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Oxidative dehydrogenation of ethane with CO₂ over Cr supported on submicron ZSM-5 zeolite

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ABSTRACT

A series of submicron ZSM-5-supported chromium oxide catalysts were prepared and characterized by XRD, N₂ adsorption, ²⁷Al MAS NMR, SEM, XPS, laser Raman spectroscopy and diffuse reflectance UV-Vis spectroscopy. The catalytic performance of these materials during ethane dehydrogenation in the presence of CO₂ was investigated. The catalysts exhibited both high activity and stability, with an ethane conversion of ~65% and ethylene yield of ~49% without any obvious deactivation following 50 h. Characterization results show that the excellent catalytic performance results from the high degree of dispersion of CrO_x species on the submicron ZSM-5 surface. Both a high Si/Al ratio and the use of the Na-form of the ZSM-5 support were found to favor CrO_x dispersion. The promotional effect of CO₂ on the dehydrogenation reaction was quite evident and can be attributed to the reverse water-gas shift reaction.

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1. Introduction

The catalytic conversion of light alkanes such as ethane and propane into the corresponding value-added alkenes has gained much attention over the past several decades because of the growing demand for light alkenes. The dehydrogenation of alkanes is endothermic and is inevitably controlled by the thermodynamic equilibrium, thus relatively high temperatures are required to obtain high yield of alkenes, resulting in high energy consumption and ready deactivation of the catalyst. For this reason, oxidative dehydrogenation using oxygen has been proposed as an alternative process. However, the over-oxidation of alkanes to carbon dioxide is unavoidable during this process, leading to a decrease in the targeted product selectivity. However, it has been reported that these disadvantages can be overcome by replacing O₂ with milder oxidants, such as N₂O

[1–4] and CO₂ [5–11].

The dehydrogenation of ethane over In [5], Cr [6,7], Ga [8,9], Co [10] and Mn [11]-containing catalysts in the presence of CO₂ has been studied intensely for some time now. Cr-based catalysts in particular show excellent activity for the dehydrogenation of ethane, and CO₂ can markedly promote the reaction, leading to a significant increase in ethylene yield in the presence of CO₂ over Cr-based catalysts. Because of the low surface area of bulk crystalline chromium oxides, Cr species are often dispersed on supports with high surface areas, such as Al₂O₃ [7], SiO₂ [7], ZrO₂ [12,13], TS-1 [14], mesoporous silicas like SBA-1 [15], SBA-15 [16], MSU-x [17], MCM-41 [18] and oxidized diamond [19,20], so as to prepare a catalyst with an abundance of active sites.

ZSM-5 plays a very important role both in industrial processes and in academic studies as either a catalyst or a catalyst

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support, owing to its three-dimensional microporous structure, high surface area and high thermal and hydrothermal stability. ZSM-5-supported metal oxide catalysts have been investigated with regard to ethane or propane dehydrogenation using CO₂, and H-form ZSM-5 with a Si/Al ratio over 1900 has been reported to be preferred as the support [21]. More recently, Cr supported on Na-type ZSM-5 having a smaller crystal size (*ca.* 400 nm) was found to be more effective when applied to the dehydrogenation of propane in the presence of CO₂, although the stability of the catalyst system was still not satisfactory [22].

In our present work, a series of Cr catalysts supported on submicron H- or Na-form ZSM-5 materials having various Si/Al ratios were prepared and characterized by X-ray diffraction (XRD), nitrogen adsorption, laser Raman spectroscopy, X-ray photoelectron spectroscopy (XPS), diffuse reflectance UV-Vis spectroscopy (DRS) and temperature-programmed reduction (TPR). The catalytic performance of each of these submicron ZSM-5-supported Cr-based catalysts during the dehydrogenation of ethane to ethylene in the presence of CO₂ was also investigated. The relationship between catalytic behavior and physicochemical properties is discussed herein on the basis of the experimental results.

2. Experimental

2.1. Catalyst preparation

Submicron ZSM-5 zeolite was prepared using procedures previously reported in the literature [23], employing tetrapropylammonium hydroxide (TPAOH, 25% aqueous solution, Yixing Dahua) as the template. Typically, NaAlO₂ (CP, Sinopharm Chemical) was dissolved in an aqueous TPAOH solution, after which tetraethylorthosilicate (TEOS, AR, Shanghai Lingfeng) was added. The resulting mixture was stirred for 6 h at room temperature, followed by heating at 50 °C with further stirring to evaporate the ethanol resulting from the reaction. A clear gel was obtained with the molar composition 120SiO₂:*x*Al₂O₃:48TPAOH:3600H₂O. This gel was transferred to an autoclave and crystallized by heating at 170 °C for 2 d. The obtained product was centrifuged, washed, dried at 110 °C overnight and then calcined in air at 600 °C for 6 h to remove the template.

The supported chromium oxide catalysts were prepared by impregnating ZSM-5 with an aqueous solution of Cr(NO₃)₃·9H₂O (AR, Sinopharm Chemical) using the incipient wetness method. The impregnated samples were dried at 110 °C overnight and calcined in air at 650 °C for 6 h. The obtained catalysts are denoted as *y*Cr/ZSM-5-*c*, where *y* represents the mass fraction of Cr₂O₃ in the catalysts, and *c* represents the Si/Al ratio in gel.

