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Article

Rod-shaped porous alumina-supported Cr_2O_3 catalyst with low acidity for propane dehydrogenation

Xin-Qian Gao, Wen-Duo Lu, Shou-Zhao Hu, Wen-Cui Li, An-Hui Lu *

State Key Laboratory of Fine Chemicals, School of Chemical Engineering, Dalian University of Technology, Dalian 116024, Liaoning, China

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ABSTRACT

Direct catalytic propane dehydrogenation (PDH) to obtain propylene is a more economical and environmentally friendly route for propylene production. In particular, alumina-supported Cr_2O_3 catalysts can have better potential applications if the acidic properties could be tuned. Herein, a series of rod-shaped porous alumina were prepared through a hydrothermal route, followed by calcination. It was found that the acidity of the synthesized alumina was generally lower than that of the commercial alumina and could be adjusted well by varying the calcination temperature. Such alumina materials were used as supports for active Cr_2O_3 , and the obtained catalysts could enhance the resistance to coke formation associated with similar activity in PDH reaction compared to the commercial alumina. The amount of coke deposited on a self-made catalyst (Cr-Al-800) was 3.6%, which was much lower than that deposited on the reference catalyst (15.7%). The lower acidity of the catalyst inhibited the side reactions and coke formation during the PDH process, which was beneficial for its high activity and superior anti-coking properties.

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1. Introduction

Propylene is one of the most important building blocks in petrochemical industry [1,2], with a global production capacity of 127 million metric tons per year. Currently, the industrial process for propylene production is mainly based on the steam cracking and fluid catalytic cracking (FCC) of naphtha, light diesel, and other oil byproducts [2,3], which inevitably involves extensive energy consumption and significant emission of CO_2 [1,4]. Compared with the thermal or catalytic cracking, direct catalytic propane dehydrogenation (PDH) to obtain propylene is a more economical and environmentally friendly route [5] and has been commercialized by UOP and ABB Lummus in the 1990s [6]. Three types of direct catalytic PDH technologies, CATOFIN, Oleflex and STAR, have been developed on an indus-

trial scale in more than 14 installations [4]. In addition, many new facilities are already under construction, or their prospective constructions have been announced [7].

In commercialized PDH technologies, the CrO_x -based catalysts have been widely used because of their low price and outstanding performance [4,8]. However, these catalysts suffer from fast deactivation by coke deposition, which has become one of the major problems in the existing PDH processes [9,10]. The spent catalysts need to be frequently regenerated in a high-temperature oxidative atmosphere to remove coke [9]. Thus, it is of great significance and highly desirable to prepare thermally stable CrO_x -based catalysts with anti-coking properties [10]. This can be achieved by a flexible design over supports.

The catalyst support not only serves as a scaffold but also

* Corresponding author. Tel/Fax: (0411)84986112; E-mail: anhuilu@dlut.edu.cn

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provides a complex microenvironment, which is a key factor in determining the catalytic function [3]. The catalyst support should be thermally stable enough to maintain the morphology of the catalyst, in addition to providing an open structure for the catalyst to allow easy access to the reactants and preventing the blockage of the pore by coke [4,11]. Following these lines, porous alumina is one of the most widely used material in the industries with desirable textural properties and thermal stability [9,11]. Unfortunately, the acidic nature of alumina always leads to coke formation and side reactions, inevitably leading to catalyst deactivation [9]. It has been reported that Lewis acids are generated after the dehydration/dehydroxylation of the surface and are present in the form of coordinatively unsaturated Al^{3+} , which in turn depends on the nanostructure and morphology of alumina [12–14]. The properties of alumina depend on the initial aluminum hydrates, and the calcination step dictates the properties of the final product by controlling the stepwise removal of water and OH groups [15]. However, owing to the structural complexity and diversity of phase transition, it is still challenging to precisely figure out the relationship between the structure and preparation conditions. In our previous work, a series of alumina such as Al_2O_3 nanorods with rough surface and Al_2O_3 nanosheets rich in pentacoordinate Al^{3+} were prepared through a hydrothermal approach, which could nicely disperse and stabilize gold and platinum, respectively. When used in CO oxidation and PDH reactions, the catalysts displayed excellent activities and superior stabilities [5,16]. Therefore, we conceive that alumina prepared by a similar approach could also be beneficial to the CrO_x -based catalysts.

