, they developed vehicle exhaust gas purification catalysts with the active components comprising rare earth metal, non-noble metal, and trace noble metal. They established the preparation technologies for the key materials, such as high performance rare earth oxygen storage materials and composite alumina, as well as monolithic catalysts with vacuum coating and vacuum extraction [120,121]. The related technologies have successfully achieved industrialization in Wuxi Weifu Lida Catalytic Converter Co., Ltd, Jinhua Oulun Catalytic Technology Co., Ltd, and Shanghai Langt Autocatalyst Co., Ltd.

3.4.3. Catalytic purification of indoor air

Efficient nano-photocatalyst: By using methods to enhance surface acidity, to regulate component and structure, to form semiconductor composites, to forming heterojunctions as well as to make use of nano-quantum size effect, Fuzhou University developed a series of novel nano-photocatalysts such as solid superacid photocatalysts with which the efficiency of the photocatalytic process is greatly improved. Through technological integration of the sol-gel process, membrane dialysis and super acidification of the surface, they developed a novel processing technology of nano-photocatalysts for industry, as well as designed and built a photocatalyst production line for industrial production. On the basis of these novel efficient nano-photocatalysts, they integrated photocatalysis, chemical oxidation, adsorption and low temperature plasma technologies, and developed a variety of air purification technologies and products for indoor confined space use. In addition, they collaborated with enterprises to design and build a large scale

production line of a photocatalytic air purifier, which has achieved industrialization.

Catalytic oxidation of formaldehyde and catalytic sterilization at room temperature: Formaldehyde is one of the most serious pollutants in indoor air in China. There are also some contaminations by pathogenic microorganisms in indoor air. These pollutants pose a serious hazard to human health. Research Center for Eco-Environmental Sciences, CAS, Institute of Process Engineering, CAS and Perking Yadu Air Pollution Control Technology Co., Ltd [78] have invented new highly dispersed supported noble metal catalysts for the catalytic oxidation of formaldehyde at room temperature, as well as a series of Ag loaded inorganic catalytic materials for catalytic sterilization at room temperature. They have also developed their large scale preparation technology. This invention has been industrialized in collaborating companies such as Perking Yadu Air Pollution Control Technology Co, Ltd. It has achieved good social and economic benefits.

3.4.4. Catalysis in water treatment

Photocatalytic degradation of toxic and refractory organic pollutants: Institute of Chemistry, CAS [122] has a number of achievements on the photocatalytic degradation of toxic and refractory organic pollutants by solar light. (1) They successfully achieved the effective photocatalytic degradation and mineralization of dye pollutants by TiO_2 under the irradiation of visible light, and proposed a mechanism of dye pollutant visible light photocatalytic degradation which is different from that of the UV photocatalytic reaction. (2) They designed and synthesized a series of novel Fe-N complexes and their supported visible light photocatalysts, which effectively activated H_2O_2 and O_2 , as well as degraded and mineralized toxic organic pollutants under the irradiation of visible light. In addition, they proposed the corresponding mechanism of photocatalytic reaction under visible light. (3) They successfully developed a TiO_2 -based visible light photocatalyst prepared using the binary synergistic modification of non-metallic boron and nickel oxide, which can effectively activate O_2 and degrade toxic organic pollutants such as chlorophenol under the irradiation of visible light. With the systematic and thorough investigation of the TiO_2 surface and its bulk modification, they clarified many controversial scientific problems.

Highly stable and refractory organic pollutants are important pollutants that adversely affect water quality in urban China. Harbin Institute of Technology invented a series of pollutant elimination methods by ozone heterogeneous catalytic oxidation. By utilizing special surface properties of a transition metal oxide, ozone can be converted to radicals with a strong oxidizing ability, which improves the decomposition efficiency of highly stable organic pollutants by 2 to 4 times over that of simple ozone oxidation. The ozone catalytic oxidation method can effectively eliminate highly stable organic pollutants in water, decrease water mutagenic activity, and significantly improve the safety of drinking water. At present, the integrated pollutant elimination technology of the ozone catalytic oxidation method is applied in our waterworks. It has significantly improved the water quality. Polluted water sources of class III

and IV can be treated to reach the drinking water standard.

3.4.5. Method for the improvement of energy efficiency in photocatalytic environmental pollution control

The efficient treatment of toxic and hazardous pollutants is a difficulty in international environmental engineering. Photocatalysis is considered as one of the most promising new technology to control these pollutants. However, a low energy efficiency restricts its practical application. In order to solve the key scientific problem, "How to improve the energy efficiency", Dalian University of Technology and Tsinghua University [123,124] explored methods to improve energy efficiency in photocatalytic environmental pollution control processes and investigated its applications. They obtained innovative results.

3.5. Coal-based syngas chemistry

Coal-based syngas chemistry refers to the use of coal and syngas as the raw materials for the chemical industry. By using coal, the industrial chain can be continued when oil reserves get depleted. By the development of suitable catalysts, hundreds and even thousands of chemical products and fuel oils can be produced. The industry has the properties of a long industry chain, large value-added opportunities, high correlation, good scale and economic benefits, and broad development prospects. In the past three decades, important progress has been made.

3.5.1. Methanol to olefins (MTO)

In the early 1980s, DICP investigated catalysts for the conversion of methanol or dimethyl ether to alkene and its process technology. In the 1990s, they successfully developed an inexpensive synthesis technology for a silicoaluminophosphate zeolite (SAPO-34), a microsphere catalyst preparation technology and a fluidized bed reactor process technology. They have completed the pilot-scale test. On the basis of the basic research and catalyst performance improvement, they developed a new generation of catalyst for the conversion of methanol or dimethyl ether to low carbon olefins, which improved the selectivity to olefins. DICP, Shanxi Xinxing Coal Chemical Industry Technology Development Company and SINOPEC Luoyang Petrochemical Engineering Corporation together completed a MTO industrial test with the scale of ten thousand tons, which was a first in the world. This was named the DMTO technology. The project scale and process performance have achieved a leading position in the world. The world's first set of a MTO industrial unit with a capacity of 1.8 million tons/year in Shenhua Company (Baotou) was successfully tested, and the methanol conversion was 100%. 2.96 tons of methanol can produce 1 ton of ethylene and propene. Later on, the DMTO unit was officially operated in a commercial operation stage. This is a complete set of technology for the mass production of petrochemical raw materials, such as ethylene and propene, from coal instead of petroleum oil [125].

3.5.2. Catalyst for coal-to-oil

In 1953, DICP did the pilot test of a circulating fluidized bed

for producing synthetic oil with a capacity of 3000 tons/year. Since the mass production of fossil oil, the investigation of synthetic oil was temporarily stopped. In the early 1980s, Shanxi Institute of Coal Chemistry, CAS resumed the research and development of the coal-to-oil technology [126,127], and made technological advances with a fixed bed two-stage synthesis process, a slurry phase synthetic oil technology, microspherical Fe-Cu-K/SiO₂ (20–150 μm) catalysts suitable for a low temperature slurry phase Fischer-Tropsch synthesis, and microspherical (30–150 μm) Fe-based catalysts suitable for a high temperature slurry phase Fischer-Tropsch synthesis. The space time yield reached 1.2–1.5 g/g. The production capacity of each ton of catalyst achieved 1500–1800 ton oil. The activity of this catalyst was over 10 times higher than that of the traditional fixed bed Fischer-Tropsch synthesis catalyst and 4–5 times higher than that of the low temperature slurry phase Fischer-Tropsch synthesis catalyst. In 2006, Synfuels China was established to form the technology supporting entity of our coal-to-oil industrial development. Three synthetic oil demonstration plants with the capacity of 160–200 thousand ton/year were built in Yitai, Luan and Shenhua companies. These have passed the acceptance test by China International Engineering Consulting Corporation, which shows that China has mastered an advanced efficient coal-to-oil industrial technology

3.5.3. Technology of syngas methanation to natural gas (SNG)

On the basis of the industrial application of the catalyst and technology for water-gas partial methanation under atmospheric pressure, DICP carried out comprehensive research and development of the catalyst and process technology for a coal-to-gas process at high temperature and under high pressure. They developed a series of methanation catalyst and carried out long term (8000 h) catalyst performance testing. The industrial testing verified the catalyst performance and the feasibility of the process technology. They have developed a complete set of processing software for a SNG industrial unit with the production capacity of 120 thousand m³ per day, and have integrated the production line of the catalyst for syngas methanation, which achieved mass production of the catalyst. This technology has satisfied all the conditions for the industrial application. The technology of syngas methanation (DNL-0901-S2M) passed the verification of Liaoning Science & Technology Department in 2011.

3.5.4. Coal-to-ethylene glycol

In collaboration with enterprise, Fujian Institute of Research on the Structure of Matter, CAS successfully developed a complete set of technology for the catalytic synthesis of oxalic ester from CO in the vapor phase with a ten thousand ton scale and the catalytic hydrogenation of oxalic ester to ethylene glycol [128–131]. Fujian Institute of Research on the Structure of Matter, CAS and Shanghai Jin Coal Chemical Technology Co, Ltd have sold the coal-to-ethylene glycol technology to Tongliao Jin Coal Chemical Co, Ltd. The world's first set of coal-to-ethylene glycol demonstration unit with an annual output of 200000 ton was established in Tongliao, Inner Mongolia. However, there is still a technical bottleneck in the process. With more effort, it is

expected that it will be the largest ethylene glycol production plant in China.

3.5.5. Natural gas desulfurization by the dry method

For use with natural gas, oil field-associated gases, coal gas, refinery gas and industrial gases containing H₂S, DICP initiated an investigation of H₂S mass transfer and successfully developed a high sulfur capacity catalytic oxidative desulfurization agent by the dry method. They studied DCL sulfur fixative of coal combustion and carried out production and industrial testing. They also developed the localization technology of a selective catalytic reduction DeNO_x catalyst for thermal power plants, as well as an impregnated activated carbon as a high sulfur capacity desulfurization agent of the dry method and its application. The successful promotion and application of the catalytic oxidation desulfurization agent resulted in desulfurization cost savings. At the same time, it reduces the secondary environmental pollution from the desulfurization process. At present, this technology has been applied in four major oil fields in China.

4. Conclusions and prospects

After many years of research and endeavor by catalytic colleagues, especially in the last three decades that saw rapid development, China has become an important contributor to catalysis. However, to further develop to become a regular contributor of important advances is the main mission for all our catalytic colleagues in the future.

Spurred by surface science, especially recently developed nano-science and technology, the exploration of catalytic nature and the development of catalytic theory are still the goals that scientists will pursue. Catalytic research will include new catalytic reactions, novel catalytic materials, and new catalytic characterization methods, especially in situ characterization methods in real time and with high space resolution. By combining computational chemistry with modern in situ physical chemistry methods such as ultra-high resolution analytical electron microscopy and in situ spectroscopy technology, we seek to better investigate the industrial catalyst. By learning and using the theory and technology of condensed matter physics, we will seek to develop novel catalysts and investigate their mechanisms, which are important research directions.

In view of the importance of catalytic science and technology in the national economy, the environment, and the quality of human life, the major catalytic research fields are closely tied to the urgent needs of the country, such as the optimized use of coal, petroleum oil, natural gas, hydrogen, environment, petrochemicals, energy, and so on.

Given that catalysis is an old discipline that has accumulated much academic and technical experiences, the development of the discipline requires us not to only focus on the discipline itself. We also need to develop interdisciplinary connections since there must be cross links between different disciplines, such as in the development of various functional materials. I believe there will be a prosperous new world with the efforts of our catalytic colleagues.

