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Review (Special Column on New Porous Catalytic Materials)

Ethylbenzene to styrene over ZrO₂-based mixed metal oxide catalysts with CO₂ as soft oxidant

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ARTICLE INFO

Article history:

Received 1 March 2015

Accepted 4 May 2015

Published 5 January 2016

Keywords:

Oxidative dehydrogenation

Carbon dioxide activation

Zirconia-based mixed oxide

Acid-base properties

Redox properties

ABSTRACT

ZrO₂-based mixed metal oxide catalysts for the industrially important dehydrogenation process of ethylbenzene to styrene monomer have been explored by our group for the past 20 years. These efforts were subjected to the activation of CO₂ over mixed metal oxide catalysts and resulted in several promising benefits to the dehydrogenation processes, such as stabilized conversion and selectivity, suppressed coke formation and commercially-acceptable longevity. In this review, we summarize the most recent developments on ZrO₂-based mixed metal oxide catalysts, including the further optimization of sol-gel process in the synthesis of catalysts, rationalizing acid-base properties by doping, co-operative properties between redox and acid-base active sites and additional promoters towards the effective improvement of the longevity of catalysts.

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1. Introduction

1.1. Technologies for dehydrogenation of ethylbenzene to styrene monomer

Styrene is one of the most important monomers in polymer chemistry. Global styrene monomer (SM) consumption is driven by the production of its polymer or copolymer products, such as polystyrene (PS), polystyrene-butadiene rubber (SBR), polyacrylonitrile-butadiene-styrene (ABS). Styrene-based polymer materials offer unique characteristics, such as durability, high performance, versatility of design, simplicity of production and economy. They can also provide excellent hygiene, sanitation, and safety benefits. Owing to its usefulness, the demand of SM has been increasing every year. The SM capacity in 2012 was estimated to be over 32.7 million tonnes (Merchant Research and Consulting Group). To provide feedstock for products, the SM capacity usage rates are predicted to grow

rapidly in the near future and are expected to reach ~94% (Merchant Research & Consulting, 2015).

Catalytic dehydrogenation, one of the 10 most important petrochemical processes, produces more than 90% of the SM required for application [1]. The dehydrogenation of ethylbenzene (EB) is performed over a K-promoted iron oxide catalyst at around 600–650 °C, just below the decomposition temperature of the reactant [2]. Owing to the high endothermic (125 kJ/mol) nature and volume increasing character of the reaction, in an adiabatic reactor, a large amount of superheated and pressurized steam (steam/EB = 7–15 mol/mol) is necessary to supply the heat and lower the partial pressure of reaction to shift the equilibrium towards the SM product [3]. The large amount of steam acts as a diluent to lower the partial pressure of the product mixture, to shift the equilibrium to SM and to avoid (or remove) the formation of carbon deposits [4]. However, at the gas-liquid separator, a large amount of latent heat steam is wasted [5]. Consequently, the estimated hike in pro-

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DOI: 10.1016/S1872-2067(15)60901-9 | http://www.sciencedirect.com/science/journal/18722067 | Chin. J. Catal., Vol. 37, No. 1, January 2016

duction cost is about 10% and, in addition, the development of hotspots abates the overall activity and catalyst lifetime. Several technological advancements have emerged for the improvement of the existing commercial process by varying the other diluents apart from steam, such as co-feeding of O_2 and by introducing coupled reactions (SM Monomer Advanced Reheat Technology, SMART, by Lummus/UOP) [1]. Unlike conventional steam-reheat processes, the SMART process involves reactants that leave the dehydrogenation catalyst bed being reheated by selectively oxidizing part of the co-produced H_2 [6]. The reaction is fed by air or by oxygen-rich air and takes place over a proprietary UOP high selectivity catalyst with a selectivity of 92%–96%, and conversion in the range of 77%–93%. The exothermic oxidation reaction of H_2 with O_2 provides the heat required for the subsequent EB dehydrogenation. The removal of H_2 from the process shifts the reaction equilibrium in the dehydrogenation unit to substantially increase the single-pass EB conversions while maintaining high SM selectivity. Advantages of the Styro-Plus process include high conversion, high SM selectivity and reduced steam requirements, thus making it an energy efficient process. Disadvantages of the process include the need for two catalysts in the reactor, and that the reactor design and catalyst loading are more complicated for this system. Additionally, there is a danger of explosion owing to the side reaction of the complete oxidation reaction and the violent reaction of oxygen and the reactants.

To overcome such barriers of the oxidative dehydrogenation (ODH) of EB, a variety of oxidizing agents (such as air, CO_2 , N_2O , SO_2 and so forth) have also been widely investigated over novel catalysts [7–10]. Recently, there have been reports on O_2 -promoted dehydrogenation with metal-free carbon nanotubes. Su et al. [11] reported a very highly stable and selective catalyst for the synthesis of C4 olefins from *n*-butane, and the same group reported the hierarchical carbon materials which can be operated at lower temperatures, below 350 °C, under O_2 . A few other promising catalytic systems have been developed with other soft oxidant concepts. First, sulfur was reported as a soft oxidant for methane activation reported by Neurock and Marks with co-workers. The formation of metal sulfides lowered the activation energy which improved the selectivity of the products in methane coupling. This sulfur system exhibited a decrease in surface coke formation and high carbon balance [12]. Later, N_2O and N_2 were also reported as soft oxidants in the ODH of EB to SM [13,14]. These innovative findings open new possibilities for building new systems and developing catalysts suitable for these reactions, which may include a combination of these components. After all the research on the ODH, a lot of questions have arisen regarding whether the present oxidative system, with CO_2 as soft oxidant or in combination with other oxidants, is commercially credible.

As an emerging alternative technology, ODH of EB with CO_2 instead of steam has been under intensive investigation [11–15]. Although the dehydrogenation of EB process with CO_2 has currently only been performed on a laboratory scale, it is of interest, as this process can have a direct impact on both the economics and the environmental aspect during commercialization.

1.2. ODH of ethylbenzene with CO_2

Dehydrogenation of light alkanes or alkane groups of aromatics is a very important process in petroleum, polymer and industrial chemistry [11]. CO_2 is used as a feedstock replacing the previously used partial oxygen–steam or oxygen–nitrogen streams. CO_2 possesses a much weaker oxidizability as compared with the oxygen molecule but can still be used as a mild oxidant to remove the H_2 by-product in the dehydrogenation unit and lower the reaction temperature without decreasing the conversion and selectivity.

There are two possible pathways for EB dehydrogenation with CO_2 . One is ODH of EB through the oxygen species dissociated from CO_2 in a single step route and the other is dehydrogenation of EB coupled with a reverse water–gas shift reaction (RWGS) in the two-step process [16–20]. The result of the reaction is that the CO_2 is not hydrogenated but converted to CO and H_2O molecules.