Herein, we investigated the relationship between the structure and preparation conditions of Al_2O_3 and focused on adjusting the acidity of alumina by varying the calcination temperature. A series of rod-shaped porous alumina were prepared by a hydrothermal route, followed by calcination at different temperatures. The synthesized alumina, as a support for Cr_2O_3 , possessed low acidity and exhibited excellent stability and anti-coking ability in the PDH process.

2. Experimental

2.1. Alumina preparation

Typically, $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and $\text{CO}(\text{NH}_2)_2$ at a molar ratio of 1:9 were dissolved in deionized water, and the obtained solution was transferred to a Teflon-lined stainless-steel autoclave and heated at 100 °C for 24 h. Then, the white precipitates were washed with deionized water and anhydrous ethanol to remove the ion impurities and dried at 80 °C. After calcination at different temperatures of 700, 800, and 900 °C for 2 h, the final products were obtained and named as Al_2O_3 -T, where T represents the calcination temperature of alumina.

2.2. Catalyst preparation

Using $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ and KNO_3 as the precursors, a series of catalysts were prepared using the incipient co-impregnation

method, in which the theoretical amounts of Cr_2O_3 and K_2O loaded were 18 wt% and 1.5 wt%, respectively. After impregnation, the samples were maintained at room temperature for 2 h and then dried at 50 °C for 12 h. This was followed by calcination in 20% O_2/N_2 at 600 °C for 4 h and then reduced in 20% H_2/N_2 atmosphere at 600 °C for 2 h. The obtained unreduced and reduced samples were named as Cr-Al-T-C and Cr-Al-T, respectively. For comparison, commercial alumina (denoted as Al_2O_3 -Ref) was calcined at 800 °C and used to prepare the reference samples, which were named as Cr-Al-Ref-C and Cr-Al-Ref.

2.3. Characterization

X-ray powder diffraction (XRD) measurements were operated on a PANalytical X'Pert3 Powder diffractometer using $\text{Cu K}\alpha$ radiation ($\lambda = 0.15406 \text{ nm}$). The tube voltage was 40 kV, and the current was 40 mA. Nitrogen adsorption-desorption isotherms were obtained using a Micromeritics TriStar 3000 adsorption analyzer. The specific surface areas (S_{BET}) were calculated from the adsorption data in the relative pressure range of 0.05–0.3 using the Brunauer-Emmett-Teller (BET) method. Pore size distributions (PSDs) were determined based on the non-local density functional theory. Transmission electron microscopy (TEM) images were recorded on a FEI TECNAI F30 microscope, operating at an accelerating voltage of 300 kV. Scanning electron microscopy (SEM) investigations were carried out with a Hitachi FESEM SU8220 instrument. Ultraviolet-visible (UV-vis) spectra were recorded on a Cary 5000 UV-Vis-NIR spectrophotometers (Agilent, Japan) using diffuse reflectance spectroscopy (DRS) in the range of 200–1000 nm. BaSO_4 (AR) was used as white standards to dilute the samples to minimize the effect of the highly different extinction coefficients. Temperature-programmed reduction of hydrogen (H_2 -TPR) was performed on a Micromeritics AutoChem II 2920 apparatus with a thermal conductive detector by passing 8% H_2/Ar (flow rate of 50 mL min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$ up to 900 °C. Before H_2 -TPR, the samples were pretreated at 150 °C for 1 h under an Ar flow to ensure a clean catalyst surface. The system was then cooled to ambient temperature under Ar flow. Temperature-programmed desorption of ammonia (NH_3 -TPD) was carried out on a Micromeritics AutoChem II 2920 apparatus. Typically, the sample was pretreated in a flow of He (50 mL min^{-1}) at 500 °C for 1 h. After the temperature lowered to 100 °C, the sample was pulsed by NH_3 gas six times. Then the gas phase NH_3 was removed by He purging for 1 h, after which TPD was performed in He flow (50 mL min^{-1}) at a heating rate of $10 \text{ }^\circ\text{C min}^{-1}$. The desorbed mixture was monitored by a TCD detector, and the desorption of NH_3 was monitored by on-line mass spectrometry (MS). The amount of coke deposited was determined by the combustion of the deposited material monitored on a thermogravimetric (TG) analyzer STA 449 F3 (NETZSCH). Prior to combustion, the spent catalyst was pre-treated with flowing He (40 mL min^{-1}) at 200 °C for 1 h, and then cooled to ambient temperature under He. Finally, the sample was exposed to a mixture of 20% O_2 in N_2 flowing at 20 mL min^{-1} and oxidized from ambient tem-