References

- [1] Editorial Committee of Chinese Chemical Society. Fifty Years of Chemistry in China: 1932–1982. Beijing: Sci Press (中国化学会编辑委员会. 中国化学五十年: 1932–1982. 北京: 科学出版社), 1985
- [2] Wang H L, Xin Q. *Appl Catal A*, 1999, 178: 133
- [3] Lin L W, Liang D B, Wang Q X, Cai G Y. *Catal Today*, 1999, 51: 59
- [4] Zhang D Y. Theoretical Study on Surface Bond in Heterogeneous Catalysis. In: Collection of Reports for the 3rd Conference of Department of Technical Science, Chinese Academy of Sciences (张大煜. 多相催化研究中的表面键理论. 见: 中国科学院第三次技术科学部学部大会报告汇编). 1960. 48
- [5] Zhang D Y, Guo X X. Highlights for Surface Bond Theory. In: Collection of Reports for Forum of Catalysis Theory, Dalian, Chinese Academy of Sciences (张大煜, 郭燮贤. 表面键理论的基本要点. 见: 中国科学院大连催化理论座谈会报告汇编). 1961. 4
- [6] Guo X X, Xin M, Zhai R S, Cao Y M, Zhang L H, Wang D Zh. *Progr Nat Sci* (郭燮贤, 辛梅, 翟润生, 曹玉明, 张林虎, 王德峰. 自然科学进展), 1994, 4: 665
- [7] Guo X X, Xin M, Zhai R S. *J Phys Chem*, 1994, 98: 7175
- [8] Fu G, Chen Z N, Xu X, Wan H L. *J Phys Chem A*, 2008, 112: 717
- [9] Tsai K R, Wan H L. In: Tsutsui M, Ishii Y, Huang Y Z eds. *Fundamental Research in Organometallic Chemistry*. New York: Sci Press, 1982. 1
- [10] Chen S Y, Lü X L, Peng Sh Y. *Chin J Catal* (陈诵英, 吕秀莲, 彭少逸. 催化学报), 1982, 13: 165
- [11] Min E Z. Research and Development of Industrial Catalysts: My Practice and Exploration. Beijing: China Petrochem Press (闵恩泽. 工业催化剂的研制与开发——我的实践与探索. 北京: 中国石化出版社), 1997
- [12] Min E Z. Way of Seeking in Industry Catalysis. Shijiazhuang: Hebei Edu Press (闵恩泽. 工业催化之路的求索. 石家庄: 河北教育出版社), 2003
- [13] Wu Y. Catalytic Chemistry. Beijing: Sci Press (吴越. 催化化学. 北京: 科学出版社), 1998
- [14] Wu Y, Yang X G. Modern Catalysis Principles. Beijing: Sci Press (吴越, 杨向光. 现代催化原理. 北京: 科学出版社), 2005
- [15] Wu Y. Fundamental and Applied Catalysis. Beijing: Chem Ind Press (吴越. 应用催化基础. 北京: 化学工业出版社), 2009
- [16] Fang X P, Li Sh B, Lin J Zh, Gu J F, Yang D X. *J Mol Catal (China)* (方学平, 李树本, 林景治, 顾靖芳, 杨得信. 分子催化), 1992, 8: 255
- [17] Fang X P, Li Sh B, Lin J Zh, Chu Y L. *J Mol Catal (China)* (方学平, 李树本, 林景治, 褚衍来. 分子催化), 1992, 6: 427
- [18] Chen P, Zhang H B, Lin G D, Hong Q, Tsai K R. *Carbon*, 1997, 35: 1495
- [19] Wu H, Yuan Q, Zhu B L. *J Chem Ind Eng (China)* (吴华, 袁权, 朱葆琳. 化工学报), 1984, 35: 283
- [20] Tang Y Q, Xie Y Ch, Gui L L. *Progr Nat Sci* (唐有祺, 谢有畅, 桂琳琳. 自然科学进展), 1994, 4: 642
- [21] Chen Y, Zhang L F. *Catal Lett*, 1992, 12: 51
- [22] Bao X H, Deng J F, Dong S Z. *Acta Chim Sin*, 1986, 44: 619
- [23] Shen Zh Q, Yang M J, Cai Y P, Shi M X. *Sci Chin, Ser B* (沈之荃, 杨慕杰, 蔡一平, 石明孝. 中国科学B辑), 1983, 13: 119
- [24] Shen Zh Q, Yang M J, Shi M X, Cai Y P. *J Polym Sci, Polym Lett Ed*, 1982, 20: 411
- [25] Zhang Y F, Chen X H, Shen Zh Q. *Inorg Chim Acta*, 1989, 155: 263
- [26] Shen Zh Q, Zhang Y F, Peng J D, Ling L. *Sci Chin, Ser B* (沈之荃, 张一烽, 彭建德, 凌琬. 中国科学B辑), 1989, 19: 1028
- [27] Li W Zh, Liang Ch H, Zhou W J, Qiu J Sh, Zhou Zh H, Sun G Q, Xin Q. *J Phys Chem B*, 2003, 107: 6292
- [28] Zhou W J, Zhou Z H, Song Sh Q, Li W Zh, Sun G Q, Tsiakaras P, Xin Q. *Appl Catal B*, 2003, 46: 273
- [29] Li W Zh, Liang Ch H, Qiu J Sh, Zhou W J, Han H M, Wei Zh B, Sun G Q, Xin Q. *Carbon*, 2002, 40: 791
- [30] Zhou W J, Song S Q, Li W Z, Zhou Z H, Sun G Q, Xin Q, Douvartzides S, Tsiakaras P. *J Power Sources*, 2004, 140: 50
- [31] Jiang L H, Sun G Q, Zhou Z H, Zhou W J, Xin Q. *Catal Today*, 2004, 93: 665
- [32] Jiang L H, Sun G Q, Sun Sh G, Liu J G, Tang Sh H, Li H Q, Zhou B, Xin Q. *Electrochim Acta*, 2005, 50: 5384
- [33] Zhou W J, Zhou B, Li W Z, Zhou Z H, Song S Q, Sun G Q, Xin Q, Douvartzides S, Goula M, Tsiakaras P. *J Power Sources*, 2004, 126: 16
- [34] Wu G, Chen Y S, Xu B Q. *Electrochem Commun*, 2005, 7: 1237
- [35] Zhao D, Xu B Q. *Angew Chem, Int Ed*, 2006, 45: 4955
- [36] Fu Q, Li W X, Yao Y X, Liu H Y, Su H Y, Ma D, Gu X K, Chen L M, Wang Z, Zhang H, Wang B, Bao X H. *Science*, 2010, 328: 1141
- [37] Pan X L, Fan Zh L, Chen W, Ding Y J, Luo H Y, Bao X H. *Nature Mater*, 2007, 6: 507
- [38] Xie X W, Li Y, Liu Zh Q, Haruta M, Shen W J. *Nature*, 2009, 458: 746
- [39] Qiao B T, Wang A Q, Yang X F, Allard L F, Jiang Zh, Cui Y T, Liu J Y, Li J, Zhang T. *Nat Chem*, 2011, 3: 634
- [40] Xin Q, Guo X X, Silvy R P, Grange P, Delmon B. *Proc Int Congr Catal*, 1988, 1: 66
- [41] Xin Q, Gao X T. *Progr Natural Sci*, 1995, 5: 317
- [42] Yan Y Sh, Xin Q, Jiang Sh C, Guo X X. *J Catal*, 1991, 131: 234
- [43] Xin Q, Luo M F. Modern Catalytic Research Methods. Beijing: Sci Press (辛勤, 罗孟飞. 现代催化研究方法. 北京: 科学出版社), 2009
- [44] Xin Q. Research Methods for Solid Catalysts. Beijing: Sci Press (辛勤. 固体催化剂研究方法. 北京: 科学出版社), 2005
- [45] Xin Q. In-Situ Technology in Research of Catalysis. Beijing: Peking Univ Press (辛勤. 催化研究中的原位技术. 北京: 北京大学出版社), 1993
- [46] Zhang W P, Xu Sh T, Han X W, Bao X H. *Chem Soc Rev*, 2012, 41: 192
- [47] Zhang L, Ren Y H, Yue B, He H Y. *Chem Commun*, 2012, 48: 2370
- [48] Wang Ch Y, Li W Zh. Six Decades of Applied Research on Heterogeneous Catalysis at Dalian Institute of Chemical Physics, CAS (王承玉, 李文钊. 中科院大连化物所多相催化应用研究六十年). 2010. 123
- [49] Mu R T, Fu Q, Jin L, Yu L, Fang G Z, Tan D L, Bao X H. *Angew Chem, Int Ed*, 2012, 51: 4856
- [50] Fan F T, Feng Zh Ch, Li C. *Acc Chem Res*, 2010, 43: 378
- [51] Zhao Y H, Sun K J, Ma X F, Liu J X, Sun D P, Su H Y, Li W X. *Angew Chem, Int Ed*, 2011, 50: 5335
- [52] Wang B, Ma X F, Caffio M, Schaub R, Li W X. *Nano Lett*, 2011, 11: 424
- [53] Wang H F, Liu Zh P. *J Am Chem Soc*, 2008, 130: 10996
- [54] Wang L Sh, Tao L X, Xie M S, Xu G F, Huang J S, Xu Y D. *Catal Lett*, 1993, 21: 35
- [55] Zhao D B, Kou Y, Min E Z. *Catal Today*, 2002, 74: 157
- [56] Yang G Y, Ma X F, Xu J. *J Am Chem Soc*, 2004, 126: 10542
- [57] Tong X L, Xu J, Miao H. *Adv Synth Catal*, 2005, 347: 1953
- [58] Chen Ch, Xu J, Zhang Q H, Ma Y F, Zhou L P, Wang M. *Chem Commun*, 2011, 47: 1336
- [59] Zhou L P, Yang G Y, Zhang W, Sun Zh Q, Gao J, Miao H, Chen Ch, Ma H, Li X Q, Zhang Q H, Wang F, Tong X L, Xu J. *Progr Nat Sci* (周利鹏, 杨贯羽, 张伟, 孙志强, 高进, 苗虹, 陈晨, 马红, 李晓强, 张巧红, 王峰, 全新利, 徐杰. 自然科学进展), 2007, 17: 281
- [60] Xi Z W, Ning Zh, Yu S, Li K L. *Science*, 2001, 292: 1139
- [61] Chen H, Li Y Z, Li R X, Cheng P M, Li X J. *J Mol Catal A*, 2003, 198: 1
- [62] Yuan M L, Chen H, Li R X, Li Y Z, Li X J. *Appl Catal A*, 2003, 251: 181
- [63] Ma H X, Chen H, Zhang Q, Li X J. *J Mol Catal A*, 2003, 196: 131
- [64] Jiang H Y, Yang C F, Li C, Fu H Y, Chen H, Li R X, Li X J. *Angew Chem, Int Ed*, 2008, 47: 9240
- [65] Shao Z P, Yang W Sh, Cong Y, Dong H, Tong J, Xiong G X. *J Membr Sci*, 2000, 172: 177
- [66] Yang W Sh, Wang H H, Zhu X F, Lin L W. *Top Catal*, 2005, 35: 155
- [67] Xu X C, Yang W Sh, Liu J, Lin L W. *Adv Mater*, 2000, 12: 195
- [68] Li Y S, Yang W Sh. *J Membr Sci*, 2008, 316: 3
- [69] Liu X L, Li Y S, Zhu G Q, Ban Y J, Xu L Y, Yang W Sh. *Angew Chem, Int Ed*, 2011, 50: 10636

Graphical Abstract

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Progress in catalysis in China during 1982–2012: Theory and technological innovations

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From 1982 to 2012, the major contributions of catalysis works (theory and technological innovations) in China are presented. The historical evolution of research and development work in catalysis in China is also described.

- [70] Yin Y Q, Hu B, Zhang W Q, Zhang Y H, Zhang J. The Metal Fragment Exchange Reaction. New York: Nova Sci Publishers, 2006
- [71] Xia Ch G, Tang Z H, Chen J, Zhang X Z, Li Z, Guo Y X. US Patent 7 244 854. 2007
- [72] Chen J, Tang Z H, Xia Ch G, Zhang X Z, Li Z. US Patent 7 560 599. 2009
- [73] Wang D E, Jiang H F, Zong X, Xu Q A, Ma Y, Li G L, Li C. *Chem Eur J*, 2011, 17: 127
- [74] Yan H J, Yang J H, Ma G J, Wu G P, Zong X, Lei Z B, Shi J Y, Li C. *J Catal*, 2009, 266: 165
- [75] Zhang J, Xu Q, Feng Zh Ch, Li M R, Li C. *Angew Chem, Int Ed*, 2008, 47: 1766
- [76] Zong X, Yan H J, Wu G P, Ma G J, Wen F Y, Wang L, Li C. *J Am Chem Soc*, 2008, 130: 7176
- [77] Ji N, Zhang T, Zheng M Y, Wang A Q, Wang H, Wang X D, Chen J G. *Angew Chem, Int Ed*, 2008, 47: 8510
- [78] Ding K L, Du H F, Yuan Y, Long J. *Chem Eur J*, 2004, 10: 2872
- [79] Ding K L, Wang Z, Wang X W, Liang Y X, Wang X S. *Chem Eur J*, 2006, 12: 5188
- [80] Long J, Hu J Y, Shen X Q, Ji B N, Ding K L. *J Am Chem Soc*, 2002, 124: 10
- [81] Wang X W, Ding K L. *J Am Chem Soc*, 2004, 126: 10524
- [82] Yang Q H, Han D F, Yang H Q, Li C. *Chem Asian J*, 2008, 3: 1214
- [83] Xie Y Ch, Tang Y Q. *Adv Catal*, 1990, 37: 1
- [84] Wang Ch Y, Li W Zh. Six Decades of Applied Research on Heterogeneous Catalysis at Dalian Institute of Chemical Physics, CAS (王承玉, 李文钊. 中科院大连化物所多相催化应用研究六十年). 2010, 40
- [85] Tian H J, Zhang T, Sun X Y, Liang D B, Lin L W. *Appl Catal A*, 2001, 210: 55
- [86] Tao K Y, Li W, Li H X, Qi X M. *Appl Catal A*, 1996, 139: 43
- [87] Xie Z K. Porous Catalytic Materials with New Structure and Improved Performance. Beijing: Sinopec Press (谢在库. 新结构高性能多孔催化材料. 北京: 中国石化出版社), 2010
- [88] Xiao F Sh, Han Y, Yu Y, Meng X J, Yang M, Wu S. *J Am Chem Soc*, 2002, 124: 888
- [89] Han Y, Wu S, Sun Y Y, Li D S, Xiao F Sh, Liu J, Zhang X Z. *Chem Mater*, 2002, 14: 1144
- [90] Wu S, Han Y, Zou Y C, Song J W, Zhao L, Di Y, Liu S Z, Xiao F Sh. *Chem Mater*, 2004, 16: 486
- [91] Xiao F Sh, Wang L F, Yin C Y, Lin K F, Di Y, Li J X, Xu R R, Su D S, Schlögl R, Yokoi T. *Angew Chem, Int Ed*, 2006, 45: 3090
- [92] Wang X Sh, Guo H Ch. ACS Symposium Series. Chapter 14. 2000. 738
- [93] Wang H F, Guo Y L, Lu G Zh, Hu P. *Angew Chem, Int Ed*, 2009, 48: 8289
- [94] Li H Y, Wang H F, Gong X Q, Guo Y, Guo Y, Lu G Zh, Hu P. *Phys Rev B*, 2009, 79: 193401/1
- [95] Wang J Z, Zhao L W, Shi H M, He J. *Angew Chem, Int Ed*, 2011, 50: 9171
- [96] Shi H M, He J. *J Catal*, 2011, 279: 155
- [97] Shi H, Yu C G, He J. *J Catal*, 2010, 271: 79
- [98] Zhang F Z, Zhao X F, Feng C H, Li B, Chen T, Lu W, Lei X D, Xu S L. *ACS Catal*, 2011, 1: 232
- [99] Peng J J, Deng Y Q. *Tetrahedron Lett*, 2001, 42: 5917
- [100] Peng J J, Deng Y Q. *New J Chem*, 2001, 25: 639
- [101] Yang H Z, Gu Y L, Deng Y Q, Shi F. *Chem Commun*, 2002: 274
- [102] Qiao K, Deng Y Q. *J Mol Catal A*, 2001, 171: 81
- [103] Shi F, Deng Y Q. *J Catal*, 2002, 211: 548
- [104] Shi F, Zhang Q H, Ma Y B, He Y D, Deng Y Q. *J Am Chem Soc*, 2005, 127: 4182
- [105] Tian Zh J, Liang D B, Lin L W. *Chin J Catal* (田志坚, 梁东白, 林励吾. 催化学报), 2009, 30: 705
- [106] Tian Zh J, Wang L, Xu Zh Sh, Xu Y P, Hu Sh, Qu W, Wang B Ch, Lin L W (田志坚, 王磊, 徐竹生, 徐云鹏, 胡胜, 曲炜, 王炳春, 林励吾). CN Patent 1 721 074. 2006
- [107] Wei Y, Tian Zh J, Gies H, Xu R Sh, Ma H J, Pei R Y, Zhang W P, Xu Y P, Wang L, Li K D. *Angew Chem, Int Ed*, 2010, 49: 5367
- [108] Ma H J, Tian Zh J, Xu R Sh, Wang B Ch, Wei Y, Wang L, Xu Y P, Zhang W P, Lin L W. *J Am Chem Soc*, 2008, 130: 8120
- [109] Wang L, Xu Y P, Wei Y, Duan J Ch, Chen A B, Wang B Ch, Ma H J, Tian Zh J, Lin L W. *J Am Chem Soc*, 2006, 128: 7432
- [110] Xu Y P, Tian Zh J, Wang Sh J, Hu Y, Wang L, Wang B Ch, Ma Y Ch, Hou L, Yu J Y, Lin L W. *Angew Chem, Int Ed*, 2006, 45: 3965
- [111] Liang Q H, Wen X W, Lin Z Q. Overview on Science and Technology of Contemporary China. Beijing: China Sci Technol Press (梁清海, 文兴吾, 林子卿. 当代中国科学技术总览. 北京: 中国科学技术出版社), 1992
- [112] National Office for Science and Technology Award. The National Three Awards Catalog (Annual Directory). Beijing: China Science and Technology Press (国家科学技术奖励工作办公室资料. 国家三大奖目录(年度目录). 北京: 中国科学技术出版社)
- [113] He H, Li J H, He H, Shangguan W F. Environmental Catalysis: Principles and Applications. Beijing: Sci Press (贺泓, 李俊华, 何洪, 上官文峰. 环境催化——原理及应用. 北京: 科学出版社), 2008
- [114] Chen Y X, Liu Zh Sh, Wang X, Yang Y. *Petrochem Safety Environ Protect Technol* (陈玉香, 刘忠生, 王新, 杨英. 石油化工安全环保技术), 2009, 25(3): 48
- [115] Zhao M, Li X, Zhang L H, Zhang C, Gong M C, Chen Y Q. *Catal Today*, 2011, 175: 430
- [116] Chen Y Q, Guo J X, Gong M Ch (陈耀强, 郭家秀, 龚茂初). CN Patent 1 824 384A. 2006
- [117] Gong M Ch, Chen Y Q, Xu Q H, Li X W (龚茂初, 陈耀强, 许清淮, 李孝维). CN Patent 1 408 645A. 2003
- [118] Chen Y Q, Gong M Ch, Wang M, Zhao M (陈耀强, 龚茂初, 王敏, 赵明). CN Patent 1 817 447A. 2006
- [119] Lü Zh, Chen Y Q, Gong M Ch, Zhao M (吕臻, 陈耀强, 龚茂初, 赵明). CN Patent 1 695 798A. 2005
- [120] Li H Y, Wang H F, Guo Y L, Lu G Z, Hu P. *Chem Commun*, 2011: 6105
- [121] Zhan W Ch, GUO Y, Gong X Q, Guo Y L, Wang Y Q, Lu G Zh. *Sci Sin*