The estimated energies required in this CO_2 applied process is 190 kcal/kg of SM ($EB/CO_2 = 1/9$). This is much lower than the commercial steam process which is 1500 kcal/kg of SM ($EB/H_2O = 1/9$). Consequently, the dehydrogenation in the presence of CO_2 should be an energy-saving process. As an estimation, a simple replacement of water steam with CO_2 in an SM installation should decrease the energy consumption from 6.4 to 0.8 GJ/t of SM [3]. Obviously, using CO_2 as a mild oxidant, ODH of EB to SM possesses both environmental and economic benefits [11,21].

CO_2 use offers several advantages in catalysis, such as acceleration of the reaction rate, enhancement in product selectivity, alleviation of thermodynamic equilibrium limitations, suppression of total oxidation, prolonging of catalyst lifetime and prevention of hot spots on the catalyst surface [3,17,22]. Based on these unique characteristics, CO_2 has been coined as a soft oxidant [16,23]. Additionally, industrial use of CO_2 is increasingly important in many aspects especially the greenness of the process where CO_2 is consumed during the process [14].

In view of these points, CO_2 applied to the EB dehydrogenation process could be considered as an industrially viable process.

1.3. Catalysts for ODH of ethylbenzene with CO_2

Commercial Fe-based catalysts are not effective for the dehydrogenation of EB in the presence of CO_2 owing to the decomposition of the active phase of the catalyst [2,24]. Intensive studies have been performed to improve the commercial catalytic system of alkali metal-promoted iron oxides, by supporting them onto Al_2O_3 and activated carbon materials [18,25–29]. These catalysts showed compatible catalytic activities effectively activating CO_2 . Recently, various metal or metal oxide systems were investigated further for exploitation of ODH of EB by means of CO_2 as soft oxidant [5,10,15,30–34]. In this direction, a variety of active metal components (Fe-, Cr-, V-, La-oxides and so forth.) have been investigated, supported on different materials such as carbonaceous materials, MgO, SiO_2 (mesoporous silica), Al_2O_3 , Ga_2O_3 , ZrO_2 , TiO_2 hydrotalcite-type

compounds, zeolites and so forth [35–42]. The most recent studies have related to active carbon sites from carbonaceous deposits [43,44] and synergetic effects from redox active sites [45,46].

Park and co-workers have studied several high performance catalytic systems for CO₂ applied effective ODH of EB, such as Fe-, V- and Cr-based catalysts [34]. These systems were based on designing a redox surface to activate CO₂, dissociate it on the surface of catalysts and use the oxygen for the RWGS reaction. Among these catalysts, Al₂O₃-supported vanadium and vanadium–antimony oxide catalysts have been intensively studied and the results showed reasonable activities [47–54]. The significance of these catalyst systems for the title reaction has been consolidated. However, the deactivation owing to coke deposition and the deep reduction of the surface vanadium species still restrains the practical use of VO_x/Al₂O₃-based catalysts.

2. Scope of this review

To design a better catalyst system in terms of activity, selectivity and stability for time-on-stream experiments, Park et al. [5,55–60] developed several ZrO₂-based composite oxides; in particular, MnO₂–ZrO₂, TiO₂–ZrO₂, CeO₂–ZrO₂, SnO₂–ZrO₂, effect of Cl on Fe₂O₃/TiO₂–ZrO₂, effect of redox promoters (V₂O₅, CeO₂, Sb₂O₃) and effect of alkali doping in TiO₂–ZrO₂. These catalysts with acid-base properties exhibited interesting and improved catalytic properties for this reaction. Based on these catalytic achievements, the continuous work was supported by SABIC toward commercialization of this effective system. In this review, we will briefly summarize our recent basic studies on ZrO₂-based catalysts for CO₂ applied ODH of EB and the further application to light paraffin for the production of olefins (Scheme 1).

3. Acid-base bifunctional ZrO₂-based binary metal oxides

Based on the systemic research of alumina-supported vanadia (VO_x/Al₂O₃) catalysts with redox surface properties, we

developed ZrO₂-based metal oxide catalysts for ODH of EB with CO₂, and proposed that the acid-base surface of zirconia metal oxides could activate EB and CO₂ simultaneously, to observe the positive effects of CO₂ in directing the EB conversion, product selectivity and prolonged catalytic activity.

In a primary study, Park et al. [61] found amphoteric ZrO₂ was active for the dehydrogenation of EB, especially in the presence of CO₂. This positive effect of CO₂ was highly dependent on the tetragonal phase of crystalline ZrO₂. A higher EB conversion and SM selectivity were obtained with increased surface area and CO₂ affinity, which was related to surface basicity.

Additionally, mixing the pure oxides is beneficial to either modulate the properties of the component oxides or to create new active sites. Several theories have been proposed for the enhanced acid-base properties and their activities [62–65].

In the exploration of ZrO₂-based mixed metal oxide catalysts, our studies have focused on the various ZrO₂-based binary metal oxide catalysts at the same time. These binary oxides are namely TiO₂–ZrO₂, MnO₂–ZrO₂, CeO₂–ZrO₂ and SnO₂–ZrO₂.

3.1. MnO₂–ZrO₂ binary metal oxides

In our recent report, we described the influence of CO₂ over ZrO₂, wherein an enhancement in the conversion of EB and the selectivity towards SM in the presence of CO₂ oxidant were observed [61]. Furthermore, the catalytic activity of ZrO₂ was significantly improved when it was mixed with other transition metal oxides [66–68]. Our study on MnO₂–ZrO₂ binary metal oxides was focused on enhancing the acid-base properties and also the introduction of the redox nature.

MnO₂–ZrO₂ mixed oxides with various compositions (5–50 wt%) have been prepared by a co-precipitation method [55]. The precipitate was washed thoroughly with water and dried at 120 °C for 12 h, then calcined at 550 °C for 6 h. MnO₂–ZrO₂ mixed oxides are X-ray amorphous or poorly crystalline, whereas both MnO₂ and ZrO₂ are purely crystalline. The increase in surface area of the mixed oxide suggested the formation of solid solution. The surface areas of all the mixed oxides were more than 4 times higher than those of the individual oxides. Additionally, the temperature programmed desorption (TPD; NH₃ and CO₂) measurements reveal that the 10% MnO₂–ZrO₂ mixed oxide possessed a higher number of acidic as well as basic sites compared with the individual oxides.