2.2. Catalyst characterization

XRD patterns were acquired with a Persee XD-2 X-ray diffractometer using nickel-filtered Cu K_α radiation at 40 kV and 30 mA. The BET surface areas and micropore volumes of the

catalysts were determined by N₂ adsorption at −196 °C using a Micromeritics ASAP 2000 instrument. Scanning electron microscopy (SEM) images were recorded digitally on a Philips XL 30 microscope operating at 30 kV. Laser Raman spectra were obtained with a Horiba JY XPloRA spectrometer using the 532 nm radiation from an air-cooled solid state laser as the excitation source. The other parameters included a laser power of 25 mW, a data acquisition time of 30 s, an accumulation number of 8 and a spectral resolution of 2 cm^{−1}. The spectra were obtained at room temperature under ambient conditions. DRS spectra were collected on a Shimadzu UV-2450 spectrometer equipped with an integrating sphere attachment. XPS data were acquired using a Perkin-Elmer PHI 5000C spectrometer with Mg K_α radiation as the excitation source. All binding energy values were referenced to the C 1s peak at 284.6 eV.

TPR profiles were obtained on a Micromeritics AutoChem II apparatus loaded with 100 mg of catalyst. The TPR experiments were carried out in a 30 mL/min flow of 10% H₂-90% Ar with a ramp rate of 10 °C/min. H₂ consumption was monitored using a thermal conductivity detector. Thermogravimetric (TG) analysis was performed under an air flow on a Perkin-Elmer 7 Series Thermal Analyzer to determine the amount of coke deposited on the catalyst following the reaction.

2.3. Catalytic testing

Catalytic tests for ethane dehydrogenation with CO₂ were performed at 650 °C in a fixed-bed flow microreactor at atmospheric pressure. The catalyst load was 200 mg, and each sample was pretreated at 650 °C for 2 h under a nitrogen flow prior to the reaction. The gaseous reactant contained 3% ethane and 15% CO₂ with the balance consisting of nitrogen at a total flow rate of 30 mL/min. The hydrocarbon reaction products were analyzed using an on-line gas chromatograph (GC) equipped with a 6 m Porapak Q packed column and a flame ionization detector (FID). The gaseous products were analyzed on-line using a second GC equipped with a thermal conductivity detector (TCD) and a carbon molecular sieve 601 column. The reverse water-gas shift reaction was performed in a fixed-bed flow microreactor at atmospheric pressure using a catalyst load of 200 mg. The H₂:CO₂:N₂ molar ratio was 1:1:1, and the total flow rate of the gaseous reactants was 30 mL/min. The reaction temperature was in the range of 500–650 °C. The amounts of CO₂ before and after the reaction were determined by on-line analysis with a GC equipped with a carbon molecular sieve 601 column and a TCD. The reaction data in this work were reproducible, with a variation of less than 5%.

3. Results and discussion

3.1. Structural Characterization

Figure 1 shows the XRD patterns of the various ZSM-5-supported chromium oxide catalysts. All exhibit well-crystallized MFI structures with characteristic reflections at 2θ = 8.0°, 8.9°, 23.1°, 23.4° and 24.0° [24]. No diffraction patterns corresponding to chromium oxide were observed, suggesting that

Fig. 1. XRD patterns of (1) 3Cr/NaZSM-5-60, (2) 3Cr/NaZSM-5-100, (3) 3Cr/NaZSM-5-160 and (4) 3Cr/HZSM-5-160.

the chromium oxide was well dispersed on all the ZSM-5 supports.

SEM images of the ZSM-5 supports are presented in Fig. 2. All samples were well crystallized without any presence of amorphous materials and exhibit a rod-like morphology with a uniform crystallite size distribution. The average crystallite size was approximately 400 nm for all the ZSM-5 zeolites.

The textural properties of the ZSM-5-supported chromium oxide catalysts are summarized in Table 1. These catalysts, regardless of whether the ZSM-5 support was the Na- or H-form or had a low or high Si/Al ratio, exhibit similar BET surface areas and micropore volumes, showing that the supports had similar crystallinities and that their micropore channels were not blocked by the supported CrO_x species.

^{27}Al MAS NMR spectra of the ZSM-5 supports were acquired to characterize the local coordination environment of the aluminum atoms in the zeolites. An intense line at $\delta = 55$, assigned to ZSM-5 framework aluminum atoms in tetrahedral coordination, can be observed in the spectra of all the samples, while no discernable signal at $\delta = 0$, attributed to extra-framework aluminum atoms in octahedral coordination, is evident (Fig. 3). The absence of extra-framework aluminum atoms indicates that all of the Al species have been incorporated into the zeolite framework.

3.2. State of Cr species

XPS was employed to investigate the oxidation states of Cr species. The Cr $2p_{2/3}$ spectra obtained from the catalysts were deconvoluted into two bands at approximately 576.5 and 579.5

Table 1

Textural properties of supported chromium oxide catalysts.