perature to 900 °C at a heating rate of 10 °C min⁻¹. The CO₂ generated was monitored by on-line MS.

2.4. Catalytic tests

Catalytic performance was tested in a tubular fixed-bed quartz reactor (I. D. = 8 mm) at atmospheric pressure. The temperature of the reactor was controlled by a Yudian AI temperature controller (Series 708P). 100 mg of catalyst was used in each experiment. A feed gas composition of C₃H₈ at 8 mL min⁻¹ was passed through the catalyst bed at 600 °C for the reaction to take place. The products were analyzed by an on-line gas chromatograph. GDX-105 and molecular sieve 5A columns were used to analyze N₂, H₂, C₃H₈, C₃H₆, C₂H₄, C₂H₆, and CH₄ in the products.

$$\text{Con.} = \{[F_{\text{in}}(\text{C}_3\text{H}_8) - F_{\text{out}}(\text{C}_3\text{H}_8)] / F_{\text{in}}(\text{C}_3\text{H}_8)\} \times 100\%$$

$$\text{Sel.} = [(n_i / 3) \times F_{\text{out}}(i)] / \sum_i [(n_i / 3) \times F_{\text{out}}(i)] \times 100\%$$

Here, i is hydrocarbon product in the effluent gas stream, n_i is the number of carbon atoms of component i , and $F(i)$ is the corresponding flow rate.

A first-order deactivation model was used to evaluate the catalyst stability:

$$k_d = \left\{ \ln \left[(1 - X_{\text{final}}) / X_{\text{final}} \right] - \ln \left[(1 - X_{\text{initial}}) / X_{\text{initial}} \right] \right\} / t$$

Here, X_{initial} and X_{final} are the conversion measured at the

start and end, respectively, of an experiment, t is the reaction time (h), and k_d is the deactivation rate constant (h⁻¹). Higher k_d values are indicative of rapid deactivation, and hence, low stability.

3. Results and discussion

3.1. Propane dehydrogenation

A series of Cr-Al-T catalysts were prepared, as mentioned in the experimental section, and the propane dehydrogenation reactivities over these catalysts as well as the reference catalysts were plotted (Fig. 1). All Cr-Al-T catalysts showed better activities compared with the reference catalysts (Fig. 1a). Among the three Cr-Al-T catalysts, Cr-Al-800 exhibited the optimal initial propane conversion of 33.2%, with 90.4% propylene selectivity. After 170 min of the reaction, the propane conversion and the propylene selectivity slightly decreased to 20.4% and 84.7%, respectively. For the Cr-Al-Ref catalyst, the propane conversion dramatically dropped from an initial 40.4% to 12.8%, with the propylene selectivity decreasing from 87.7% to 71.0%. The deactivation rate constant for the Cr-Al-800 catalyst (0.26%) was much lower than that for the reference catalyst (0.61%). The amount of coke deposited on the spent catalysts was determined by thermogravimetric