As a result, MnO₂–ZrO₂ binary metal oxides exhibited greatly elevated catalytic activity for the conversion of EB than those of the individual oxides in the presence of CO₂ (Fig. 1). The MnO₂–ZrO₂ binary metal oxide catalyst exhibited conversion of 73% with a selectivity of 98% at 650 °C. However, in the absence of CO₂, poor catalytic activity and stabilities were observed. A gradual enhancement of activity was demonstrated for the higher CO₂ to EB ratios. The increase or optimization of the CO₂/EB ratios showed an increase in conversion along with a preservation of the high selectivity. Hence, CO₂ had an active role as a soft oxidant by improving both activity and stability in the dehydrogenation of EB over MnO₂–ZrO₂ mixed oxide catalysts.

Scheme 1. Development of zirconia-based metal oxide catalysts.

Fig. 1. Effect of MnO₂ content in MnO₂-ZrO₂ for the conversion of EB. (1) 5% MnO₂-ZrO₂; (2) 10% MnO₂-ZrO₂; (3) 20% MnO₂-ZrO₂; (4) 50% MnO₂-ZrO₂. Reaction conditions: Catalyst weight = 1.0 g, temperature = 600 °C, CO₂/EB = 5.1 (molar ratio), W/F = 16.73 (g_{cat}·h)/mol. Reproduced from Ref. [55].

The superior activity of MnO₂-ZrO₂ mixed oxide over its respective individual oxides might arise from the generation of active sites during the stages of mixed oxide catalyst preparation as described above. The combination of redox and acid-base bi-functional mechanism might be responsible for the higher activity of MnO₂-ZrO₂ mixed oxides. However, further studies are necessary for the elucidation of the mechanism.

3.2. TiO₂-ZrO₂ binary metal oxides

The combination of TiO₂-ZrO₂ has attracted considerable attention as an active catalyst as well as support for a wide variety of reactions, as was summarized in a recent review by Reddy et al. [69]. The mixing of TiO₂ and ZrO₂ exhibits high surface area, improved surface acid-base properties and enhanced hydrothermal and mechanical robustness. TiO₂-ZrO₂ mixed oxides are proven to be highly active and selective for dehydrogenation reactions. Particularly, TiO₂-ZrO₂ catalysts were used for the oxidative and non-oxidative dehydrogenation of EB and cyclohexane. We have studied TiO₂-ZrO₂ binary metal oxides with various compositions, modified its catalytic properties with K and B, and finally combined surface modification with textural property control in the sol-gel process by using the digestion method [56–58,70].

3.2.1. Effect of composition on TiO₂-ZrO₂ binary metal oxides

We have prepared TiO₂-ZrO₂ binary metal oxide catalysts with different compositions by the co-precipitation method then calcined at 550 °C [56]. XRD patterns showed the mixed metal oxides phase changed from monoclinic ZrO₂ to tetragonal, amorphous and TiO₂ anatase phase with incremental increase of TiO₂ content from 10% to 30%. Between the ratios 40%–60%, the catalysts showed amorphous nature and further increase of the Ti content only showed anatase TiO₂ phase. The amorphous phase was crystallized to clear TiZrO₄ phase when the calcination temperature was raised to higher than 650 °C.

Through the addition of TiO₂ to ZrO₂, the surface area increased sharply and reached to about 5–9 times that of its individual oxides. The NH₃ and CO₂-TPD profiles demonstrated that the strength and number of acid-base sites of TiO₂-ZrO₂ binary metal oxides were much higher than that of its individual oxides (TiO₂ and ZrO₂).

In the dehydrogenation of EB with CO₂, the 60% TiO₂-ZrO₂ amorphous catalyst exhibited superior activity than that of other loadings (Fig. 2). The amorphous TiO₂-ZrO₂ gave the compatible catalytic sites that are comparable to TiZrO₄ phase catalysts obtained at high temperature calcination [56]. The catalytic activity was almost double those of the individual oxides and stable even at elevated temperatures in the presence of CO₂. The high selectivity arose from the suppressed cracking and hydrogenolysis reactions. Formation of benzene and toluene by-products was minimized.

The formation of amorphous TiZrO₄ phase, enhancement in the specific surface area, and increase in the number and strength of acid-base sites are some of the reasons for the observed high catalytic activity and selectivity [68]. These results indicate that the dehydrogenation of ethyl benzene to SM followed the acid-base bi-functional mechanism, wherein Zr ion acts as Lewis acid site and Ti ion as a base site [64]. The coke deposition on the surface of the catalyst was lower in the presence of CO₂ than that of its absence and resulted in better catalytic activity and selectivity.

3.2.2. Boron oxide modified TiO₂-ZrO₂ binary metal oxides

The dehydrogenation of EB to SM in the presence of CO₂ has been shown to proceed effectively on acid-base bi-functional catalysts with a balanced strength and number of acidic and basic sites. Various amounts of B₂O₃ (2.5–15 wt%) were supported on to amorphous TiO₂-ZrO₂ bifunctional catalysts with the wet-impregnation method [57]. The impregnated samples were dried, then calcined at 550 °C to activate the surface. The specific surface area of the TiO₂-ZrO₂ decreased with the im-

Fig. 2. Effect of TiO₂ content in TiO₂-ZrO₂ for the conversion of EB. Reaction conditions: Weight of the catalyst = 1 g, ethylbenzene flow rate = 1 ml/h, CO₂/ethylbenzene = 5.1 (molar ratio), pressure = 1 atm, temperature = 600 °C. Reproduced from Refs. [56,58].

pregnation of B₂O₃. The XRD patterns revealed that the addition of B₂O₃ influenced the crystallization and stabilization of the anatase TiO₂. The addition of B₂O₃ increases the acidic strength and number of acidic sites on TiO₂-ZrO₂ catalyst. The 5 wt% B₂O₃/TiO₂-ZrO₂ catalyst did not exhibit good conversion or selectivity in comparison to TiO₂-ZrO₂ catalysts. Benzene and toluene were the two major side products, which mainly arise from the influence of the strong acid-base centers on the surface of the catalysts [66]. Strong basic sites can abstract the β -H of the adsorbed EB which facilitates the cleavage of the C-C bond of the side chain resulting in the formation of toluene (Scheme 2), whereas the strong acid centers abstract the α -H of EB and facilitate the cleavage of the phenyl-C bond resulting in the production of benzene (Scheme 2).

B₂O₃ could not promote the TiO₂-ZrO₂ catalysts for the CO₂ applied dehydrogenation of EB. However, these results indicate an alternative direction for promoting TiO₂-ZrO₂ with base moieties.

3.2.3. K₂O promoted TiO₂-ZrO₂ binary metal oxides

Based on the studies of TiO₂-ZrO₂ binary metal oxide catalysts, we realized that these TiO₂-ZrO₂ binary metal oxide catalysts could be further improved for the dehydrogenation of EB with CO₂ by neutralizing the strong acidic sites. Amorphous TiO₂-ZrO₂ binary metal oxide with a specific composition (60:40 molar ratio) was impregnated with 1, 2, 3, and 4 wt% K₂O [58]. After the impregnation, all these samples were dried at 120 °C for 12 h, and calcined at 600 °C for 6 h in air.