- (Chim) (詹望成, 郭耘, 龚学庆, 郭杨龙, 王艳芹, 卢冠忠. 中国科学: 化学), 2012, 42: 433
- [122] Chen C C, Ma W H, Zhao J C. *Chem Soc Rev*, 2010, 39: 4206
- [123] Yu H T, Quan X. *Progr Chem* (于洪涛, 全燮. 化学进展), 2009, 21: 406
- [124] Zhang L W, Zhu Y F. *Catal Sci Technol*, 2012, 2: 694
- [125] Ondrey G. *Chem Eng*, 2011, 118(2): 16
- [126] Zhang C H, Yang Y, Teng B T, Li T Z, Zheng H Y, Xiang H W, Li Y W. *J Catal*, 2006, 237: 405
- [127] Teng B T, Chang J, Zhang C H, Cao D B, Yang J, Liu Y, Guo X H, Xiang H W, Li Y W. *Appl Catal A*, 2006, 301: 39
- [128] Yao Y G, Lin L, Pan P B, Li Zh J, Zhou Zh F, Yang J X, Tan Y Y (姚元根, 林凌, 潘鹏斌, 李兆基, 周张锋, 杨锦霞, 覃业燕). CN Patent 102 463 122. 2012
- [129] Yao Y G, Yang J X, Li Zh J, Pan P B, Zhou Zh F, Lin L, Tan Y Y (姚元根, 杨锦霞, 李兆基, 潘鹏斌, 周张锋, 林凌, 覃业燕). CN Patent 102 247 847. 2011
- [130] Yao Y G, Lin L, Pan P B, Li Zh J, Zhou Zh F, Yang J X, Tan Y Y (姚元根, 林凌, 潘鹏斌, 李兆基, 周张锋, 杨锦霞, 覃业燕). CN Patent 102 139 213. 2011
- [131] Li Zh J, Yao Y G, Pan P B, Lin L, Zhou Zh F, Tan Y Y, Cheng J K (李兆基, 姚元根, 潘鹏斌, 林凌, 周张锋, 覃业燕, 程建开). CN Patent 101 869 838. 2010

中国催化三十年进展: 理论和技术的创新

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摘要: 中国的催化科学与技术始于 20 世纪初, 经过先辈的努力使其经历了发展初期和稳定发展阶段, 在历史上由于人为因素的严重破坏使其处于停滞并失去了宝贵的十余年大好发展时机。20 世纪 80 年代, 中国催化事业进入了快速发展时期。在这一历史时期, 迅速恢复和建立了以中科院、高校和产业部门研究院组成的三个方面军的研究队伍。开展了以形式动力学为主要方法和手段的研究, 基础研究方面提炼出新催化材料、新催化表征方法和新催化反应为主要研究方向。表面科学、纳米科学的出现大大促进和深化了催化的基础探索, 催化正从艺术走向科学……。在应用催化研究方面, 在不同历史时期结合国家重大需求, 在煤、石油、天然气优化利用, 先进材料, 环境, 人类健康等领域做出了重大贡献。当前的中国已成为催化大国并正在走向催化强国。

关键词: 催化; 进展; 理论; 技术

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1. 前言

建国以来, 以张大煜、蔡镭生、蔡启瑞、余祖熙、闵恩泽等老一辈科学家为代表的中国科学院、高校和产业部门的研究院构成了催化研究队伍的三个方面军。但其在文革期间遭到严重破坏: 研究设备残缺陈旧, 研究队伍断层, 经费短缺^[1~3]。自 20 世纪 80 年代改革开放以来, 经过中科院、教委和科委精心策划, 先后筹建了以郭燮贤、辛勤、徐奕德、熊国兴等为学术带头人的催化基础国家重点实验室和林励吾、李文钊、王弘立、郑禄彬等中国科学院大连化学物理研究所(以下简称大连化物所)团队; 以蔡启瑞、万惠霖、张鸿斌等为学术带头人的固体表面物理化学国家重点实验室和厦门大学团队; 以彭少逸、钟炳、陈诵英等为学术带头人的煤转化国家重点实验室和中国科学院山西煤炭化学研究所团队; 以李树本、殷元骥、王弘立、陈英武、沈师孔、寇元等为学术带头人的羰基合成和选择氧化国家重点实验室和中科院兰化所团队; 以吴越、谢小凡、张曼征等为学术带头人的中科院长春应化所团队; 以邓景发、高滋、郑绳安、李全芝等为学术带头人的复旦大学团队; 以庞礼、

李宣文、谢有畅、林炳雄等为学术带头人的北京大学团队; 以陈懿、须沁华、颜琪洁等为学术带头人的南京大学团队; 以蔡镭生、郑作光、丁莹茹、甄开吉、吴通好等为学术带头人的吉林大学团队; 以金松寿、郑小明、沈之荃等为学术带头人的浙江大学团队; 以朱启明等为学术带头人的清华大学团队; 以张鏐、赵九生、秦永宁、钟顺和等为学术带头人的天津大学团队; 以李赫晷、项寿鹤、陶克毅等为学术带头人的南开大学团队; 以王祥生、蔡天锡、何仁、金子林等为学术带头人的大连理工大学团队; 以刘化章等为学术带头人的浙江工业大学团队; 以黄钟涛、曾绍愧等为学术带头人的华南理工和中山大学团队; 以汪仁、李承烈等为学术带头人的华东理工大学团队; 以魏可镁、付贤智等为学术带头人的福州大学团队; 以闵恩泽、李大东、何鸣元、汪燮卿、舒兴田等为学术带头人的石油化工科学研究院团队; 以张式、关兴亚、陈庆龄等为学术带头人的上海石油化工研究院团队; 以胡永康、韩崇仁等为学术带头人的中石化抚顺石油化工研究院团队; 以毛炳权、刘新香、杨元一等为学术带头人的北京化工研究院团队。从而形成了以上述团队为代表的一批高素质的中国催化研究队伍。

中国石化总公司、国家基金委的建立进一步促进了中国催化科学技术的发展. 研究生制度的恢复促进了催化人才培养,造就了一批催化界的精英. 在这样一批学术带头人的精心策划和努力下,全方位地开展国际合作,大批人被选送出国学习、工作、吸收先进国家的科学技术,他们之中相当多的人成长为遍布世界各发达国家的精英.

为使中国催化界走向国际催化学术舞台,中国催化界学者积极参加和主办国际学术会议,先后主办了“中日美催化会议”(后来发展成为“泛太平洋国际催化会议”)、“国际溢流学术会议”、“催化和膜科学大会”等. 推动、签订了诸多同日本、欧洲、美国、俄罗斯的双边和多边等国际科技合作项目.

鉴于石油资源的日趋匮乏,李文钊等组织了“天然气转化利用”国家八五计划项目. 为了争取研究经费、凝练学术命题和聚集人才,郭燮贤、蔡启瑞、彭少逸、闵恩泽、陈懿等人策划了“煤、石油、天然气优化利用的科学基础”八五攀登项目,该项目得到中石化和国家基金委的资助. 它是国家当时对催化领域的最大支持项目,其命题也是中国在相当一段历史时期的永恒主题,后来的九五重大、重大基金、“973”、“863”等项目给催化科学技术的发展以极大的支持. 在这期间创刊(复刊)了“催化学报”、“分子催化”、“燃料化学学报”、“天然气化学”“石油学报”、“石油炼制”“工业催化”、“石油化工”等主流催化杂志;恢复成立了催化委员会及常设秘书处;设立了中国催化终身成就奖和青年奖,2010年又增设了面向35岁以下青年科学家的“中国催化优秀青年奖”;确立了每两年举办一次的全国催化会议,现已举办了14届,参会人数从百余人发展至今1500余人,促进了学术和技术交流. 目前,我国同国际上主要催化大国、强国建立了实质性的合作关系;几乎所有国际催化主流杂志都有中国催化学者任编委和国际顾问;亚太催化委员会的秘书处常设在中国;蔡启瑞、郭燮贤、陈懿、何鸣元和李灿代表中国催化学会先后任国际催化理事会理事;2004年李灿当选国际催化理事会副主席,2008年升任主席,这是中国催化学者第一次当选国际催化理事会主席,表明中国催化受到国际催化界的重视. 上述种种举措和老一代催化界精英们追求卓越的奋发努力和献身精神为造就现今中国催化界的辉煌奠定了基础.

2. 催化基础研究

2.1. 催化理论的探讨

20世纪80年代科学的春天到来,得益于改革开放政策的支持,我国催化领域的学者通过国内外学术交流,接触国际催化理论的新思想,把注意力集中在催化新材料、新反应、新表征方法的开拓研究上. 自从张大煜先生^[4,5]提出“表面键”概念,并在多年工业催化剂研发的基础上提出了“催化剂库”的概念,阐述了工业催化剂研发中催化剂移植的作用后,陈荣、郭燮贤等^[6]发表了“化学吸附覆盖度和动力学关系”,认为空的活性中心对反应物分子的活化也起重要作用. 继之,郭燮贤等^[7]研究了吸附促进脱附机理,即“AAD机理”,进一步研究了吸附分子与活性中心之间的相互作用. 蔡启瑞、万惠霖等^[8,9]分别对合成气制乙醇催化反应的中间物种、机理和低碳烷烃氧化反应的活性物种开展了系统性的研究. 彭少逸等^[10]则提出超细粒子催化剂对CO加氢产物分布的解释及惰性气体脱氧剂的研制发挥了重要作用. 闵恩泽^[11,12]指导开展新催化材料、催化新反应和新反应工程的导向性基础研究(包括非晶态合金、纳米分子筛等),为炼油、石油化工催化剂制造技术奠定了基础,同时他还指导化纤单体己内酰胺成套绿色制造技术的开发. 由于对我国石油炼制、石油化工等的巨大贡献,闵恩泽荣获“中国催化成就奖”和2007年度“国家最高科学技术奖”,成为中国催化界的泰斗. 林励吾等^[3]对多金属重整、加氢异构裂化、长链烷烃脱氢等工业过程催化剂的活性相及其调变规律的系统研究结果在工业上取得了成功的应用,继闵恩泽之后也获得“中国催化成就奖”. 吴越等^[13–15]对氧化物及复合氧化物催化剂的活性相结构和相互作用模型进行了深入系统的研究. 周望岳、尹元根、李树本等针对当时国家的需求开展了丁烯氧化脱氢制丁二烯新反应的研究. 李树本等^[16,17]研究的甲烷氧化偶联制烯烃用W-Mn-SiO₂系催化剂处于当时世界先进水平,受到同行的重视.