Fig. 1. Propane conversion and selectivity to propylene after 170 min of the reaction for Cr-Al-T and Cr-Al-Ref catalysts (a), TG-MS profiles of the spent Cr-Al-800 and Cr-Al-Ref catalysts (b, d), and dehydrogenation-regeneration cycles over the fresh Cr-Al-800 catalyst (c). Dehydrogenation conditions: reaction temperature = 600 °C, catalyst weight = 100 mg, feed gas C₃H₈ (8 mL min⁻¹). Regeneration conditions: spent catalyst for each cycle was regenerated at 600 °C in a flow of air (40 mL min⁻¹) for 240 min.

analysis (TG) in a temperature-programmed oxidation mode (TPO) (Fig. 1b). It was observed that the amount of coke deposited on the Cr-Al-800 catalyst (3.6%) was much lower than that on the Cr-Al-Ref catalyst (15.7%). To further investigate the location of coke deposit, the concentration of CO₂ under TPO was detected by MS. Generally, the coke deposited at low temperatures is mainly the one that covers the active metal, while that deposited during combustion at higher temperatures is the one that is present on the external surface of the support [5,17,18]. Fig. 1d shows that the spent Cr-Al-800 and Cr-Al-Ref catalysts presented a similar desorption peak ranged between 250 and 550 °C, which indicated that coke was deposited in the same location, although the amount of coke deposited varied greatly. Furthermore, five dehydrogenation-regeneration cycles over the fresh Cr-Al-800 catalyst were investigated to examine the regenerative ability and stability; the recycles for the PDH reactions are presented in Fig. 1c. Cr-Al-800 catalyst exhibited superior regenerative ability, with the initial propane conversions being above 33% in all recycles, and the propylene selectivity remaining almost unchanged.

3.2. Textural and structural characterization of supports and catalysts

To investigate the effect of different calcination temperatures for alumina and the corresponding catalysts, a series of characterization techniques were carried out. Fig. 2a shows that Al₂O₃-700 and Al₂O₃-800 have the main diffraction peaks at 37.6°, 45.8°, and 66.9°, which were assigned to the γ -Al₂O₃ phase (COD: 01-079-1158) [18]. As the temperature increased,

the intensity of the reflection at 66.9° became stronger, indicating an increase in the crystallite size [15]. The change in the nature of lattice from Al₂O₃-800 to Al₂O₃-900 suggested the occurrence of phase transition, and this transition may correspond to the formation of δ -Al₂O₃ phase [15]. The diffraction peaks corresponding to the crystal phase of Cr₂O₃ were present in the XRD patterns of the Cr-Al-T catalysts (COD: 01-084-1616) (Fig. 1b). After the reaction, the spent catalysts retained their structure (Fig. S1, Supporting Information). Nitrogen adsorption-desorption isotherms (Fig. 1c) exhibited type IV adsorption isotherms with H₂-shaped hysteresis loops, indicating the typical mesoporous structure with ink-bottle-like mesopores [19]. The corresponding PSDs suggested a mesopore size centered in the range of 5–10 nm. Textural properties of the samples are summarized in Table 1. Specific surface area and pore volume of alumina decreased with increasing calcination temperature, while the pore diameter roughly increased. The decrease in the surface area is because of sintering [20]. The increase in pore size and decrease in pore volume contributed to the change in the crystal structure of alumina [21]. The specific surface area and pore volume of catalysts also decreased after loading active metal oxides. The mesopore size distributions were centered at 3.8, 5.0, and 5.9 nm for Cr-Al-700, Cr-Al-800, and Cr-Al-900, respectively, which allowed easy access to the reactants and prevented the blockage of the pore by coke (Table S2). More importantly, the total acidity of the synthesized alumina was generally lower than that of the commercial alumina. A higher calcination temperature caused a significant decrease in the total acidity (Table 1).

Furthermore, the morphologies of the samples were char-

Fig. 2. XRD patterns (a, b) and N₂ adsorption isotherms (c, d) of alumina (a, c) and the corresponding catalysts (b, d).

Table 1

Textural properties of alumina.