An increased amount of K₂O loading will diminish the BET surface areas of TiO₂-ZrO₂ binary metal oxide which might arise from the blockage of micropores. Through the addition of K₂O, excess TiO₂ in the amorphous TiO₂-ZrO₂ binary metal oxide was crystallized into the anatase phase [71]. The motiva-

tion was to use a basic alkali promoter for the activation of CO₂. For the over 3% K₂O/TiO₂-ZrO₂ catalyst, unified effects of K₂O and CO₂ were observed. At a minimum loading (1 wt%) of K₂O, the strong acidic sites were poisoned, while increasing K₂O loading resulted in the neutralization of some weak to moderate acidic sites [3,4]. In the presence of N₂, the conversion of EB over the TiO₂-ZrO₂ catalyst was 52.19%. In the presence of CO₂, the conversion of EB over a 3% K₂O/TiO₂-ZrO₂ catalyst was increased to 71.95%. The increase in the conversion is almost 20% and selectivity had almost reached 100% (99.63%). Deactivation of the K₂O/TiO₂-ZrO₂ catalyst was prolonged and the benzene formation was almost negligible. Such high selectivity was usually observed at lower conversion levels of EB [72]. The high SM selectivity of the K₂O-promoted catalyst arose from the suppression of the dealkylation reaction by neutralizing the strong acidic sites and converting hydrogen into water by the coupling of the RWGS reaction (Fig. 3) [58].

As mentioned earlier, an acid-base bi-functional mechanism was proposed by several authors for the dehydrogenation of EB [5,10]. It is clear that there should be a balance of number and strength between acidic and basic sites either for simple dehydrogenation or ODH of EB with CO₂.

3.2.4. TiO₂-ZrO₂ binary oxides by digestion

Amorphous TiO₂-ZrO₂ binary metal oxides will provide more acid-base active sites by increasing their surface area. This will bring compatible benefits to the dehydrogenation of EB proposed by an acid-base bi-functional mechanism. There is a well-known method to improve surface area of metal oxides by amorphization with alkali metal doping (Scheme 3) [70].

Using KOH solution as a hydrolyzing agent as well as a digestion medium, a high surface area TiO₂-ZrO₂ (50%) was prepared. Highly crystalline phases of ZrO₂ are observed for the undigested TiO₂-ZrO₂ catalyst (calcined at 600 °C) [70]. After digestion with KOH solution, TiO₂-ZrO₂ was transformed to amorphous TiZrO₄ phase, which was confirmed from the Raman spectra [70]. After digestion, the particle size decreased from 25 to 5 nm. Surprisingly, the specific surface area was increased to 166 m²/g which was higher than previously re-

Scheme 2. Cracking and hydrogenolysis of EB.

Fig. 3. Effect of K_2O content in $\text{TiO}_2\text{-ZrO}_2$ for the conversion of EB. Reaction conditions: Weight of the catalyst = 1.0 g, ethylbenzene flow rate = 1 ml/h, CO_2/EB = 5.1 (molar ratio), pressure = 1 atm, temperature = 550 °C. Reproduced from Ref. [58].

ported for the undoped catalyst. The phase transformation from the crystalline to amorphous phase is the crystallization-amorphization-reorganization process which is the Ostwald ripening process induced by K (or Na) in the digestion media [73]. The alkali metal was doped into $\text{TiO}_2\text{-ZrO}_2$ metal oxides during digestion which showed a broadness in the 01s species of the catalysts as evidenced in the references which consequently showed the increase in activity and selectivity along with improved CO_2 conversion [70]. The digestion process helped in adjusting the acid-base properties of the catalysts.

The catalysts were applied to the dehydrogenation of methylbenzene. The highest conversion, selectivity and CO_2 consumption were observed simultaneously over properly digested $\text{TiO}_2\text{-ZrO}_2$ catalyst.

$\text{TiO}_2\text{-ZrO}_2$ catalysts were also prepared by NaOH digestion [74]. Compared with KOH digestion, a higher surface area of 188 m^2/g was achieved. The particle size of the $\text{TiO}_2\text{-ZrO}_2$ catalyst was even decreased to 3–5 nm, which is slightly smaller than that observed with KOH digestion. Acid-base sites were increased in both number and strength. In the dehydrogenation of EB with CO_2 , during 15 h time-on-stream, NaOH digested catalyst showed high conversion (>60%), good selectivity (>95%) and apparent CO_2 consumption (>10%) (Fig. 4).

Digested $\text{TiO}_2\text{-ZrO}_2$ is highly desirable toward dehydrogenation reactions, especially for CO_2 applied ODH of EB.

3.3. $\text{CeO}_2\text{-ZrO}_2$ binary metal oxides

CeO_2 is one of the most popular transition metal oxides in

Scheme 3. Formation of solid solution over digestion. Reproduced from Ref. [70].

the application of heterogeneous catalysis as the active component, additives or the support [75,76]. CeO_2 and ZrO_2 mixed oxides could generate definite benefits to the catalytic properties owing to the redox properties of CeO_2 , acid-base properties of ZrO_2 and the formation of new crystal phase [65,77]. The CeO_2 phase is able to store more active oxygen species in the catalyst system and is expected to suppress the coke formation more effectively.

A catalyst comprised of 25 mol% CeO_2 and 75 mol% ZrO_2 (25CZ), as a binary metal oxide, was prepared by the co-precipitation method [59]. According to the XRD patterns of 25CZ, the solid solution formed with tetragonal symmetry, and

Catalyst	A_{BET} (m^2/g)	Acidic sites (mmol/g)	Basic sites (mmol/g)	CO_2 conversion (%)
$\text{TiO}_2\text{-ZrO}_2$ (TZ)	144	0.52	0.04	1
$\text{TiO}_2\text{-ZrO}_2$ (KOH digestion, K-24)	166	0.14	0.44	11
$\text{TiO}_2\text{-ZrO}_2$ (NaOH digestion, Na-24)	188	0.42	0.46	9

Fig. 4. Digested $\text{TiO}_2\text{-ZrO}_2$ for the dehydrogenation of EB. Reaction conditions: Weight of the catalyst = 1.0 g, ethylbenzene flow rate = 1 ml/h, CO_2/EB = 5.1 (molar ratio), pressure = 1 atm, temperature = 600 °C. Reproduced from Ref. [73].

no tetragonal or monoclinic forms of ZrO_2 were observed [64]. This arose from a facile solid phase reaction between CeO_2 and ZrO_2 . The surface area of 25CZ binary metal oxide ($37 \text{ m}^2/\text{g}$) is approximately the same as the sum of the constituent individual oxides (25 and $19 \text{ m}^2/\text{g}$ for ZrO_2 and CeO_2 , respectively) [59].