蔡启瑞、张鸿斌等^[18]开展了在固氮酶作用下和铁催化剂作用下固氮成氨以及碳纳米管合成的研究. 吴华、袁权、朱葆琳等^[19]开展了催化剂颗粒的工程设计基础——活性非均匀分布催化剂颗粒性能的研究. 唐有祺、谢有畅等^[20]在国际上首先发现表面单层分散现象并进行了系统深入的研究. 陈懿等^[21]提出氧化物催化剂的嵌入模型,对氧化物催化剂制备规律进行了系统研究. 梁娟、李赫晷、须沁华、高滋、林炳雄、庞文琴等分别对分子筛多孔材料的结构、表面酸性及催化性能和制备规律进行了深入系统研究. 邓景发等^[22]对非晶态和银催化剂表面物种进行了深入研究. 刘汉范进行了高分子稳

定金属纳米簇的合成及催化研究. 沈之荃等^[23–26]进行了稀土催化剂在分子合成中的应用研究: 进行了稀土催化剂定向聚合研究, 提出用稀土化合物作双烯烃定向聚合催化剂的组分, 发展了 Z-N 催化合成顺丁橡胶三元镍系催化剂, 成为中国万吨级顺丁橡胶聚合工艺的基础, 将稀土络合催化聚合研究推进到炔烃、环氧烷烃、环硫烷烃、交脂内脂和极性单体等聚合以及固定二氧化碳制备聚碳酸酯等新领域. 辛勤和孙公权等^[27–33]在直接醇类燃料电池电极催化剂研究中率先将多壁碳纳米管用于电催化剂载体, 发展了制备高含量多金属催化剂的 EG 方法, 采用超高分辨分析电镜显微学技术系统深入研究了纳米粒子大小、微区组成和形貌对电催化性能的影响规律. 这是催化技术与燃料电池电极交叉研究的创新成果, 相关论文引起国内外同行的大量引用和认同. 徐柏庆等^[34,35]发现单壁碳纳米管用作 Pt 电催化剂载体, 显著提高了 Pt 电催化剂的活性和稳定性, 并通过与多壁碳纳米管和常规碳黑进行对比, 为发展低贵金属纳米结构催化剂提供了新思路. 包信和、潘秀莲和傅强等^[36,37]利用纳米合成技术(如碳纳米管的剪裁、碳纳米管内组装金属催化剂、Pt/FeO 催化剂制备和调控技术等)、超高分辨分析电镜等新技术研究了纳米粒子的大小、形貌、微区组成、微环境对催化剂性能的影响规律, 并同密度泛函(DFT)等计算化学方法相结合, 提出的“限域效应”概念较好地解释了实验结果. 申文杰等^[38]合成晶面择优取向的 Co_3O_4 , 发展了氧化物催化剂的形貌控制技术; 张涛团队^[39]首次制备出氧化铁担载的单原子铂催化剂, 以 CO 氧化反应为探针, 发现单原子铂催化剂在相同条件下 CO 氧化活性高于纳米铂催化剂, 并与刘景月、李隽等合作, 利用超高分辨电镜和 DFT 计算对负载型单原子催化剂的结构进行了研究, 从而提出了单原子催化的新概念.

2.2. 催化剂表征新方法的建立和应用

催化理论的深化是同现代表征技术、计算化学、材料科学尤其是 20 世纪 90 年代发展起来的纳米科学密切相关. 所以, 中国催化界同仁始终十分重视新表征技术的发展. 辛勤等^[40–45]利用双分子探针的原位红外光谱方法研究硫化态 Co-Mo/ Al_2O_3 催化剂, 发现 Co-Mo 活性相之间的氢溢流作用, 该方法可有效地研究活性相间的相互作用和反应机理(在第九届国际催化大会的总结报告中被评为催化研究方法重要进展之一); 他们发展了系列原位分子光谱方法, 先后被国内外百余实验室采用, 编撰出版了六本专著, 促进了催化原位表征技术在国内外

的普及推广. 李灿等研发了紫外拉曼光谱技术, 并将其应用于催化材料研究, 发现紫外拉曼光谱是探测金属氧化物表面层物相的一种灵敏技术, 建立了鉴定杂原子分子筛活性中心的紫外共振拉曼光谱表征新方法, 在国际上最早将紫外拉曼光谱应用于催化研究, 取得了重要进展; 利用紫外共振拉曼光谱首次获得钛硅分子筛中骨架钛物种存在的直接证据, 建立了国际公认的鉴定微孔和中孔分子筛骨架中过渡金属杂原子的拉曼光谱研究方法; 在国际上首次对分子筛的合成过程实现了原位紫外共振拉曼光谱研究, 发现了催化材料合成的重要转化过程和活性中心中间物种, 提出了催化材料合成的机理; 发现许多氧化物的表面与体相结构不同, 尤其在重要的光催化剂氧化钛体系中, 基于紫外拉曼光谱的研究, 提出“表面异相结增强光催化活性”的新概念, 并将紫外拉曼光谱仪推向产业化, 使我国拉曼光谱的催化表征研究处于国际领先水平. 包信和等^[46]、贺鹤勇等^[47]将原位固态 NMR 技术应用于催化剂和催化反应研究(多孔材料的酸性表征、中间物种识别等), 取得了新进展. 丁莹茹、林励吾、章素、沈俭一等发展了原位穆斯堡尔谱, 并用于催化剂的原位表征(见文献[48]). 光发射电子显微镜(Photoemission Electron Microscopy, PEEM) 是以紫外光或 X 射线来激发固体表面原子中的电子, 采用电磁透镜系统记录光电子发射并进行成像研究, 是一种对表面结构、电子态、化学反应等表面物理化学性质进行原位、动态研究的新技术, 在化学、物理、材料等研究领域有着重要的应用. 现有的 PEEM 空间分辨能力一般在 20–50 nm 间. 众所周知, 许多表面的物理和化学过程都是发生在非常小的空间尺度上, 例如 10 nm 以下. 现有的 PEEM 空间分辨能力大大限制了 PEEM 的广泛应用. 大连化物所包信和、傅强等^[49]首次将我国科学家自主研制的深紫外激光光源(DUV) 应用于 PEEM 技术中, 利用深紫外激光的高能量、高强度等特点获得了 3.9 nm 的空间分辨率, 这是目前国际上报道的最高水平, 同时实现了 0.102 eV 的能量分辨率. 该系统已成功应用于催化、材料、能源等领域的原位和动态观察, 实现在变温和气氛条件下的表面过程研究, 在某些领域中显示了不可替代的作用. 与常规拉曼光谱相比, 紫外拉曼光谱具有灵敏度高和避开荧光干扰等优势, 同时由于很多化合物的电子吸收带在紫外区, 还可以进行共振拉曼光谱的研究, 已被应用于催化、材料以及生命科学等领域, 紫外拉曼光谱的研究越来越受到人们的关注. 但这些工作中所用的激光光源大都是 200 nm 以上的紫外激光. 发展

激光波长更短的拉曼光谱一直是科学家们追求的目标。Sanford Asher 等发展了波长低至 193 nm 的深紫外拉曼光谱,对蛋白质的二级结构进行了深入地研究(见文献[2])。大连化物所在国际上最早将紫外拉曼光谱应用于催化及材料科学研究,利用紫外共振拉曼光谱技术解决了一系列重要分子筛材料研究的科学难题。在国家重大科研装备研制项目的支持下,中科院物理化学技术研究所和中科院大连化物所利用 KBBF 晶体对 1064 nm 激光进行 6 倍频输出获得 177.3 nm 的激光。利用我国自主研制的 177.3 nm 深紫外激光光源,采用外光路椭圆反射深紫外区收集镜和深紫外区 170~400 nm 光谱响应的三联光栅成像单色仪研制出国际上首台 177.3 nm 深紫外区拉曼光谱仪、193~240 nm 波长连续可调的共振拉曼光谱仪,并将其应用于催化材料、半导体材料等领域,初步的结果已显示出深紫外拉曼光谱独特的优势,有望在宽禁带半导体以及分子筛含铝、镓原子等活性位研究中发挥巨大作用。李灿、冯兆池等^[50]研发的深紫外拉曼光谱仪为催化剂表征提供了新手段。傅强、李微雪和包信和等^[36,51,52]将 DFT 计算和实验相结合,研究了“纳米氧化物-金属”的界面催化机理,发现 Pt 与 FeO 纳米岛界面之间存在强相互作用。利用这种强相互作用可以稳定配位不饱和的高活性铁物种,具有很好的低温催化氧化 CO 活性。文章发表后,美国 C&E News、英国 Chemistry World,以及中国科学基金以“让催化剂设计的梦想照进现实”为题给予了专题报道。该工作对于如何优化催化剂的设计,推进催化基础理论研究的进展,具有重要启发价值。合成气转换的选择性是多相催化反应里最具挑战性的课题之一,其中关键的科学问题有 CO 活化、碳链增长、含氧化物生成、以及催化剂积碳失活等。李微雪等人利用 DFT,以 Rh, Co 催化剂为对象,对该反应中的重要中间体甲酰基展开研究。研究发现,甲酰基作为一种重要的中间体,不单是生成含氧化物的重要中间体,而且也是碳链增长的重要中间体。该结果修正并补充了人们长期以来公认的合成气转化中含氧化物经由 CO 插入、碳链增长经由烷基偶联的机理。

刘智攀等^[53]采用新发展的过渡态搜索方法,以乙醇燃料电池催化机理为背景,研究了计算复杂反应选择性的理论方法,考察了 3 种不同 Pt 表面上乙醇的化学反应,包括乙醇所有的 C-C, C-O 键断裂, O-H 或 C-H 键在催化剂表面的断键次序,以及不同中间产物的稳定性。理论结果首次发现了乙醇在 Pt 表面协同断 C-H, O-H 键的动力学优先,解释了乙醇氧化选择性的关键问题。提出并

解释了乙醇氧化的表面敏感效应,证明了 Pt(100) 面独有的全氧化乙醇的能力,已有部分结果被实验和其他理论计算证实。该发现改变了传统表面科学中得出的一些基本认识。

目前,国内催化界主流实验室已能在较高层次上掌握原位 X 射线衍射、能谱、分子光谱、磁共振和超高分辨分析电镜等催化剂表征技术,计算化学在催化研究中也得到广泛应用,水平有了实质性的提高。

2.3. 开发的新催化反应

在国内外热衷于发展甲烷氧化偶联制烯烃的热潮中,王林胜、谢茂松和徐奕德等^[54]首先发现甲烷在无氧条件下可在分子筛负载的催化剂上芳构化生成芳烃和氢气,引起国内外催化界的重视,进一步与包信和、林励吾等合作进行了系统深入研究,初步确认与分子筛骨架发生交换作用的双核钼物种为该反应的活性中心,并提出反应机理。寇元等^[55]提出了多相催化剂液相负载的新设计思想,将纳米粒子催化剂“固定”在离子液体中,而不是负载在固体表面上以创造出三维的多相催化剂;费托合成是煤制液体燃料的关键技术,但催化剂效率低,采用此方法制备的金属纳米粒子催化剂,在水相反应条件下,反应温度降低 100 °C,效率却提高了十多倍。该成果已技术转让给企业。徐杰等^[56–59]在开展烃类选择氧化催化剂活性相结构、催化剂表面有机修饰效应、设计有机含氮非金属系列催化体系的研究基础上,成功进行了山梨醇制乙二醇、环己烷氧化制环己酮、对二甲苯(PX)氧化制对苯二甲酸(PTA)等过程的工业应用研究。其中,利用醌类化合物为电子转移助剂与 *N*-羟基邻苯二甲酰亚胺(NHPI)组成非金属有机催化体系,这是第一个不使用计量还原剂和自由基引发剂的用于温和条件下烃类氧化反应的有机催化体系。继而利用邻菲罗啉、吡啶黄、甲基紫、甲基蓝等的含氮正离子,在 NHPI(或少量 NaBr 或 Br₂)的存在下,实现烃类氧化过程中的氧化-还原循环。所开发的非金属催化体系在环己烷氧化制环己酮关键技术开发上取得进展,成功完成 7 万吨/年规模的工业化应用试验。奚祖威团队^[60]于 2001 年发现用过氧化氢丙烯环氧化“反应控制相转移催化过程”,发明了一类兼有均相催化与多相催化优点的杂多酸催化剂,为解决均相催化剂难以分离的关键问题提供了一条新途径。相关技术正在工业开发中。李贤均等^[61–64]在水溶性有机金属配合物催化研究中,提出了烯烃氢甲酰化的两相催化体系中“介稳态胶束-离子对作用机理”、“两相界面分子自组装和烯烃氢甲酰化的高区域选择性关系”的理论解释,

并将乙烯氢甲酰化生产丙醛和正丙醇等过程工业化。杨维慎、熊国兴和林励吾^[65–69]在国际上较早地开展了无机膜催化分离一体化的规律性研究,设计合成了具有国际领先水平的 $\text{Ba}_{0.5}\text{Sr}_{0.5}\text{Co}_{0.8}\text{Fe}_{0.2}\text{O}_{3-\delta}$ 透氧膜材料;实现了膜反应器中烃类部分氧化制合成气或氢,甲烷氧化偶联制乙烯以及乙烷氧化脱氢制乙烯等。杨维慎等在国际上率先应用微波合成技术成功地合成了无缺陷分子筛膜,用于乙醇、高碳醇的脱水并实现产业化;探索新型基于纳米分子筛粒子的混合基质渗透气化膜,有望在第二代生物燃料(丁醇)的高效富集中取得重要应用。殷元骐等^[70]对多核金属簇化合物的合成、结构表征及催化性能进行了深入的研究,在不对称羰基化和烯烃羰基化等反应实现了工业应用。夏春谷和陈静^[71,72]实现了国际上首例离子液体催化甲醛合成三聚甲醛的工业试验,以及国内首个离子液体催化环氧化合物和 CO_2 环加成合成环状碳酸酯的工业应用。李灿等^[73–76]启动太阳能光催化制氢和转化 CO_2 的研究,在基础研究方面取得进展,并牵头组织中国科学院太阳能行动计划。2008 年张涛团队^[77]首次发现在镍促进的碳化钨催化剂上纤维素可以被高选择性地转化为乙二醇的新反应,转化率可达 100%,乙二醇收率达 61% 以上;相关技术正在工业开发中。

2.4. 催化新材料的应用和开发

闵恩泽、宗保宁等研发的“非晶态合金催化剂和磁稳定床反应工艺的创新与集成”包括非晶态合金催化剂和磁稳定床反应工艺。将晶态催化剂的结构非晶化,使广泛应用的雷尼镍催化剂加氢性能产生质的飞跃。通过加入原子半径大的稀土提高晶化势能垒,然后用碱抽提除铝制成多孔催化剂,突破了非晶态合金作为实用催化材料热稳定性差、比表面积小的限制。开发关键生产设备,优化生产工艺,建成百吨级非晶态镍生产装置。实现了高效链式操作状态的控制和均匀磁场的放大,提出了不同反应所适用的工艺流程。非晶态镍已用于己内酰胺加氢精制过程替代进口雷尼镍;用于改造国外己内酰胺氧化精制技术为加氢精制;部分替代 Pd/C 催化剂用于苯甲酸加氢过程;还用于多家药物中间体和葡萄糖加氢的生产企业。

丁奎岭等^[78–81]在基于组合方法与组装策略的新型手性催化剂研究方面,系统地将不对称活化和毒化、手性传递和放大等概念与组合化学方法结合,进行手性催化剂库的设计与评价,发展了多个系列新型、高效、高选择性手性催化剂,发现并阐明了催化体系中的不对称放大效应、添加物的活化作用及其机制等;基于分子组