Sample	S_{BET} ($\text{m}^2 \text{g}^{-1}$)	V_{total} ($\text{cm}^3 \text{g}^{-1}$)	D_{peak} (nm)	Total acid sites ^a ($\mu\text{mol NH}_3 \text{g}^{-1}$)
Al ₂ O ₃ -700	217	0.43	5.6	267
Al ₂ O ₃ -800	165	0.37	6.3	178
Al ₂ O ₃ -900	117	0.36	9.8	90
Al ₂ O ₃ -Ref	189	0.92	14.5	281

^a Acid sites estimated based on NH₃-TPD profiles (Fig. S3).^b Commercial alumina was calcined at 800 °C.

acterized by SEM, TEM, and HRTEM. It can be clearly seen in Fig. 3a, b, and c that the representative Al₂O₃-800 sample displayed rod-shaped structure and quite a rough surface that possessed numerous small mesopores with the average sizes of 5.0 nm. The results were consistent with nitrogen sorption measurement. After the loading of Cr species, the roughness of the surface seemed to disappear, implying the uniform distribution of Cr species on the surface (Fig. 3e and f). The Al₂O₃-Ref showed large bulk particles (Fig. S4a) and a relatively smooth surface (Fig. S4d). The introduction of Cr species had little impact on the morphology (Fig. S4e). After the activity test, the spent catalysts were observed by SEM, TEM, and HRTEM images. The morphology of the Cr-Al-800 catalyst was unchanged after the reaction (Fig. 3d and g), while the particle size of Cr-Al-Ref catalyst decreased significantly (Fig. S4b and c), which indicated that the synthesized alumina as a support for Cr₂O₃ possessed excellent structural stability. The absence of any obvious difference in the surface of the catalyst after the reaction suggested that Cr species were still uniformly distributed on the rough surface (Fig. 3h and i). The unique nanostructure of the synthesized rod-shaped alumina with quite a rough surface may contribute to the outstanding stability of the Cr-Al-800 catalyst.

Fig. 3. SEM images (a, d, g), TEM images (b, e, h), and HRTEM images (c, f, i) of Al₂O₃-800, Al₂O₃-Ref, and the corresponding catalysts.

3.3. Local structure of Cr₂O₃ catalysts

To identify the origin of the difference in the catalytic performance of the Cr-Al-800 and Cr-Al-Ref catalysts, a series of analyses were performed. The diffuse reflectance UV-vis spectra for the fresh catalysts were recorded to confirm the coordination state of the Cr species (Fig. 4a). All the samples exhibited four absorption bands in the range of 240–260, 350–370, 450–470, and 590–610 nm. The intense bands centered at 257 and 367 nm were assigned to the O → Cr (VI) charge transfer in isolated Cr₂O₃ with a tetrahedral symmetry [22,23]. The band at 461 nm was assigned to the d-d transition ($A_{2g}-T_{1g}$) in Cr³⁺ with octahedral symmetry [23]. Another obvious band at 600 nm could be assigned to the d-d transition ($A_{2g}-T_{2g}$) in Cr³⁺ with octahedral symmetry, which was attributed to the Cr₂O₃ crystal [24]. The UV-vis spectra indicated that Cr-Al-800 and Cr-Al-Ref possessed the similar Cr species.

The reduction behavior of Cr-Al-800-C and Cr-Al-Ref-C was investigated by H₂-TPR experiments (Fig. 4b). Cr-Al-Ref-C exhibited two major peaks due to hydrogen consumption at 296 and 373 °C. In the case of Cr-Al-800-C, the corresponding reduction peaks shifted to 327 and 420 °C. The signals of hydrogen consumption in the temperature range 210–460 °C were attributed to the reduction of the dispersed Cr⁶⁺ to Cr³⁺ species [25]. It was worth noting that the reduction temperature of Cr-Al-800-C was higher as compared with that of Cr-Al-Ref-C, suggesting that the Cr species in the former is difficult to reduce. Also, the Cr-Al-Ref-C sample showed an obvious peak at a higher temperature, which can be attributed to the formation of dichromate phases [26,27]. Extensive research proved that the surface acidity of Cr₂O₃ catalysts was an important feature that affected the chromia-support interaction [19,28]. These observations indicated the presence of different metal-support interaction on Cr-Al-800-C and Cr-Al-Ref-C samples, which could be caused by the different surface acidities [28].