25CZ catalyst exhibited better activity than CeO_2 and ZrO_2 . The enhancement of catalytic activity could be explained where a kind of stress between the bonded atoms (Ce-O-Zr) was developed by variation of the ionic sizes (effective ionic radii of $\text{Ce}^{4+} = 0.97 \text{ \AA}$, $\text{Ce}^{3+} = 1.14 \text{ \AA}$, $\text{Zr}^{4+} = 0.84 \text{ \AA}$). The mixed metal oxide tends to form fine particles or amorphous mixtures, and will improve the acid-base property. The catalytic result was not comparable to $\text{MnO}_2\text{-ZrO}_2$ and $\text{TiO}_2\text{-ZrO}_2$ systems. Further investigations on $\text{CeO}_2\text{-ZrO}_2$ binary metal oxides are necessary.

3.4. $\text{SnO}_2\text{-ZrO}_2$ binary metal oxides

A series of $\text{SnO}_2\text{-ZrO}_2$ nanocomposite catalysts were prepared over the full range from 0 to 100% of SnO_2 by careful hydrolysis of both metal salts with NH_3 solution [60]. The gel was precipitated and calcined at 600°C . The sizes of the binary metal oxide particles were in the range of 10–15 nm with uniform spherical morphology. Pure monoclinic ZrO_2 phase and cassiterite SnO_2 phase co-existed in the nanocomposite catalysts containing 10%–40% of SnO_2 . However, at 50%–90% SnO_2 content, the nanocomposite catalysts exhibited only cassiterite SnO_2 phase. No significant XRD reflections were related to ZrO_2 . There was a strong interaction between the two metal oxides. Owing to the strong interaction, the binary metal oxides showed greater surface acidity and moderate basicity compared with those of the single component oxides (Fig. 5). The highest catalytic activity was obtained over 15% $\text{SnO}_2\text{-ZrO}_2$ (15% SnO_2 , 85% ZrO_2). The beneficial role of CO_2 as a diluent and as a soft oxidant was apparent over the $\text{SnO}_2\text{-ZrO}_2$ binary metal oxide catalyst.

3.5. Mesoporous silica-supported binary metal oxides

The properties of metal oxide nanoparticles were greatly in-

Fig. 5. EB conversion over SnO_2 , ZrO_2 , $\text{SnO}_2\text{-ZrO}_2$. Reaction conditions: Catalyst weight 1.0 g, 600°C , 1 atm, $\text{CO}_2/\text{EB} = 6$ (molar ratio), $W/F = 17.6 \text{ (g}_{\text{cat}}\text{h)}/\text{mol}$. Reproduced from Ref. [60].

fluenced by the number of atoms at the surface. However, at high temperatures, the metal oxide nanoparticles were easily sintered and dramatically lost their activities. One solution is to support the metal oxides on high surface area and thermally stable mesoporous materials, such as SBA-15 or mesoporous silicalite-1 [59,78,79].

3.5.1. SBA-15-supported $\text{CeO}_2\text{-ZrO}_2$

Supported metal or metal oxides have been used and studied in various reactions. Mesoporous silica, used as support, was chosen to disperse the mixed metal oxide system for overcoming the diffusion limitation to improve the activity. In the preparation of the $\text{CeO}_2\text{-ZrO}_2/\text{SBA-15}$ catalyst, $\text{Ce}(\text{NO}_3)_3$ and $\text{ZrO}(\text{NO}_3)_2$ were hydrolyzed with NH_3 solution in the presence of calcined SBA-15. Mixed metal hydroxide gels will form inside the mesopore or on the outer surface of SBA-15. The 25/25CZS catalyst (25 wt% of 25CZ on the SBA-15) was calcined at 650°C for 12 h [59]. Undoubtedly, the supported 25/25CZS catalyst is X-ray amorphous revealing that $\text{CeO}_2\text{-ZrO}_2$ binary metal oxides were highly dispersed on the SBA-15. In the dehydrogenation of EB with CO_2 , the 25/25 CZS catalyst showed superior activity than those of the individual oxides and binary metal oxides in terms of turn over frequencies (TOF). Owing to the high dispersion of the binary metal oxides on the SBA-15, the active sites were easily accessible to the reactants. The TOF of 25/25CZS catalyst was elevated 10–20 times when compared with its bulk oxides. The catalytic activity of this supported catalyst was stable during 10 h of time-on-stream, while the activity of the unsupported metal oxides was decreased within 8 h of time-on-stream [59]. The improved lifetime of the supported 25/25CZS catalyst was mainly owing to the suppressed sintering of metal oxide nanophases at high temperatures and facile transportation of reactant or product in the mesoporous SBA-15. Further optimization of synthesis procedures and more detailed characterization are required to improve this novel catalyst system.

3.5.2. Mesoporous silicate-1-supported $\text{TiO}_2\text{-ZrO}_2$

Among our studies on ZrO_2 -based binary metal oxide bulk catalysts, the results over $\text{TiO}_2\text{-ZrO}_2$ are promising. They were supported onto the thermally stable mesoporous silicalite-1 [79]. The XRD pattern of TZ/CS-1 did not show any crystalline phase of TiO_2 or ZrO_2 , only a typical reflectance for the MFI-type zeolite from mesoporous silicalite-1 support. $\text{TiO}_2\text{-ZrO}_2$ binary metal oxides were highly dispersed within the silicalite-1 crystals and showed a high proportion of strong acid-base sites which might arise from the formation of solid solutions (ZrTiO_4). In the dehydrogenation of EB to SM with CO_2 , this catalyst showed poor catalytic activity and selectivity to SM. However, the amount of coke deposition was less owing to the well-developed porosity of the mesoporous silicalite-1 support.

4. Multi metal oxides for combination of acid-base with redox properties

The $\text{TiO}_2\text{-ZrO}_2$ composite oxides are of great interest as ac-

tive catalysts as well as supports in the design of heterogeneous catalysts for a wide range of reactions [69]. The significant features of $\text{TiO}_2\text{-ZrO}_2$ -based mixed oxides include a high specific surface area, improved acid-base properties when compared with those of the individual oxides, and improved redox properties, together with a high thermal stability and strong mechanical strength. Our fundamental studies revealed that $\text{TiO}_2\text{-ZrO}_2$ binary metal oxides were dependable catalysts with excellent catalytic activity and selectivity for dehydrogenation of EB with CO_2 as a soft oxidant [5]. However, there is still some concern regarding the fast deactivation of $\text{TiO}_2\text{-ZrO}_2$ binary metal oxide catalysts by carbonaceous deposits [80].