装原理,首次提出了手性催化剂“自负载”概念,实现了包括羰基-烯、氧化和氢化等在内的多个非均相催化反应的高选择性、高活性,为手性催化剂的负载化开辟了新思路,为多种手性药物关键中间体的合成提供了有效的方法。李灿和杨启华等^[82]在国内较早开展多相手性催化方面的研究并取得重要研究进展,分别在纳米粒子表面、乳液催化体系和纳米反应器中的手性催化方面取得新进展,特别是利用纳米孔道的空间限阈效应及孔道微环境的修饰使纳米孔道内的手性催化剂表现出比均相催化剂更高的对映选择性和活性,实现了纳米反应器中的手性催化,在国际催化学术界产生重要影响。

谢有畅等^[83]根据发现的自发单层分散原理,广泛应用于催化剂、吸附剂和纳米材料研究中。将 CuCl 单层分散在分子筛表面,制得 CO 高效吸附剂,使我国变压吸附分离 CO 技术跃居世界领先水平;进一步开发出空分制氧高效吸附剂,此吸附剂用于大型变压吸附空分制氧,使我国变压吸附空分制氧技术达国际先进水平。舒兴田和何鸣元等开发成功 ZRP-1 分子筛,系采用 REY 分子筛作晶种,异晶导向直接合成晶体内含稀土元素和磷元素的,具有 Pentasil 结构的 ZRP-1 分子筛。稀土元素在分子筛晶格内起到稳定骨架结构的作用,使分子筛在水热条件下保持晶格结构的完整性,从而抑制或减缓分子筛的脱铝失活过程。稀土元素的引入使 ZRP-1 分子筛的孔径比 HZSM-5 分子筛更窄,并具有孔径约 4 nm 的二次中孔体系。孔径较大的二次孔为裂化原料油中的大分子烃类提供一定的裂解空间,从而提高了重质油转化能力。CHZ(SRNY) 分子筛催化剂的研究获国家创造发明二等奖; β 分子筛及其新合成方法获 1999 年国家发明三等奖。

杨宝山、周业慎和张涛等历时四十年研制成功的航天系列肼分解催化剂,解决了航天飞行器姿态和轨道控制的难题,是航天技术的一大飞跃(见文献[84])。张涛等^[85]采用复合氧化物取代金属催化剂,获得了高浓度过氧化氢分解的高效催化剂。拓展了航天航空催化技术应用的新领域,利用过氧化氢催化分解作为化学激光引射气源,发明了耐高温氧化的过氧化氢复合氧化物催化剂和环式薄层催化分解反应器,解决了大规模工程应用中反应物床层均匀分布和热管理的问题,实现了无毒催化分解技术的首次工程应用,为我国化学激光发展做出重要贡献。李赫晔等^[86]发明了不用有机胺模板剂合成 NKF 分子筛 (ZSM-5) 的新合成方法,大大降低了原料成本,并解决了使用有机胺所带来的环境污染问题;该法

生产的分子筛开发的多种工业催化剂已在生产中使用。徐龙伉和王清遐等发明了“复合模板剂组装”,“晶化速率控制”等多孔材料合成新方法,成功合成出 MCM-22, MCM-49, ZSM-35, 以及 MCM-22/ZSM-35 和 ZSM-5/ZSM-11 等系列超细及共结晶分子筛材料,解决了分子筛可控合成、功能化及工业化等技术关键,开发成功了催化干气制乙苯;(2) 醛氨缩合生产吡啶;(3) 液化气芳构化生产 BTX 芳烃/高辛烷值汽油等多个过程新型高效催化剂及成套技术,并获大规模推广应用,为石油与化学工业的可持续发展提供重要科技支撑(见文献[87])。肖丰收等^[88–91]利用沸石分子筛的结构单元与表面活性剂的自组装,系统地合成了具有无序微孔与有序介孔复合的催化材料,对大分子的催化转化显示出优异的催化性能。进一步,他们又成功地在无模板条件下合成出 β 沸石,这可以大幅度地降低 β 沸石催化材料的成本,同时也大大降低了 β 沸石合成过程中污染物的排放。王祥生等^[92]研究了高硅择形沸石的研制及其在烃转化应用中发现用氨水体系合成的 ZSM-5 沸石具有合适的酸强度和孔道弯曲度,适于作为选择性烷基化催化剂的基质;混合稀土能调节择形性,降低烧炭温度;超细粒子 ZSM-5 沸石的晶间孔是积炭优先生成的部位。从分子水平上阐述了四丙基铵离子在导向合成钛硅沸石中的关键作用。首创了以混合稀土为主的组合改性方法,用于氨水法合成 ZSM-5 的改性并制成合成高纯度(98%)对二乙苯催化剂,创建了乙苯-乙烯合成对二乙苯工业技术。赵东元和唐颐等在研究有序排列的纳米多孔材料的组装合成和功能化中基于纳米和分子组装化学、模板导向化学、表面活性剂化学,研究和建立了微孔、介孔和多级有序分子筛材料的构筑方法,在材料形貌、孔结构和孔内活性位等几个层次上,提出了“酸碱对”和电荷匹配理论,发明了适合微介孔材料的造孔工程方法,提出了低维纳米材料有序排列和组装概念,发展了层叠层、电泳沉积、微纳米浇注和再生长等多种纳米沸石组装技术。合成了数十种新型介孔、微孔、金属有机配合物的纳米孔材料,大孔-微孔沸石材料和沸石仿生材料,可控介观结构的纳米管等阵列。谢在库和杨为民等多级复合孔催化材料、超水热稳定分子筛、小晶粒择形催化材料、沸石形貌控制进行了系统的研究,并应用于甲苯择形歧化、C4 烯烃裂解、苯与丙烯烷基化制异丙苯等实现了工业化(见文献[87])。汪仁和卢冠忠等^[93,94]研究了稀土复合氧化物的储放氧性能及作用原理,发现铈离子可促使过渡金属离子以高价态稳定地存在,又能在较低的温度下被还原;

并开发了应用于工业源 VOCs 净化和机动车尾气净化的整体式稀土复合氧化物催化剂;卢冠忠等还合成了系列稀土掺杂的 SAPO-5, MCM-41, MCM-48 和 SBA-15 等分子筛,发现稀土的掺杂对介孔材料的氧化-还原性能和表面酸碱性起到了很好的调节作用,在烯烃选择性氧化、烷烃氧化、含氯 VOCs 的催化净化等方面表现出较好的性能,开发了以稀土为主催化剂的反应。段雪课题组^[95–98]在层状及超分子插层结构催化材料研究中,充分利用层状及层柱结构的可设计性和调控性,创制了具有新型结构的层状固体酸酯化催化剂、层状介孔固体碱催化剂、酶层柱催化材料、插层结构手性催化剂及高分散负载型金属催化剂;层状结构固体酸酯化催化剂已广泛应用于工业生产。邓友全等^[99–104]率先成功地开展了合成室温离子液体及其应用和金催化剂的研究。田志坚等^[105–110]利用离子热合成在离子液体中成功合成了系列分子筛和分子筛膜。

近 30 年是我国的催化基础研究从打基础到走向国际学术舞台的过程。在这期间催化学术和技术界队伍从几千人扩大到 2 万余人(工程师以上人员);在国内催化主流期刊上发表了 13000 余篇论文,在国际催化主流刊物上发表 3000 余篇论文(约占国际上发表论文总数的 5%);单篇引用超过 100 次的有 60 余篇。中国学者在 Science 杂志发表有关催化的论文 6 篇;Nature 1 篇。出版了 100 余部催化方面的专著,其中国外专著 10 余部。1982~2010 年间国家发布自然科学奖 914 项,催化界获 19 项;科技发明奖 2762 项,催化界获 64 项;科技进步奖 10139 项,催化界获 121 项。

3. 三十年来工业化重大成果

3.1. 炼油催化技术^[111,112]

我国炼油工业催化剂研发始于 20 世纪 60 年代;进入 80 年代,炼油逐步走出“引进仿制”阶段,使我国炼油工业得到新的、更快的发展,炼油能力、产品品种、产品质量均得到很大的提高。这个时期是我国炼油催化技术从仿制为主到自主创新的转变时期。此时,我们必须提到石化领域侯祥麟的贡献,他长期负责石油工业的科研组织领导工作,主持研究解决了影响国产航空煤油自给的关键,并与当时大连化物所研制成功的重油加氢裂化生产低冰点航空煤油工艺一起解决了国家急需的喷气燃料的生产和应用问题;组织国内相关单位共同研究开发成功被誉为“五朵金花”的催化裂化、铂重整等炼油系列新技术;还主持研制开发成功数十种特殊润滑材

料,及时满足了我国国防工业的需要;积极建议和推动“用好1亿吨油”,为发展我国的石油加工和石油化学工业作出了突出贡献。

20世纪90年代,单项技术开发转向成套技术开发,不仅能大部分满足国内需要,而且自主开发的炼油技术走向国际市场。一批技术和催化剂陆续进入东南亚、中东和欧美市场,并实现了炼油厂成套技术出口,显示了我国石化技术在国际上的竞争力。

进入21世纪,我国进口原油猛增而世界原油劣质化趋势明显,硫含量和金属含量越来越高,加工难度越来越大;重油深度加工与高效转化生产轻质油品、产品的清洁化和生产过程的清洁化;炼油与化工一体化以及形成替代燃料的生产是炼油工业的发展趋势,我国炼油能力跃居世界第二位,突破5亿吨。目前,中国炼油技术已经形成完整的体系,能采用自主技术建设现代化的千万吨级炼油厂,炼油过程的主要技术,如催化裂化系列技术、加氢系列技术、连续重整技术及与工艺过程配套的催化剂已经达到世界先进水平。此间,新过程、新催化剂和新工艺应运而生,其中突出的部分介绍如下。

3.1.1. 催化裂化和加氢裂化

石油化工科学研究院研发的MIP(Maximizing Iso-paraffins)技术:用于生产清洁汽油的催化裂化技术。MIP工艺从催化裂化过程的化学反应机理出发,独创性地提出了裂化和转化(异构化、氢转移、烷基化)两个反应区的新概念,由此设计出具有两个反应区的串联提升管新型反应器,并形成了相应的工程技术。从理论到实践,用工艺技术手段在促进重油裂化基础上,有效地降低了催化裂化汽油的烯烃含量,增加了异构烷烃含量,并使汽油中的硫含量有所降低,同时具有重油转化能力提高、增产汽油,提高总液收等优点。围绕该技术先后申请了100多项中国发明专利,其中授权专利为80件,在美国和日本等国家申请数件专利并获授权,形成了具有我国自主知识产权的生产清洁汽油组分的成套工艺技术,并逐步成为催化裂化工艺技术开发平台。MIP技术属国际领先水平,已应用到近30多套工艺技术,并已转让到古巴石油公司。

石油化工科学研究院研发的催化裂解制取低碳烯烃(DCC)技术:以重质馏分油为原料,采用提升管加床层的方式,在相匹配的工艺技术条件下,研究开发了大量生产丙烯的新技术、工艺条件、反应器型式及配套使用的专用催化剂(CHP-1),形成了使用重质原料生产以丙烯为主的低碳烯烃的新工艺路线,架起了炼油与化

工之间的桥梁,现已在国内外技术转让,建成多套工业生产装置。

抚顺石油化工研究院开发的系列加氢裂化催化剂:先后开发了30多个牌号的系列加氢裂化催化剂。包括大量生产化工石脑油的轻油型催化剂,灵活生产化工石脑油和中间馏分油的灵活型催化剂,大量生产中间馏分油的中油型催化剂,以及用于单段加氢裂化工艺过程的无定形和分子筛型催化剂等,其中有22个牌号的加氢裂化催化剂在60多套工业装置上使用,均产生了良好的效果。开发的9种牌号的加氢裂化预精制催化剂在40多套工业装置使用亦取得了很好的结果。这些催化剂的开发成功并应用,适应了企业的需求,提高了我国加氢裂化技术水平。

抚顺石油化工研究院开发的缓和加氢裂化催化剂(3882):两剂串联工艺流程处理减压馏分油,可生产优质的蒸气裂解制乙烯原料,并联产部分柴油和石脑油。采用缓和加氢裂化技术处理VGO,其尾油作为蒸气裂解制乙烯原料,乙烯和三烯收率都有了大幅度的提高;“MCI催化柴油加氢转化技术”是一种可大幅度提高柴油十六烷值的柴油加氢处理技术。其主要特点是通过选择特殊的工艺条件组合将反应控制在使柴油中的多环芳烃饱和、开环而不断链的阶段,从而既可大幅度提高柴油的十六烷值、降低密度,又使硫含量符合欧V标准,是国际首创的技术。

抚顺石油化工研究院的加氢裂化尾油异构脱蜡(WSI)技术:针对用加氢裂化尾油生产API二类、三类润滑油基础油和工业级、食品级白油产品的需要,开发的加氢裂化尾油异构脱蜡(WSI)技术设置两个串联使用的反应段,第一段装填专门的以特种择形分子筛为酸性组分的贵金属加氢异构脱蜡催化剂,用于降低加氢裂化尾油进料的凝点;第二段装填高加氢脱芳活性的贵金属加氢补充精制催化剂,用于异构脱蜡产物的深度加氢脱芳。该工艺具有原料适应性强、生产灵活性大、催化剂活性高、稳定性好、目的产品选择性高、产品质量好等特点,已于2005年在10万吨/年装置上实现工业应用。

上海石油化工研究院、中国石化工程建设公司研发的裂解汽油一段、二段加氢催化剂及其成套工艺技术:将乙烯装置副产裂解汽油经一段、二段加氢后,生产芳烃抽提原料。针对原料复杂性和高苛刻度,通过研制特定复合大孔结构氧化铝载体、疏水改性及贵金属晶粒粒径控制与精修,大幅度提高了一段选择加氢催化剂的耐水/胶质能力,延长催化剂运行寿命;研制的高比例活性

相的复合床层二段加氢催化剂,较好地解决了运行中易结焦、芳损高和阶段性低硫工况下易失活问题,一段、二段催化剂及成套工艺技术已成功应用于国内百万吨级乙烯装置,整体技术水平处于国际先进水平。