NH₃-TPD experiments were carried out to analyze the number and strength of the acid sites. It was observed from Fig. 4c and 4d that all the samples presented a broad desorption peak ranged between 100 and 500 °C. The shapes of the profiles were complex and asymmetric, suggesting the presence of different acid sites. To further investigate the distribution of acid sites, we fitted the asymmetric profiles by a Gaussian function. The patterns exhibited three desorption peaks, and the peak centered between 170 to 190 °C was assigned to the desorption of NH₃ bonded by weak acid sites, while the peak centered between 220 to 290 °C was assigned to the desorption of medium-strong acid sites. The temperature maximum (T_{max}) of each desorption peak and the fraction of different acid sites for each sample are listed in Table 2. The table also lists the total acidities, which were estimated from the NH₃-TPD profiles. The distribution of surface acidity was similar in Al₂O₃-800 and Al₂O₃-Ref, and the fraction of medium-strong acid sites in the former significantly decreased with the loading of active metal oxides. The decrease of these acid sites could improve the propylene selectivity [29]. It was worth noting that the total acidities of pure Al₂O₃-800 and Al₂O₃-Ref were 178 and 281 $\mu\text{mol NH}_3 \text{g}^{-1}$, whereas in the case of the correspond-

Fig. 4. UV-vis spectra for Cr-Al-800 and Cr-Al-Ref catalysts (a), H₂-TPR profiles for unreduced Cr-Al-800-C and Cr-Al-Ref-C (b), NH₃-TPD profiles for Al₂O₃-800 and Al₂O₃-Ref (c), and NH₃-TPD profiles for Cr-Al-800 and Cr-Al-Ref catalysts (d).

Table 2

Acid strength distribution in different catalysts.

Sample	$T_{\max}$ (°C)			Total acid sites ($\mu\text{mol NH}_3 \text{ g}^{-1}$)	Area fraction (%)	
	I	II	III		Weak acid	Medium-strong acid
Al ₂ O ₃ -800	170	220	281	178	28	72
Al ₂ O ₃ -Ref	179	237	280	281	24	76
Cr-Al-800	180	228	264	64	43	57
Cr-Al-Ref	171	220	290	140	32	68

ing catalysts, these values distinctly decreased to 114 and 141 $\mu\text{mol NH}_3 \text{ g}^{-1}$, respectively. This indicated that the surface acidity could be changed considerably after loading active metal oxides [30]. The total acidity of the Cr-Al-800 catalyst (64 $\mu\text{mol NH}_3 \text{ g}^{-1}$) was much lower than that of the Cr-Al-Ref catalyst (140 $\mu\text{mol NH}_3 \text{ g}^{-1}$), and the fraction of medium-strong acid sites for Cr-Al-800 catalyst was lower than the reference catalyst. Previous studies have demonstrated that the coke deposits were mainly formed through polymerization of olefins during the dehydrogenation reaction, which could be catalyzed on the acid sites [7,17,18]. Therefore, it can be inferred that the lower acidity of the Cr-Al-800 catalyst rendered it a better anti-coking ability.

4. Conclusions

Rod-shaped porous alumina was hydrothermally synthesized, and the corresponding Cr₂O₃ catalysts were used in the PDH process to investigate their catalytic performance. The calcination temperature played a crucial role in modifying the surface-physicochemical properties of alumina, subsequently affecting the catalytic activity. The Cr-Al-800 catalyst exhibited excellent stability because of the inhibitory effect of low acidity toward side reactions and coke formation, thus leading to better anti-coking ability. Therefore, the synthesized alumina for CrO_x-base catalysts could facilitate the PDH reaction.

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Graphical Abstract

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Xin-Qian Gao, Wen-Duo Lu, Shou-Zhao Hu, Wen-Cui Li, An-Hui Lu *

Dalian University of Technology

Rod-shaped porous alumina supported chromium oxide exhibited high activity and superior anti-coking ability in propane dehydrogenation process because of the low total acidity of alumina surface.