One of the generally accepted hypotheses for ODH is that the reaction proceeds over redox active sites following a Mars–Van Krevelen mechanism and the rate-determining step is the breaking of the C–H bond (Schemes 4 and 5) [81,82]. Further, it is generally agreed that hydrocarbon oxidation over metal oxide catalysts involves the participation of lattice oxygen species or oxygen vacancies.

Therefore, in the subsequent investigations, redox metal oxide-promoted $\text{MO}_x/\text{TiO}_2\text{-ZrO}_2$ catalysts, where MO_x is Fe_2O_3 , V_2O_5 , CeO_2 , $\text{V}_2\text{O}_5\text{-CeO}_2$ and $\text{V}_2\text{O}_5\text{-Sb}_2\text{O}_5\text{-CeO}_2$, were synthesized and evaluated for the ODH of EB using CO_2 as the soft oxidant [80,83–85].

4.1. $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst: influence of Cl

The $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ catalyst was explored and the influence of chloride ions in $\text{TiO}_2\text{-ZrO}_2$ binary metal oxide was discussed (Fig. 6). Calcined $\text{TiO}_2\text{-ZrO}_2$, which was synthesized by a co-precipitation method, was wet impregnated with 15 wt% Fe_2O_3 . After calcination, the chlorine-containing $\text{TiO}_2\text{-ZrO}_2$ showed less surface area and revealed a slightly crystalline phase of ZrTiO_4 . The iron oxides were highly dispersed over the chlorine-containing $\text{TiO}_2\text{-ZrO}_2$ support as evidenced by the XRD pattern. Fe_2O_3 impregnation did not change the pore structure, crystal phase or particle morphology of chlo-

Scheme 4. Proposed dehydrogenation mechanism over $\text{TiO}_2\text{-ZrO}_2$.

Scheme 5. Reduction and re-oxidation step in the Mars-van Krevelen mechanism.

rine-containing $\text{TiO}_2\text{-ZrO}_2$. In the dehydrogenation of EB with CO_2 , the order of activity on various catalysts was found to be $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ (Cl) > $\text{TiO}_2\text{-ZrO}_2$ (Cl) > $\text{TiO}_2\text{-ZrO}_2$. Cl ions exhibit a strong influence on the physicochemical and catalytic properties of the $\text{TiO}_2\text{-ZrO}_2$ and revealed a good catalytic efficiency of the $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ combination. From the results of high and stable activity without rapid deactivation, the iron chloride species are expected to play a role as redox active sites and this can be coupled with the acid-base $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ [83].

4.2. $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ combination catalysts

The ceria component in the mixed metal oxides is able to

Sample	Surface area (m^2/g)
$\text{TiO}_2\text{-ZrO}_2$ (TZ-1)	207
$\text{TiO}_2\text{-ZrO}_2$ (TZ-2)	146
$\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$ (FTZ)	132

TZ-1: Cl-free $\text{TiO}_2\text{-ZrO}_2$
 TZ-2: Cl containing $\text{TiO}_2\text{-ZrO}_2$
 FTZ: 15 wt.% $\text{Fe}_2\text{O}_3/\text{TiO}_2\text{-ZrO}_2$

Fig. 6. Effect of chlorine and Fe_2O_3 in $\text{TiO}_2\text{-ZrO}_2$ for the conversion of EB. Reaction conditions: Catalyst weight = 1.0 g, temperature = 600 °C, pressure = 1 atm, CO_2 = 20 ml/min, EB = 9.8 mmol/h. Reproduced from Ref. [83].

promote the oxidizability of catalysts and can suppress catalyst deactivation by preventing coke formation in the ODH reactions [80]. In the high temperature gas phase dehydrogenation reaction, bulk cerium and vanadium oxides undergo sintering easily and deactivate rapidly. The combination of vanadia (known for its redox properties) and ceria (known for its oxygen storage and release functions) is expected to provide better catalytic systems.

On the acid-base $\text{TiO}_2\text{-ZrO}_2$ binary metal oxides, vanadium oxide and cerium oxide were supported individually or together for the ODH of EB to SM using CO_2 as a soft oxidant. Here, by control of the sol-gel process, a high specific surface area ($207 \text{ m}^2/\text{g}$) $\text{TiO}_2\text{-ZrO}_2$ was synthesized by a co-precipitation method. The $\text{TiO}_2\text{-ZrO}_2$ was calcined at 550°C . Based on the surface area of $\text{TiO}_2\text{-ZrO}_2$, a monolayer equivalent of V_2O_5 (15 wt%), CeO_2 (15 wt%) and $\text{CeO}_2\text{-V}_2\text{O}_5$ (7.5 wt% + 7.5 wt%) were deposited by adopting a standard wet impregnation method, then calcined again at 550°C . These mixed metal oxides showed an X-ray amorphous phase, but contained an amorphous TiZrO_4 phase and smaller amounts of ZrV_2O_7 and CeVO_4 phase. In the $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ catalyst, the co-addition of ceria with vanadium oxide onto the $\text{TiO}_2\text{-ZrO}_2$ support gave rise to a strong solid-state reaction, which influenced the particle size of the $\text{TiO}_2\text{-ZrO}_2$, and promoted the vanadium oxide dispersion and the reducibility.

The $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ catalyst showed superior activity with higher selectivity than those of the individual metal oxide-supported catalysts (Fig. 7). In this combination catalyst system, 56% conversion and 98% product selectivity were achieved during 10 h time-on-stream. Addition of CeO_2 to $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ prevented catalyst deactivation and helped to maintain a high and stable catalytic activity.

4.3. $\text{V}_2\text{O}_5\text{-Sb}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ catalysts

The redox behavior of V_2O_5 as a catalyst is known in ODH. Sb_2O_5 is able to stabilize highly dispersed V_2O_5 species on the catalyst support. Antimony oxides and highly dispersed vana-

Fig. 8. Activity comparison of the present VSC/TZ catalyst with previous results. Reaction conditions: 600°C , CO_2/EB molar ratio = 5.1. Reproduced from Ref. [85].

dium oxides could react in the solid phase and provide a new mixed oxide phase, which is likely to induce a facile redox transformation between vanadium redox pairs, and result in improved catalyst activity and stability [16]. Similar results were also observed in the catalyst of V stabilized with $\text{CeO}_2\text{-ZrO}_2$ solid solution (Fig. 8) [43].