3.1.2. 加氢精制

石油化工科学研究院研发的 RN-1 加氢精制催化剂:以 Ni-W 为活性组分,具有高加氢脱氮、加氢脱硫和加氢脱芳活性,同时具有好的活性稳定性和对各种原料的广泛适应性。RN-1 适用于高氮高硫原油的直馏馏分油和高氮、高硫原油的二次加工馏分油的加氢精制,也可用于中、高压加氢裂化或中压加氢改质工艺过程中精制段原料的加氢脱氮和芳烃饱和。基于 MAS 制备平台开发的“柴油超深度脱硫催化剂 RS-2000 催化剂”,生产国Ⅲ柴油的现有柴油加氢装置通过更换该催化剂后即可直接生产国Ⅴ柴油产品。开发了渣油加氢处理 RHT 系列催化剂,其载体孔道独特,具有超高的脱金属和容金属能力,从而获得了较国内外催化剂更长的运行周期,后续开发的 RN-10, RN-10B, RN-32V 和 RS-1000 等在馏分油加氢领域继续保持了性能优势,在国内外加氢装置上大量推广,实现了我国在该技术领域的跨越。

抚顺石油化工研究院开发的 SRH 渣油加氢处理技术及配套催化剂:使用 SRH 技术处理后的渣油作为催化裂化进料,大幅度提高了催化裂化产品的质量和目的产品的收率,FZC 系列催化剂整体水平达到了国外同类催化剂的先进水平,实现了含硫原油加工技术的重大突破。“加氢精制催化剂”包括使 W-Mo-Ni-Co 在催化剂中形成 Mo-Co 活性相与 W-Ni 活性相;引入纳米级 SiO₂ 改善催化剂活性金属分散度,提高活性中心数量等,制备了用于柴油馏分加氢精制的 FH-DS 催化剂和用于加氢裂化预处理工艺的 FF-16 催化剂。“馏分油临氢降凝催化剂”,临氢降凝是一种用于降低喷气燃料的冰点、柴油的凝固点和润滑油的倾点炼油技术。

石油化工科学研究院研发的劣质重油加氢处理催化剂:针对原油重质化、劣质化趋势,开发具有更强脱金属和沥青质转化能力的系列渣油加氢处理催化剂。通过催化剂级配专有技术,大幅提升了渣油固定床加氢装置的运转周期和效益,产品已出口海外市场。

石油化工科学研究院研发的催化裂化汽油选择性加氢脱硫催化剂和技术:催化裂化汽油轻馏分抽提脱硫工艺、重馏分选择性加氢脱硫工艺及高选择性加氢脱硫催化剂,形成了催化裂化汽油选择性加氢脱硫 RSDS 成套技术。已建成超过十套工业生产装置,产品汽油中硫

含量可以达到 $(50\sim 10)\times 10^{-6}$ 以下,是国内生产国四、国五汽油的重要技术之一。

抚顺石油化工研究院开发的临氢降凝(FDW)、加氢降凝(FHDW)和加氢改质降凝(FHUG-DW)技术:FDW 技术是在临氢、一定温度和较低压力条件下,利用特殊分子筛催化剂的独特孔道和适当的酸性中心,使原料中的正构烷烃、带短侧链的异构烷烃和带长侧链的环状烃等高凝点组分选择性地裂解成小分子,从而降低油品的凝点,适用于加工低硫低氮直馏柴油,最大降凝幅度可达 50℃ 以上。FHDW 和 FHUG-DW 工艺技术在中等压力条件下,通过加氢精制或 MCI 对原料进行预处理,不仅提高了装置对高硫、高氮直馏和/或二次加工原料油的适应能力,改善了后续临氢降凝段进料质量,缓解了临氢降凝段操作条件,延长了装置运转周期,而且还大大改善了低凝柴油产品质量,适应了柴油产品质量升级的要求。上述技术均已有多套工业装置使用。

抚顺石油化工研究院开发的液相循环加氢技术(SRH):SRH 技术不设置氢气循环系统,依靠液相产品循环时携带进反应系统的溶解氢来提供新鲜原料进行加氢反应所需要的氢气,可取消循环氢压缩机,因此大幅度降低了装置投资和操作费用。同时,由于消除了催化剂的润湿因子影响,以及利用循环油的比热容大,可大大降低反应器的温升等特点,从而可提高催化剂的利用效率,降低裂化等副反应。该技术完成了 20 万吨/年工业示范装置的试验,并在 60 万吨/年工业装置取得了生产硫含量符合欧Ⅴ柴油标准的柴油的工业试验结果,于 2009 年开始工业化试验,取得良好试验结果。

中国科学院大连化物所与中国石油化工研究院联合开发的“润滑油基础油加氢异构脱蜡催化剂”(PIC 802)及工艺在中国石油大庆炼化分公司每年 20 万吨高压加氢装置上实现了工业应用。所研制的新型异构脱蜡催化剂 PIC802 具有活性高、重质基础油收率高的特点,在大庆炼化工业应用中,与引进催化剂相比,润滑油收率、产品质量、催化剂寿命都胜过原有引进催化剂。

3.1.3. 催化重整

抚顺石油化工研究院开发的铂-铈-钨(CB-5)重整催化剂:CB-5 催化剂是为提高我国重整技术而开发的半再生铂-铈-钨重整催化剂。第三种金属——钨的合理引入也进一步增强了双金属催化剂的选择性和稳定性。该催化剂活性与国外同类催化剂相当,而选择性更优。该催化剂使我国铂-铈系催化剂提高到一个新的水平。石科院研发的石脑油催化重整成套技术连续重整的主

要目的是提供高辛烷值汽油调合组分或芳烃和氢气,直接关系到我国石油炼制与石油化工行业技术的进步与竞争力。在催化剂方面,开发了低积炭高收率连续重整系列催化剂 PS-VI 和 PS-VII; 集成催化剂、工艺、控制系统和专用设备等多项核心技术,开发了“国产连续重整成套技术”。

石油化工科学研究院研发的半再生重整催化剂及工艺技术: 研究开发了 CB-6/CB-7, CB-60/CB-70 和 PRT-C/PRT-D 三代半再生重整催化剂及催化剂分段装填、两段混氢应用工艺。自 20 世纪 80 年代起,在国内市场占有率超过 85%。通过引入新的金属助催化组元,优化载体表面及孔结构,创新多金属浸渍制备技术开发的 PRT 系列催化剂保持双金属催化剂的高活性,而选择性更好,积炭速率显著降低。使半再生重整能够在保持较高目的产品收率的基础上长周期稳定运行。

石油化工科学研究院研发的连续重整催化剂及技术: 相继研发了三代 PS 系列催化剂,在第三代 PS-VI/VII 催化剂的研发中,通过对“金属-酸性中心”的设计和调控,解决了“比表面积降低导致的催化剂寿命缩短及严重的氯流失”以及“铂含量提高导致催化剂积炭增加”等难题,实现了我国在该领域的跨越式技术进步。催化剂国内市场占有率一直保持在 80%,为企业带来显著的经济效益,为我国的清洁汽油质量升级和芳烃生产的技术进步做出了重要贡献。催化剂已经实现了出口,引起国际市场极大关注。

洛阳石油化工工程公司与石油化工科学研究院开发的石脑油催化重整成套技术: 石脑油催化重整的主要目的是提供高辛烷值汽油调合组分或芳烃和氢气,直接关系到我国石油炼制与石油化工行业技术的进步与竞争力。通过对反应过程的研究,率先提出“依据芳烃和辛烷桶进行芳烃型和汽油型装置设计”的新理念; 成功开发了再生循环气固体脱氯技术,解决了氯腐蚀问题; 开发了“硫化-脱硫”专利技术,解决了“装置无硫结焦-催化剂有硫中毒”的难题。实现了对反应、催化剂输送与再生等系统的工艺、工程技术、专用设备以及开工操作技术等自主创新; 集成催化剂、工艺、控制系统和专用设备等多项核心技术,开发了具有自主知识产权的“石脑油催化重整成套技术”,使我国成为世界上第三个拥有该技术的国家。该技术已在国内 4 家企业应用,创造了巨大的经济效益。

3.1.4. 炼厂气综合利用

为综合利用炼厂气干气资源,并生产国内紧缺的乙

苯-苯乙烯产品,中国科学院大连化物所和抚顺石化公司开发了催化裂化干气制乙苯系列技术。其中,第一代和第二代技术分别于 1993 年和 1999 年在抚顺石油二厂(3 万吨/年)和大连石化公司(10 万吨/年)工业应用,并被列入第三世界科学院创新成果; 为进一步降低乙苯生产能耗和成本,提升产品质量,延长催化剂使用寿命,大连化物所发明了高性能低温气相烷基化催化剂(ZSM-5/ZSM-11 共晶分子筛)和液相烷基转移催化剂(超细 β 分子筛),开发成功催化干气制乙苯第三代新技术,解决了直接利用干气生产优质乙苯的关键技术难题,有效提高石油资源的利用率,降低乙苯生产能耗和成本,其原料成本比纯乙烯法低 15%~20%; 目前已在 20 余家企业成功应用,年产乙苯 150 余万吨。同时,为优化利用石化行业副产的大量液化气资源,大连化物所率先提出液化气低温芳构化技术,开发了高效芳构化多级孔分子筛催化剂,并成功应用于 20 万吨/年等工业装置。

大连理工大学开发的低碳烃固定床芳构化成套技术(Nano-forming 工艺): 采用纳米 ZSM-5 分子筛研制出抗积炭失活的芳构化催化剂,有效地解决了催化剂失活快,固定床反应器切换频繁等问题,于 2006 年建成中国首套 10 万吨/年液化气芳构化生产 BTX 装置。目前,该技术已发展成高温芳构化生产富苯混合芳烃和低温芳构化生产贫苯混合芳烃两种工艺类型,在中国建成投产多套工业装置,适用原料包括正丁烷、异丁烷、混合丁烷、FCC 液化气(MTBE 抽余料)和轻石脑油原料(如重整抽余油、拔头油)等,对液化气等低碳烃资源的优化利用具有重要意义。

石油化工科学研究院研发的轻烃芳构化成套技术: 研发了特殊成型的球形芳构化催化剂,结合配套的催化剂移动床输送和再生技术,开发成功了轻烃芳构化成套技术。该技术以碳四液化气和其他轻烃为加工原料,生产以三苯为主的芳烃产品,并副产一部分氢气。该技术实现了芳构化装置的连续平稳运转,到目前已建成多套工业装置。三苯是重要的有机化工原料,主要用于生产 PX,PTA 和聚酯等化工产品。

齐鲁石化研究院研制的系列硫磺回收氧化铝基催化剂: LS-971 脱漏氧保护型硫磺回收催化剂、LS-981 多功能硫磺回收催化剂、LS-951 Claus 尾气加氢催化剂、LS-951T Claus 尾气加氢催化剂、LS-951Q Claus 尾气加氢催化剂、LSH-02 低温型 Claus 尾气加氢催化剂、LSH-03 低温耐氧型 Claus 尾气加氢催化剂等 LS 系列硫磺回收及尾气加氢催化剂,已成功应用于中石化齐鲁分

公司、燕山分公司等100余套硫回收装置。

3.2. 石油化工和精细化工^[111,112]

石油化工、精细化工同人类生活中的衣、食、住、行、健康、安全等密切相关,三十年来的发展着重在:解决重有机原料乙烯、丙烯、甲醇、苯、乙苯和对二甲苯对进口的依存度;填补关键产品和中间体的空白;提高催化过程的效率并降低污染使其绿色化。

3.2.1. 合成纤维单体和原料制备

上海石油化工研究院研发的MB-86 丙烯腈催化剂:完成了MB系列催化剂的组成设计及催化剂工业放大制备,开发出适用于较高压力和较高负荷下操作的MB-86 催化剂,获得了工业应用成功;“甲苯与重质芳烃歧化与烷基转移成套技术及催化剂”以丝光沸石为主催化剂,以甲苯、C₉芳烃、C₁₀芳烃及C₁₀以上芳烃为原料进行歧化与烷基转移制苯和二甲苯,在一个反应器内完成甲苯歧化与烷基转移过程的同时,一并实现C₁₀芳烃及其以上重芳烃轻质化过程。HAT系列催化剂成功应用于国内上海石化股份公司等八家公司,装置总处理量380万吨/年,占国内总处理量的90%。

上海石化院和齐鲁石化公司等研发的丙烯腈成套技术:通过对丙烯腈生产中各个关键单项技术的协力攻关,形成了具有自主知识产权的专利或专有技术,将已在不同装置上应用成功的单项关键技术集成在一起,包括MB-98 丙烯腈催化剂、新型空气分布板和丙烯-氨分布器、新型高效旋风分离器、复合萃取分离技术、负压脱氰塔、新型气液分离器和导向浮阀等技术。

石油化工科学研究院研发的苯和乙烯液相烷基化合成乙苯技术:研究开发了苯与乙烯液相循环烷基化工艺以及苯与乙烯液相烷基化催化剂和苯与多乙苯液相烷基转移催化剂,形成了苯和乙烯液相烷基化合成乙苯的成套技术,并建成多套乙苯生产装置,实现了乙苯生产技术的国产化。乙苯是重要的有机化工原料,主要用于生产苯乙烯和环氧丙烷。

抚顺石油化工研究院开发的丁烯水合脱氢生产甲乙酮成套技术:开发了丁烯水合脱氢生产甲乙酮成套技术及催化剂。以苯乙烯-二乙烯苯为主要原料,经过聚合、物理结构稳定化、卤化、磺化和活性基团稳定化五个过程制备出耐高温阳离子交换树脂催化剂,用于丁烯水合生产仲丁醇;仲丁醇脱氢生产甲乙酮铜催化剂采用氧化钾改性降低催化剂酸性技术。该催化剂在中国石油和中国石化等企业10多套工业装置上应用,国内市场占有率达90%以上。

北京化工研究院研发的聚乙烯催化剂系列技术:BCS-02 催化剂是一种适用于乙烯气相聚合工艺的Z-N 催化剂,可用于制备全密度聚乙烯树脂。该催化剂活性较高,氢调和共聚性能良好,树脂粉料粒形好,堆积密度高,可在冷凝与非冷凝态下使用,并且粉料不发粘,出料顺畅。BCE 催化剂是北京化工研究院研发的新一代淤浆聚合聚乙烯催化剂,用于乙烯淤浆聚合制备中、高密度聚乙烯树脂,适用于CX, Hostalen, Innovene S 和 Philips Loop 等淤浆聚合工艺。BCH 催化剂是北京化工研究院20世纪80年代开发的淤浆聚合聚乙烯催化剂,适用于CX工艺,用于生产挤塑、注塑和吹塑等产品牌号,目前催化剂大量出口东南亚国家。茂金属聚乙烯催化剂的研究始于20世纪90年代,2002年开发了负载型茂金属催化剂,并对该催化剂进行了放大制备。2011年在齐鲁石化实现工业应用,具有活性高、共聚能力强和共聚单体在聚合物中分布均匀等优点。