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棒状多孔氧化铝负载氧化铬催化丙烷脱氢反应性能

高新芊, 陆文多, 户守昭, 李文翠, 陆安慧*

大连理工大学精细化工国家重点实验室, 化工学院, 辽宁大连 116024

摘要: 丙烯是一种重要的化工原料, 目前工业上主要来自石脑油、轻质油以及其他石油副产物的蒸汽裂解和催化裂解。这些过程能耗巨大, 碳排放严重。丙烷直接脱氢制丙烯原料利用率高, 副产物少, 是一条更加经济环保的丙烯生产路线。 $\text{Cr}_2\text{O}_3\text{-Al}_2\text{O}_3$ 催化剂因其出色的性能和低廉的价格已在工业中应用, 但氧化铝表面酸位点易催化副反应及积碳的形成, 从而造成催化剂失活。因此, 调控载体氧化铝结构具有重要的意义。

氧化铝的结构性质取决于合成条件以及焙烧过程表面羟基和水分的逐步脱除。我们课题组通过水热法合成了一系列表面粗糙的棒状氧化铝和富含五配位铝离子的片状氧化铝, 以这些氧化铝为载体制备的负载型贵金属催化剂在催化反应中表现出优异的活性和稳定性。本文在前期工作基础上研究了不同焙烧温度对棒状氧化铝表面结构的影响, 采用X射线衍射(XRD)、氮吸附、电镜(SEM/TEM)、氨气程序升温脱附($\text{NH}_3\text{-TPD}$)和紫外-可见光谱(UV-Vis)等手段表征了氧化铝结构, 并探究了其负载氧化铬催化剂上丙烷脱氢反应的影响。

XRD结果表明, 低温焙烧所得主要为 γ 相氧化铝, 提高焙烧温度至 $900\text{ }^\circ\text{C}$ 时出现 δ 相氧化铝。氧化铝氮气吸附-脱附表现出IV型等温线, 随焙烧温度升高, 介孔结构保持, 但比表面积和孔体积呈减小趋势。电镜观察显示氧化铝为棒状结构, 表面粗糙。 $\text{NH}_3\text{-TPD}$ 结果表明自制氧化铝酸量低于商业氧化铝, 且随焙烧温度升高酸量下降。以上结果表明焙烧温度在氧化铝性质调控过程中起重要作用。

以不同焙烧温度下制得的氧化铝等体积浸渍氧化铬制得氧化铬催化剂。丙烷脱氢反应结果表明, 催化剂表现出优异的稳定性和再生性能。氮吸附等温线表明新鲜催化剂为介孔结构, 这有利于反应物接触活性位点, 并提供抗积碳阻塞能力。对比氧化铝负载氧化铬前后的电镜照片可知, 催化剂表面粗糙度降低, 说明活性组分均匀分散于氧化铝粗糙表面; 反应前后催化剂形貌保持不变, 催化剂在反应中表现出优异的结构稳定性。UV-Vis和 $\text{H}_2\text{-TPR}$ 结果表明, 自制氧化铝和参比氧化铝表面的铬物种以相似配位状态存在, 但铬物种在自制氧化铝表面更难还原, 表现出更强的金属与载体相互作用。 $\text{NH}_3\text{-TPD}$ 结果表明, 自制催化剂表面酸量($64\text{ }\mu\text{mol NH}_3\text{ g}^{-1}$)远低于参比催化剂($140\text{ }\mu\text{mol NH}_3\text{ g}^{-1}$)。热重分析证实反应后自制催化剂积碳量明显低于参比催化剂。自制棒状氧化铝作为载体制备的氧化铬低酸催化剂可抑制积碳形成, 提高丙烯选择性, 在丙烷脱氢反应中表现出优异的活性和抗积碳能力。

关键词: 氧化铝; 酸量; 焙烧; 氧化铬; 抗积碳

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*通讯联系人. 电话/传真: (0411)84986112; 电子信箱: anhuilu@dlut.edu.cn

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