Based on the positive role of Sb and Ce to the supported vanadium oxides, we designed a $\text{V}_2\text{O}_5\text{-Sb}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ catalyst, under the concept of combining the acid-base bi-functional nature with the redox properties [85]. In the mixed metal oxides, the highly dispersed vanadium species induced the formation of a well-crystalline ZrTiO_4 compound and some ZrV_2O_7 phase [84]. The existence of highly active VSbO_4 species was also observed.

The addition of antimony oxide to the former $\text{V}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ catalyst will give a selectivity of SM higher than 96% at the conversion levels of EB at about 50%–65%. This result is better than the data previously reported by our group.

Acid-base and redox properties, including sustained stability of active species (V^{5+}), are responsible for the high activity of

Fig. 7. Catalytic activity of $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ for the conversion of EB. Reaction conditions: Catalyst weight 1.0 g, 600°C , 1 atm, $W/F = 16.73 \text{ (g}_{\text{cat}}\cdot\text{h)}/\text{mol}$, $\text{CO}_2/\text{EB} = 5.1$ (molar ratio). Reproduced from Ref. [80].

Catalyst	A_{BET} (m^2/g)
TZ	207
VTZ	175
CTZ	189
VCTZ	170

TZ: $\text{TiO}_2\text{-ZrO}_2$

VTZ: 15% $\text{V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$

CTZ: 15% $\text{CeO}_2/\text{TiO}_2\text{-ZrO}_2$

VCTZ: 7.5% $\text{V}_2\text{O}_5\text{-7.5%CeO}_2/\text{TiO}_2\text{-ZrO}_2$

the $\text{V}_2\text{O}_5\text{-Sb}_2\text{O}_5\text{-CeO}_2/\text{TiO}_2\text{-ZrO}_2$ catalyst. The redox cycle is related to the dispersed V^{5+} and lattice reduced vanadium site in the VSbO_4 phase [85]. The antimony oxide inhibits the easy redox cycle between different vanadia species.

4.4. ODH of *p*-diethylbenzene and *n*-butane

The concept of acid-base bi-functionality and redox nature has been extended to other alkyl aromatics and lower alkanes, especially, $\text{TiO}_2\text{-ZrO}_2$ -based catalysts have been applied to other reactions, such as CeO_2 promoted $\text{TiO}_2\text{-ZrO}_2$ nano-oxide catalysts for the ODH of *p*-diethylbenzene and a novel $\text{VO}_x/\text{SnO}_2\text{-ZrO}_2$ catalyst for C4 olefins from *n*-butane. Both catalytic systems developed provide further proof that acid-base bi-functional/redox catalysts can undoubtedly be used for C-H activation [15,86,87].

4.4.1. CeO_2 promoted $\text{TiO}_2\text{-ZrO}_2$ catalysts for ODH of *p*-diethylbenzene

CeO_2 promoted $\text{TiO}_2\text{-ZrO}_2$ (CTZ-MW) mixed oxides were synthesized by the microwave hydrothermal method and compared with the conventional hydrothermal method (CTZ-HT) in the dehydrogenation of *p*-diethylbenzene with CO_2 [86]. Interestingly, microwave prepared CTZ-MW showed an improved specific surface area compared to CTZ-HT, which is not common in the case of the $\text{TiO}_2\text{-ZrO}_2$ binary metal oxide system. CeO_2 is highly dispersed onto $\text{TiO}_2\text{-ZrO}_2$. Over the CTZ-MW catalyst, the conversion and selectivity of *p*-diethylbenzene were 74% and 98%, respectively. The time-on-stream was stable up to 8 h. The unique activity of CTZ-MW was achieved through CeO_2 promotion and improved textural properties with MW synthesis (Fig. 9).

4.4.2. $\text{VO}_x/\text{SnO}_2\text{-ZrO}_2$ catalyst for ODH of *n*-butane

Vanadium oxide was supported onto the ZrO_2 , SnO_2 and $\text{SnO}_2\text{-ZrO}_2$ mixed oxide for the ODH of *n*-butane employing CO_2 as the soft oxidant [87]. The composition of catalyst was investigated and the 7.5 wt% $\text{V}_2\text{O}_5/\text{SnO}_2\text{-ZrO}_2$ (SnO_2 is 15% in the $\text{SnO}_2\text{-ZrO}_2$) catalyst exhibited the best catalytic activity. This

Fig. 9. Activity comparison over TZ and CTZ catalyst for DEB conversion. Reaction conditions: 600 °C, 1 atm, LHSV = 0.5 ml/h, CO_2/DEB = 20 (molar ratio). Reproduced from Ref. [86].

optimized catalyst has a high specific surface area and a higher number of medium strength acid-base sites than the others. Additionally, supported-vanadia species were reduced at a relatively lower temperature. The CO_2 as a diluent or oxidant also exhibited a significant promotion effect on the selective conversion of *n*-butane to C4 olefins over 7.5 wt% $\text{V}_2\text{O}_5/\text{SnO}_2\text{-ZrO}_2$ catalyst with 22.34% conversion of *n*-butane and 36.63% selectivity to C4 olefins.

5. Summary

ODH of EB to SM is of great potential and economical interest as a means of producing high yields of SM. EB dehydrogenation with CO_2 as a soft oxidant was studied intensively over ZrO_2 -based binary metal oxide catalysts. The catalytic activity of the mixed oxides is greater in the presence of CO_2 compared with its absence. These mixed metal oxides are essentially nanoparticles with improved textural properties and the newly developed acid-base bi-functionality.

The development of a catalyst system that shows promising catalytic activity for EB with selectivity towards SM and CO_2 conversion has been studied. CO_2 played a vital role in the activity and improving stability of the catalyst. The role of CO_2 can be defined as a soft oxidant, which is oxidizing the surface of the catalyst and maintaining the surface oxygen content, removing the coke on the surface of the catalyst by reverse Boudouard reaction, removing the hydrogen product by RWGS reaction and providing high heat capacity to the reaction system, which helps in overcoming the equilibrium limitation and achieve high conversions [45,54,73,88–92].

All the catalysts studied above are illustrations of ZrO_2 -based catalytic systems with improved and modified acid-base properties along with redox properties. These modifications lead to an improvement of the development of catalysts with high thermal stability, improved activities and CO_2 activation. The best result was observed from the $\text{CeO}_2\text{-V}_2\text{O}_5/\text{TiO}_2\text{-ZrO}_2$ catalyst, which combines the stabilized redox property with acid-base bi-function. This multi metal oxide system is improved further by the addition of Sb as a redox stabilizer. Doping of alkali and alkaline earth metals has enhanced the conversions and selectivities along with CO_2 conversion based by optimizing the acid-base properties and increased surface areas. In summary, based on the present status of the catalyst and the process, there is a lot of scope for further studies to meet requirements such as high per pass conversion above 75% and selectivity greater than 98% with CO_2 conversion around 30%. From the above discussion, the strategies that should be focused on are:

- (1) Stabilization and improvement of the present catalyst system for a greater than 24 h single run;
- (2) Reducing coke formation;
- (3) Regeneration of catalyst;
- (4) Improving CO_2 activation and conversion.