上海石油化工研究院、上海石油化工股份有限公司研发的对苯二甲酸加氢精制催化剂及工艺技术:精对苯二甲酸(PTA)是重要的基本有机化工原料,主要用于生产聚酯(PET)及后续产品。通过采用国际首创的乳化浸渍分散金属控制以及催化剂微晶结构稳定等技术,创制了一种性能特别优异的新型PTA加氢精制催化剂,开发了适合高负荷、长周期稳定运行的加氢工艺,解决了以往催化剂耐热、抗毒、抗干扰等关键技术难题,突破了PTA装置稳定生产及扩能的技术瓶颈,实现了PTA核心技术的国产化。所开发的催化剂已在国内近60%的PTA装置上成功应用,综合性能处于国际领先水平。

上海石油化工研究院研发的增产二甲苯系列芳烃生产技术:包括以大孔分子筛为催化活性主体的甲苯与重质芳烃歧化与烷基转移催化剂;以甲苯、C₉芳烃及其以上重芳烃为原料,在同一反应器内完成甲苯歧化与烷基转移反应、C₁₀以上重芳烃轻质化及烷基转移反应,该系列催化剂已成功应用于国内外20余套工业装置,国内市场占有率达90%,以此为基础的大型成套技术在国内建成总处理能力达1500万吨/年的歧化装置;以ZSM-5分子筛为催化活性主体,经表面和孔口修饰改性,创制的选择性歧化催化剂,可以纯甲苯为原料,高选择性生产对二甲苯,通过结晶分离高效、低成本地生产对二甲苯,通过了工业验证,该技术可与苯/重芳烃烷基转移技术组合,以择形歧化装置生产的苯与重芳烃经烷基转移生产二甲苯和甲苯,甲苯再作为择形歧化装置的原料,该组合工艺中,对二甲苯的浓度可达60%以上,可以大幅度降

低对二甲苯生产负荷,提高对二甲苯装置生产能力。

上海石油化工研究院开发的烯烃催化裂解制丙烯催化剂及成套技术:利用炼厂或乙烯装置副产 C_4 、 C_5 烯烃来增产丙烯,创制了无粘结剂复合孔分子筛催化材料,开发了超低阻力降反应器、反应-再生高温切换工艺、高效换热器、产品分离工艺等工艺技术,形成自主知识产权的烯烃裂解成套技术,在中原石化建成6万吨/年工业装置,在世界上首次将无粘结剂分子筛技术在催化领域实现工业应用。通过催化材料的创新,研制的催化剂在反应空速和稳定性方面的技术优势显著,处于国际领先水平。

上海石油化工研究院研发的新型钛系聚酯催化剂技术:采用该钛系催化剂可以降低聚酯生产过程的酯化段反应温度,达到降低能耗的作用,在国内首次工业生产环境友好的无重金属聚酯产品,并与上海石化合作生产的NEP聚酯切片已成功出口欧盟。该钛系聚酯可用于有光、半消光、全消光纤维级聚酯切片和膜级聚酯切片。

北京化工研究院开发的 C_3 加氢催化剂技术:裂解 C_3 馏分中含有1%~5%的丙炔与丙二烯(MAPD),乙烯装置中普遍使用选择加氢的方法,使MAPD转化为丙烯而脱除。北京化工研究院开发了 C_3 气相加氢催化剂BC-H-33及 C_3 液相加氢催化剂BC-L-83和BC-L-30A。上述催化剂具有使用空速高,丙烯选择性高,聚合物生成量小,再生周期长和使用寿命长等优点。同时适用工况范围宽、抗波动能力强,整体综合性能优良。目前国内仅有的两套使用 C_3 气相加氢装置都选用BC-H-33催化剂。 C_3 液相选择加氢催化剂在国内(包括台湾)共有22套装置使用,国外已在中东、东南亚、日、韩等10套装置中应用。

北京化工研究院开发的 C_2 加氢催化剂技术: C_2 馏分选择加氢除乙炔是石油烃蒸气裂解制乙烯工艺中最重要的过程之一,北京化工研究院开发了适用于顺序分离流程的BC-H-20系列 C_2 后加氢催化剂和适用于前脱丙烷前加氢分离流程的 C_2 前加氢催化剂BC-H-21B。上述催化剂具有操作条件范围宽,稳定性好,空速高,乙烯选择性好,绿油生成量少和运行周期长等优点。 C_2 加氢催化剂目前已经在燕山、上海、齐鲁、广州、中原、扬子、大庆、辽化、独山子、天津和东方等17套乙烯装置中应用,运行情况良好。2008年该催化剂走出国门,出口到伊朗BIPC公司,至今运行效果非常好,受到用户好评。2010年出口到英国SABIC UK,为国内该类催化剂首次推广到西方发达国家。

3.2.2. 加氢、脱氢

大连化物所和轻工部日用化学所、南京烷基苯厂合作研发的正构长链烷烃($nC_{10}\sim C_{13}$)NDC-2型Pt-Sn-Li/ Al_2O_3 长链烷烃脱氢催化剂:该催化剂表面具有Pt-SnO₂- Al_2O_3 夹心结构的M2活性中心,对氢有高温强吸附性能,能够抑制积炭,从而显著提高催化剂的稳定性。NDC型催化剂还出口印度,创造了巨大的经济效益。

抚顺石油化工研究院开发的顺酐酯化/加氢生产1,4-丁二醇成套技术及催化剂:催化剂经1万吨/年1,4-丁二醇工业装置上应用二十多批次,2011年又在5.5万吨/年装置上使用,与国内外同类催化剂相比,寿命延长50%以上。

北京化工研究院开发的甲醇羰基化制乙酸催化剂技术:北京化工研究院开发了铑粉经硫酸氢铑熔融离子化,再经水解转化合成三碘化铑催化剂的制备方法。2003年,完成了工业生产装置中失活催化剂的再生方法试验工作,从而形成了一套完整的催化剂加工和再生体系。工业应用表明,该催化剂的溶解性能、杂质含量物化指标及其在生产装置中的各项控制指标均达到同类进口催化剂水平。该技术的推广打破了国外公司的长期垄断,有效降低了进口催化剂价格,使国内企业从中受益。

3.2.3. 选择加氢裂解

大连化物所与长春大成集团公司合作开发出葡萄糖-山梨醇转化制低碳醇的催化新材料及其工业应用新技术:形成具有自主知识产权的非石油路线制乙二醇和丙二醇新方法。已在20万吨/年工业装置上运转多年,现已扩产至100万吨/年,它是现今唯一由生物质制多元醇的工业生产线。乙苯脱氢:上海石化院、华东理工大学等研发的苯乙烯关键技术-新型轴径向流反应器和脱氢催化剂及工业应用,并通过整体技术耦合,形成了负压脱氢制苯乙烯成套技术,实现了整套装置的国产化。

3.2.4. 催化氧化

大连化物所开发出对二甲苯氧化制对苯二甲酸新方法和新工艺:在10万吨/年规模的工业装置上稳定运行超过30个月,催化效率显著提高,溴的用量大幅度降低,减少腐蚀和环境污染,现正在厦门进行165万吨/年规模工业应用实验。上海石化院、上海石化股份公司研发的对苯二甲酸加氢精制催化剂及工艺技术,在国际上首次创制了一种性能特别优异的新型粗对苯二甲酸(TA)精制催化剂和高负荷、长周期稳定运行的加氢技术,解决了PTA生产或扩能改造的技术瓶颈,实现了PTA核心技术的国产化。

北京化工研究院开发的苯氧化制顺酐催化剂技术: BC-118 器外活化系列催化剂是一种新型稀土 V_2O_5 - MoO_3 系催化剂,用于固定床苯选择氧化生产顺丁烯二酸酐,该催化剂在生产阶段就可完成活化,可以直接装填使用,解决了企业生产效率低的难题,目前已用于国内十几个顺酐生产厂家,市场占有率达 70% 以上。

上海石油化工研究院研发的氨氧化生产芳腈催化剂及技术:苯甲腈、苯二甲腈和卤代苯腈等是具有高附加值的精细化工产品,开发了湍流流化床反应工艺及其催化剂,大幅度提高了产品收率,降低了三废排放。开发的钒系催化剂具有耐磨性能强,选择性好,整体技术水平达到国际领先水平,并在国内芳腈生产企业广泛应用,为我国的农药、医药、染料等行业提供有力的技术支撑。

北京化工研究院开发的乙烯三聚制 1-己烯催化剂技术: 1-己烯属于乙烯衍生物,是生产多种聚乙烯产品的重要共聚单体,也是一些精细化学品的原料。乙烯三聚制 1-己烯技术是在中心金属铬组成的配位催化体系作用下,在溶液中将乙烯转化为 1-己烯的过程,由于其目标产物选择性高和产品质量好,应用该技术建成的 5 万吨/年成套工业装置已在燕山石化公司投产,推动了国内聚乙烯工业的技术进步和产品升级。

北京化工研究院开发的乙烯齐聚制备高级 α -烯烃催化剂技术: 乙烯齐聚制 α -烯烃属于乙烯衍生物产品制备技术。 α -烯烃在乙烯共聚单体、表面活性剂合成中间体、增塑剂用醇、合成润滑油和油品添加剂等领域有着广泛的应用。与中科院化学所合作开发的铁系乙烯齐聚技术,经过不断改进创新,活性在 $0.81.0 \times 10^7 (g \cdot mol)/h$,具体分布为 C_4 : 19%~24%; $C_6 \sim C_{18}$: 69%~72%; C_{20+} : 7%~11%。 C_{18} 以下的线性 α -烯烃产品平均含量大于 98%,聚合物含量 < 1%。在催化剂成本大幅降低的同时,齐聚反应活性和 α -烯烃选择性等指标均达到国际先进水平。

北京化工研究院开发的 MTBE 裂解制异丁烯催化剂: MTBE 裂解制异丁烯技术属于裂解 C_4 和炼油 C_4 综合利用项目。北京化工研究院于 1981 年开始进行甲基叔丁基醚 (MTBE) 裂解制异丁烯催化剂研究,随后开发了 MTBE 裂解制聚合级异丁烯成套技术。采用 MTBE 裂解制异丁烯技术建成的燕山石化 3.5 万吨/年异丁烯生产装置每年生产高纯异丁烯 4 万多吨,创造产值 5 亿多元,为丁基橡胶装置提供了主要原料,摆脱了丁基橡胶长期依赖进口的局面,创造出了良好的经济和社会效益。

北京化工研究院开发的稀土异戊橡胶催化剂技术: 自主研发出适用于异戊橡胶的新型高活性均相稀土催

化剂,并成功开展了稀土异戊橡胶合成的全流程试验。合成的异戊橡胶中试产品各项性能指标达到国外同类产品水平,经国内科研单位及轮胎生产厂家评价,可满足工业制品的要求。北京化工研究院自主研发的稀土催化剂以羧酸铈为主催化剂,与烷基铝和卤素化合物一起经陈化反应后制得。该催化剂的特点是活性高、稳定性好,能够较长时间保持均相。

3.2.5. 醛氨合成吡啶

大连化物所开发出醛氨合成吡啶新型高性能催化剂及成套技术: 攻克了分子筛催化剂抗碱中毒关键技术难题,打破国外技术垄断,成功投产 25 千吨/年全球最大吡啶装置在内的多套装置,将我国建成全球最大吡啶碱生产基地,实现了农药、医药等诸多行业大宗关键中间体—吡啶类化合物的规模化、连续化和清洁化生产,为下游诸多行业的发展提供关键科技支撑。用于工业化生产提升了我国农药、医药等化工产业创新水平和竞争能力,加速具有国际竞争潜力的主导农药品种及大宗关键化工中间体的产业化技术的发展”。

3.2.6. 临氢氨化

大连化物所开发的乙醇胺临氢氨化制乙二胺工业技术以乙醇胺和氨为原料生产乙二胺,可以在较缓和的工艺条件下获得较高的产品选择性,并解决国内非常紧缺的二乙烯三胺和哌嗪,适合在国内推广,开发的成套技术中采用非苯脱水剂,该技术是更为环保清洁的技术。

3.2.7. 炔醛法合成

山西大学研发的炔醛法合成 1,4-丁二醇加氢催化剂: 针对国内引进炔醛法生产 1,4-丁二醇工艺中核心技术,获得了具有适宜孔道结构与表面性质,及高水热稳定的具有水解加氢双功能的加氢催化剂,该项技术成果使我国成为世界上少数几个掌握该类催化剂关键制备技术的国家之一。

3.2.8. 烯烃酯化

华南理工大学开展羧酸与烯烃直接加成酯的研究: 包括树脂、杂多酸和分子筛系列催化剂,反应包括乙酸与丙烯反应合成乙酸异丙酯,乙酸与丁烯反应合成乙酸仲丁酯,乙酸与乙烯反应合成乙酸乙酯,水杨酸与丙烯反应合成水杨酸异丙酯等,成功地用于工业生产形成巨大经济效益。

3.3. 合成氨催化剂^[111,112]

作为基本化学工业,我国化肥工业始于 20 世纪 30 年代。1980 年全国化肥总产量(折纯养分)为 1231.9 万吨; 2010 年已达 6619.8 万吨,30 年增长 4.37 倍。无论化

肥总量抑或氮肥产量均列世界第一。化肥工业中使用催化剂的主要是用于氮肥的基本原料合成氨工艺过程。根据制氨原料采用煤、石脑油、重油、渣油和天然气的不同,使用不同品种的催化剂;它包括有机硫加氢转化、无机硫吸收、天然气或石脑油一段与二段转化、高温与低温变换、甲烷化及氨合成等8种催化剂。

福州大学研制的A201型和A202型氨合成催化剂活性及稳定性适用于中小型厂;成功研制了B116型低铬一氧化碳中温变换催化剂和B121型无铬一氧化碳高温变换催化剂。

浙江工业大学在Fritz Haber 20世纪初发明氨合成熔铁催化剂70多年后,突破经典的 Fe_3O_4 体系,发明了新一代 Fe_{1-x}O 基氨合成催化剂,创立了以单相理论为核心的中国原创的 Fe_{1-x}O 催化剂理论体系,技术达到国际领先水平。

华南理工大学研究开发成功HG-1稀土氨合成催化剂,显著提高了氨合成催化剂的低温活性、耐热性和抗毒性。

上海化工研究院研制的B301一氧化碳耐硫宽温变换催化剂,它是我国第一个开发成功并广泛使用的耐硫变换催化剂。

齐鲁石化公司研究院成功开发了适用于从天然气到炼厂气、LPG、石脑油等气态、液态烃蒸气转化制氢和合成气的系列化催化剂及相关应用技术;分别开发了QCS-01和QCS-04耐硫变换催化剂,实现了我国引进大化肥装置耐硫变换催化剂的国产化。

3.4. 环境净化催化

催化科学和技术的发展在给我们带来极大的物质生活利益的同时,也使得人类活动对自然界和环境造成巨大影响,因此环境催化应运而生。环境催化的使命——用催化的手段解决人类面临的化学污染问题,成为催化科学和技术发展所面临的新挑战^[113]。

3.4.1. 固定源污染物催化消除

烟气催化脱硫脱硝:以燃煤烟气为代表的固定源 SO_2 和 NO_x 排放是造成我国大气污染的两种主要污染物,如何有效消除 SO_2 和 NO_x 是环境催化领域的研究热点。针对 SO_2 催化消除,可以采用催化氧化法将其氧化成 SO_3 并制得硫酸,实现废物资源化;也可采用催化还原法将其还原成单质硫磺,加以回收利用。针对 NO_x 催化消除,可以采用外加还原剂(如 NH_3)的方法在有催化剂作用下将其选择性催化还原为 N_2 (即 NH_3 -SCR技术),脱硝效果显著。我国在烟气脱硫脱硝领域的研究起步较晚,

早期(2000年前)所使用的烟气后处理技术往往是通过“引进-消化吸收-再创新”的模式,存在一定的知识产权壁垒。东南大学主持的“大型火电厂烟气脱硫脱硝成套关键技术的开发与应用”项目在SCR脱硝领域取得了重要进展;大连化物所研发的电厂脱硫脱硝技术也已经完成工业化试验。抚顺石油化工研究院开发的烟气脱硝催化剂已完成工业侧线试验,2012年将完成流化催化裂化(FCC)烟气脱硝工业化试验和电厂烟气脱硝工业化试验。抚顺石油化工研究院开发的挥发性有机物(VOCs)催化氧化治理技术^[114]:抚顺石油化工研究院开发了系列的VOCs催化氧化催化剂。其中WSH-1型催化剂适用于石化污水场废气的治理,已经在十几家石化企业推广应用。燕化公司开发的WSH-1F型和WSH-2型催化剂分别应用在橡胶尾气和PO/SM尾气治理工业装置上。已经形成从工艺、设计、设备加工到催化剂开发成套的催化氧化技术。

3.4.2. 机动车尾气催化净化

我国在2010年的汽车产量约为1700万辆,已成为世界第一大汽车生产国。摩托车产量已达2500多万辆,占世界40%以上。加上8000多万辆在用汽车和11000万辆在用摩托车,我国机动车污染物在城市污染物的分担率为50%~80%,是主要大气污染源。在环境催化领域,汽车尾气中的CO、碳氢化合物(HC)、 NO_x 和颗粒物(PM)均可通过催化结合颗粒物过滤的方法去除,所涉及的技术包括三效催化(TWC)、颗粒物过滤技术(DPF)、 NO_x 选择性催化还原技术(SCR)、 NO_x 储存还原技术(NSR),以及在此基础上开发的组合净化和四效催化技术。

福州大学负责研制的FD型汽车尾气催化净化器性能达到欧IV、欧V排放限值,并实现工业化生产。FD型催化净化器在与垄断我国欧IV排放限值净化器市场的美、日、德等外企竞争中进入我国的一汽、长丰等汽车制造厂推广应用;四川大学在汽油车、摩托车、压缩天然气车和柴油车尾气净化催化剂的制备科学和技术方取得了突破,在机动车尾气净化催化材料和催化剂领域取得了一系列重要的科学创新^[115-119]。在此基础上,四川大学与四川中自科技有限公司合作建立了高性能稀土储氧材料生产线、耐高温高比表面材料生产线和机动车尾气净化催化剂生产线,批量提供汽油车、摩托车、压缩天然气(CNG)汽车和柴油车通机尾气净化催化剂,成为国内整车厂和主机厂CNG车催化剂的主要供应商,其中摩托车催化剂已得到铃木和雅马哈的大量使用。

清华大学、华东理工大学和天津大学等在对“汽车

尾气净化的关键反应、催化剂构成的关键材料、稀土与(非)贵金属组分的相互作用、活性组分的设计及制备工艺”等深入研究的基础上,设计开发了“稀土-非贵金属-微量贵金属”为活性组分的汽车尾气净化催化剂,形成高性能的稀土基储氧材料和复合氧化铝等关键材料的制备技术,以及“真空喷涂-真空抽提”整体式催化剂的制备技术等^[120,121]。相关技术在合作单位无锡威孚力达催化净化器有限责任公司、金华欧仑催化科技有限公司及上海郎特汽车净化器有限公司等成功实现工业化生产。

3.4.3. 室内空气催化净化

纳米高效光催化剂:福州大学通过表面酸性增强、组成与结构调控、半导体复合、异质结形成、纳米量子尺寸效应等方法,研制开发了包括固体超强酸光催化剂在内的一系列新型高效纳米光催化剂,使光催化过程效率大大提高;采用溶胶-凝胶、膜渗析及表面超强酸化等多种技术集成,开发了全新的纳米光催化剂工业生产技术,设计建成了光催化剂生产线并投入工业生产;在新型高效纳米光催化剂的基础上,把光催化技术与化学氧化技术、吸附技术、低温等离子体技术等耦合,开发了多种室内和军事密闭空间的空气净化技术和产品,与企业合作设计并建成了大规模光催化空气净化器生产线,实现了产业化。

室温催化氧化甲醛和催化杀菌技术:甲醛是我国室内空气中典型、最严重的污染物之一,室内空气中还存在一些致病微生物的污染,这些污染物对人体健康构成严重危害。中科院生态环境研究中心、过程工程研究所和北京亚都空气污染治理技术有限公司^[78]发明了室温条件下可催化氧化甲醛的新型高分散负载型贵金属催化剂和室温催化杀菌的系列载银无机催化材料及其规模化制备技术,并在北京亚都空气污染治理技术有限公司等合作单位实现了本发明技术的产业化应用,取得了良好的社会效益和经济效益。

3.4.4. 水处理过程中的催化

有毒难降解有机污染物光催化降解,中科院化学研究所^[122]在利用太阳光催化降解有毒难降解有机污染物方面取得多项成果:(1)在可见光照射下成功实现染料污染物的 TiO_2 光催化有效降解和矿化,提出了与紫外光光催化反应不同的染料污染物可见光光催化降解机理;(2)设计并合成了一系列新型铁氮配合物及其负载型可见光光催化剂,发现其可见光照射下可有效活化 H_2O_2 及 O_2 降解并矿化有毒有机污染物,并提出了相应的可见光光催化反应机理;(3)研制成功非金属硼和氧化镍二元

协同改性的 TiO_2 基可见光光催化剂,在可见光照射下可有效地活化 O_2 降解多氯酚等有毒有机污染物,通过对 TiO_2 表面和体相改性的系统而深入的研究,澄清了一些国际上十分关注而又有争议的科学问题。

我国城市水源中高稳定性、难降解有机污染物成为影响水质的关键污染物。哈尔滨工业大学发明了一系列臭氧多相催化氧化除污染方法,利用过渡金属氧化物的某些表面特性催化臭氧转化为具有强氧化能力的自由基,对高稳定性有机污染物的分解效率比单纯臭氧氧化提高2~4倍。臭氧催化氧化可有效地分解去除水中高稳定性有机污染物,降低水的致突变活性,显著提高出厂水的安全性。目前,哈尔滨工业大学发明的臭氧催化氧化除污染集成化技术已在我国一些水厂应用,显著地改善了水质,将Ⅲ和Ⅳ类等受污染水源水处理达到生活饮用水水质标准要求。

3.4.5. 提高光催化环境污染控制过程能量效率的方法

有毒有害污染物的高效处理一直是国际环境工程领域的难点,光催化被认为是控制这类污染物最具发展前景的新技术之一,但能量效率低制约了该技术的实际应用。针对“如何提高能量效率”这一亟待解决的关键科学问题,大连理工大学、清华大学^[123,124]开展了提高光催化环境污染控制过程能量效率的方法及应用基础研究,取得了明显的规律性创新结果。

3.5. 煤基合成气化学

煤基合成气化学是指以煤和合成气为原材料的化学工业,通过对煤进行深加工,不断延长其产业链,通过催化剂的开发,可以开发出数百种乃至上千种化工产品和燃料油,具有产业链长、增值空间大、关联程度高、规模效益显著的特点发展前景广阔,三十年来取得了重要进展。

3.5.1. 甲醇制取低碳烯烃(MTO)

大连化物所在20世纪80年代初开展了由甲醇或二甲醚制烯烃催化剂及工艺技术研究。在90年代成功开发了磷硅铝(SAPO-34)分子筛廉价合成技术、微球催化剂制备技术和流化床反应工艺技术,完成了中试规模放大。在基础研究和催化剂的性能改进工作基础上,开发了新一代甲醇或二甲醚制低碳烯烃的催化剂,进一步提高了烯烃选择性。大连化物所与陕西省新兴煤化工科技发展有限公司、中石化洛阳石化工程公司合作在世界上首次完成了万吨级规模甲醇制烯烃工业性试验,并命名为DMTO技术,其项目规模和各项指标已达到世界领先水平。神华(包头)世界首套180万吨/年甲醇制烯烃工业化装置

投料试车成功,在这套装置运行过程中,甲醇转化率达到100%,由2.96吨甲醇出发生产一吨乙烯和丙烯,此后DMTO装置正式进入商业化运营阶段.这是世界上以煤炭取代石油大规模生产乙烯、丙烯等大宗石化原料的成套技术^[125].

3.5.2. 煤制油催化剂

早在1953年大连化物所进行了3000吨/年循环流化床合成油中试试验,因天然石油的大量开采,合成油的研究暂时退出舞台.20世纪80年代初,山西煤化所重新恢复了煤制油技术的研究与开发^[126,127],先后经过固定床两段合成工艺;浆态床合成油技术;适合低温浆态床费托合成的微球形Fe-Cu-K/SiO₂ (20~150 μm) 催化剂;高温浆态床微球型(30~150 μm) 铁基费托合成催化剂等的技术进步,其时空收率可达到1.2~1.5 g/g,每吨催化剂的产油能力达到1500~1800吨油,活性是传统固定床费托合成催化剂的10倍以上,是低温浆态床费托合成催化剂的4~5倍.2006年后成立了中科合成油技术有限公司,形成了我国煤制油产业发展的技术支撑实体.在伊泰、潞安和神华建成三个16~20万吨/年合成油示范厂,并通过了中国国际工程咨询公司的考核验收,这标志着我国已完全掌握了先进高效的煤制油工业技术.

3.5.3. 合成气完全甲烷化替代天然气技术(SNG)

大连化物所在常压水煤气部分甲烷化催化剂及技术工业化应用的基础上,全面开展了煤制天然气高温高压催化剂及工艺技术的研究和开发,研发了系列的完全甲烷化催化剂,并进行了长时间(8000h)的催化剂性能测试;工业性试验验证了催化剂的各项指标和工艺技术的可行性,并编制完成了日产12万立方米SNG工业装置的成套工艺技术软件包;并集成了合成气完全甲烷化催化剂生产线,实现了催化剂的批量生产,该技术已经具备了进行工业化应用的条件.“合成气完全甲烷化技术(DNL-0901-S2M)”2011年通过了辽宁省科技厅的鉴定.

3.5.4. 煤制乙二醇

福建物质结构研究所与企业联手合作,成功开发了“万吨级CO气相催化合成草酸酯和草酸酯催化加氢合成乙二醇”(简称“煤制乙二醇”)成套技术^[128–131].中科院福建物构所和上海金煤化工新技术有限公司已将全部

煤制乙二醇技术入股通辽金煤化工有限公司,在内蒙古通辽市建设全球首套年产20万吨煤制乙二醇示范装置.但是,工艺过程仍存在技术瓶颈,经过刻苦攻关有望成为国内最大的乙二醇生产企业.

3.5.5. 天然气干法脱硫

大连化物所针对天然气、油田伴生气、煤制气、炼厂气及含H₂S的工业气体,从H₂S传质入手研究开发成功了高硫容干法催化氧化脱硫剂:“DCL型燃煤固硫剂的研制、生产及工业试运行”;“火电厂SCR烟气脱硝催化剂国产化技术开发”;“一种高硫容浸渍活性炭干法脱硫剂及其应用”.催化氧化脱硫剂的成功推广应用,在节约脱硫净化成本的同时,减少了脱硫过程对环境的二次污染,目前已在我国四大油田同时使用.

4. 结论与展望

催化界同仁经过跨世纪的追求和奋进,尤其是在近三十年的快速发展,终于使当今的中国催化发展成世界催化大国!但是,如何使催化大国发展成催化强国是全体催化同仁今后的中心使命.

在表面科学尤其是近年来发展起来的纳米科学和技术的促使下,催化本质的探索和催化工作理论的发展仍然将是人们追求的目标.精心提炼的催化研究领域仍然应当是催化新反应、催化新材料、催化新表征方法,尤其是大力发展原位实时、实空间的表征方法.利用超高分辨分析电镜、原位光谱、波谱技术等现代物理化学原位方法和计算化学相结合,对实用催化剂的深化研究,学习、引用凝聚态物理的理论和技术,发展新的催化剂及其作用原理是其重要方向之一.

鉴于催化科学和技术在国民经济、环境、人类生活质量等中的重要意义,催化研究的主战场仍然是紧密结合国家的重大需求而进行.煤、石油、天然气、氢的优化利用,石油化工,环境,能源…….

又鉴于催化是一个老学科,有着丰富的学术和技术积累,学科发展要求它必需走出本学科和其他学科交叉……两山之间必有峡谷!?!例如各种功能材料的发展.相信经过催化界同仁的努力会开辟出一片繁荣的新天地.