These developed catalysts provide a foundation for scaling up the reaction systems to the commercial scale. Using CO_2 as feedstock has been a farfetched dream which can be run by using the out gas from petrochemical oxidation or the reform-

ing industry. The high selectivity of SM in this selective dehydrogenation process suggests a \$2.7 million saving for 0.6 Mt of SM monomer per year could be made, which arises from the input and the output energies in the case of the industrial steam process, and is much higher than that of the CO₂-mediated process.

6. Conclusions

The catalyst systems for the ODH have been tested only to the lab scale and are mainly based on acid-base catalysts and redox catalysts. We conclude that the oxidative dehydrogenation of EB with CO₂ is an economic and environmentally-benign process which may serve the increasing SM demand in the near future. Although using the CO₂ process has the advantage of being an energy saving process, there are still challenges that need to be overcome, such as coke formation, longevity of the catalyst and high per pass conversion. These challenges provide a lot of scope for research in this area for the development of catalysts. Another important aspect of the ODH with CO₂ is the production of CO byproducts, which is a very valuable chemical able to be used in many processes. A clear understanding of the mechanisms of the reaction, coke formation and CO₂ activation will enable us to obtain a potential catalyst that can be industrially viable. We can envisage that using CO₂ in this process may reduce the overall CO₂ production in the production of SM.

Acknowledgments

This work is funded by Saudi Arabia Basic Industries Corporation (Kingdom of Saudi Arabia), the BK21 Plus Project in 2014 and Nano-Technology Fusion Center (Inha University, Chemistry & Chemical Engineering, Lab of Nano-Green Chemistry).

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Graphical Abstract

Chin. J. Catal., 2016, 37: 3–15 doi: 10.1016/S1872-2067(15)60901-9

Ethylbenzene to styrene over ZrO₂ based mixed metal oxide catalysts with CO₂ as a soft oxidant

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Acid-base bi-functionality activation of alkyl aromatics and CO₂ is simultaneously performed on the same zirconia-based mixed metal oxide catalyst to yield high activity and selectivity.

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ZrO₂基复合金属氧化物催化剂上CO₂温和氧化乙苯制苯乙烯

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摘要: 苯乙烯(SM)是聚合物化学中最重要的单体之一,由其生产的聚合物产品(如PS, SBR和ABS等)具有独特的性能,因而SM的需求逐年增加. 乙苯(EB)催化脱氢工艺提供了90%的SM需求,该过程在K促进的氧化铁催化剂上于600–650 °C进行. 这是一个吸热且体积增大的反应,因此需要绝热反应器和大量的过热饱和蒸汽以提供热量和降低反应分压,从而有利于反应平衡向SM方向移动,也可避免或消除积碳. 同时,也造成大量潜热被浪费;热点也降低了整个反应活性和催化剂寿命. 在蒸汽中加入空气或富氧空气,使得副产H₂与O₂反应,产生的热量可供随后乙苯脱氢反应,同时H₂的移除也有利于提高EB单程转化率,并保持高的SM选择性. 但是,该过程需要2个催化剂,反应器的设计和催化剂的装填比较复杂,且存在爆炸的危险. 因此,人们尝试了多种氧化剂和新型的催化剂. 最近也有人提出软氧化剂的概念. 这为开发新催化体系提供了可能.

相对于O₂, CO₂的氧化性很弱,但可用作温和氧化剂去除脱氢单元中副产的H₂,降低了反应温度,且不影响反应活性和选择性;同时,具有较大的经济性和环保性,在工业上也是切实可行的. 除了负载型的碱金属促进的氧化铁催化剂外,各种金属或金属氧化物也用于催化CO₂氧化EB脱氢反应中,如Fe, Cr, V和La的氧化物为活性金属,碳材料、MgO、SiO₂、Al₂O₃、Ga₂O₃、ZrO₂、TiO₂、水滑石类化合物及分子筛为载体. Park课题组研究了Fe, V和Cr基催化剂,即设计氧化还原的催化剂表面以解离CO₂,产生的O用于逆水汽反应. 其中以Al₂O₃负载的V和V-Sb氧化物催化剂性能最为突出;但存在积碳失活和V物种的深度还原等问题. 为了进一步提高催化剂性能,该课题组开发了多种ZrO₂基复合氧化物催化剂,包括MnO₂-ZrO₂, TiO₂-ZrO₂, CeO₂-ZrO₂和SnO₂-ZrO₂. 这些催化剂具有酸碱特性,在反应中表现出较高的催化性能. 因此,本文简要总结了用于CO₂氧化EB脱氢反应的ZrO₂基催化剂最新研究进展.

研究发现,在CO₂氧化EB脱氢制SM反应中,CO₂在提高催化剂活性和稳定性方面起着非常重要的作用,可被定义为软氧化剂:氧化催化剂表面以保持其表面氧含量,移除催化剂表面产生的积碳和副产物H₂,为反应体系提供较高的热容以克服反应平衡限制,从而达到较高的转化率. ZrO₂基复合金属氧化物是具有改善的织构特性的纳米粒子,且具有酸碱两性和氧化还原性能. 改性可提高催化体系的热稳定性和活性. 其中CeO₂-V₂O₅/TiO₂-ZrO₂催化剂具有恰当的氧化还原性和酸碱两性,二者协同作用,因而催化性能最佳. 氧化还原稳定剂Sb的添加进一步提高了其催化性能. 碱金属和碱土金属可优化其酸碱特性,增加比表面积,从而提高反应活性和选择性以及CO₂转化率. 继续加强抑制积碳和促进CO₂活化方面的研究,可望进一步提高单程转化率(75%以上)、选择性(98%)和CO₂转化率(30%).

总之,CO₂氧化EB脱氢制SM是一个高度经济性和环境友好的新过程,在未来有望满足SM日益增长的需求. 另外,该过程的开发可减少CO₂排放,其副产的CO还可用于多种化工过程. 然而,该过程仍面临诸多挑战:如何抑制积碳,单程转化率和催化剂寿命有待进一步提高. 这些挑战也给我们未来的研究提供了方向. 深入理解反应机理、积碳机理和CO₂的活化过程也有利于我们开发出更适合工业应用的催化剂.

关键词: 氧化脱氢; CO₂活化; ZrO₂基复合氧化物; 酸碱特性; 氧化还原性

收稿日期: 2015-03-01. 接受日期: 2015-05-04. 出版日期: 2016-01-05.

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