Catalyst	Surface area (m^2/g)	External surface area ^a (m^2/g)	Pore volume (cm^3/g)	Micropore volume ^a (cm^3/g)
3Cr/NaZSM-5-60	339	53	0.27	0.17
3Cr/NaZSM-5-100	308	38	0.21	0.14
3Cr/NaZSM-5-160	356	34	0.24	0.16
3Cr/HZSM-5-160	342	36	0.24	0.15

^a Calculated by the *t*-plot method.

Fig. 3. ^{27}Al MAS NMR spectra of (1) ZSM-5-60, (2) ZSM-5-100 and (3) ZSM-5-160.

Table 2

XPS and TPR data for supported chromium oxide catalysts.

Catalyst	BE (eV)		$\text{Cr}^{6+}/\text{Cr}^{3+}$ atomic ratio ^a	H_2 consumption ^b (mmol/g)
	Cr^{3+}	Cr^{6+}		
3Cr/NaZSM-5-60	576.5	579.5	2.87	0.24
3Cr/NaZSM-5-100	576.5	579.5	1.82	0.35
3Cr/NaZSM-5-160	576.5	579.5	0.92	0.36
3Cr/HZSM-5-160	576.5	579.5	0.89	0.32

^a Calculated from XPS peak areas.

^b Obtained by TPR.

eV, assigned to Cr^{3+} and Cr^{6+} , respectively [22,25,26], and the quantitative data after fitting are listed in Table 2. All the catalysts were found to have similar binding energy (BE) values. The $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio evidently decreases with increasing Si/Al ratios and as the Na content is decreased, indicating that Na^+ cations may have a positive effect in terms of raising the $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio, similar to the action of K^+ ions in K-doped $\text{CrO}_x/\text{Al}_2\text{O}_3$ catalysts [27]. Compared with the NaZSM-5-supported catalyst, the HZSM-5 material having the same Si/Al ratio exhibited a lower $\text{Cr}^{6+}/\text{Cr}^{3+}$ ratio, which may also result from a lower Na content.

Additional information on the state of Cr species was obtained from UV-Vis diffuse reflectance measurements, and the

Fig. 2. SEM images of (a) ZSM-5-60, (b) ZSM-5-100 and (c) ZSM-5-160.

Fig. 4. Diffuse reflectance UV-Vis spectra of (1) 3Cr/NaZSM-5-60, (2) 3Cr/NaZSM-5-100, (3) 3Cr/NaZSM-5-160 and (4) 3Cr/HZSM-5-160.

results are summarized in Fig. 4. Two bands are observed for each catalyst, at approximately 272 and 370 nm, assigned to the $O^{2-} \rightarrow Cr^{6+}$ charge transfer transition of chromate species in tetrahedral coordination [25,28–32]. Bands at 468 and 605 nm, corresponding to octahedral Cr^{3+} species in Cr_2O_3 or CrO_x clusters, are not present, indicating that all Cr species were well dispersed on the submicron ZSM-5 support.

Laser Raman spectra were acquired to identify the molecular nature of the Cr species dispersed on the ZSM-5 supports, and the results are depicted in Fig. 5. A band at 551 cm^{-1} , assigned to crystalline Cr_2O_3 , appears in the spectra of the 3Cr/HZSM-5-160 catalyst [18,22,25,30–33], while the band at the same position is much weaker in the case of the NaZSM-5 supported catalysts. The intensity of the 551 cm^{-1} band decreases in the order 3Cr/HZSM-5-160 > 3Cr/NaZSM-5-60 > 3Cr/NaZSM-5-100 $\approx$ 3Cr/NaZSM-5-160. These results demonstrate that the use of a high Si/Al ratio and the Na-form of the zeolite favor CrO_x dispersion.

Two intense bands at approximately 980 and 1000 cm^{-1} are present in the spectrum of each of the catalysts, and can be ascribed to the symmetric vibrational modes of the terminal $Cr=O$ bonds of monochromates and polymeric chromates, respectively [18,22,25,30–33]. Meanwhile, a weak, broad band at

Fig. 5. Laser Raman spectra of (1) 3Cr/NaZSM-5-60, (2) 3Cr/NaZSM-5-100, (3) 3Cr/NaZSM-5-160 and (4) 3Cr/HZSM-5-160.

Fig. 6. H_2 -TPR profiles of (1) 3Cr/NaZSM-5-60, (2) 3Cr/NaZSM-5-100, (3) 3Cr/NaZSM-5-160 and (4) 3Cr/HZSM-5-160.

810 cm^{-1} , attributed to the bending mode of the $Cr-O-Cr$ linkage of polymeric chromates, also appears. The intensity of the band at 1000 cm^{-1} increases as the Si/Al ratio is increased, indicating that the dispersed $Cr(VI)$ species on the catalyst surfaces gradually transition from monochromates to polymeric chromates with increasing Si/Al ratios.

H_2 -TPR was carried out to characterize the redox ability of Cr species on the catalysts, which has a very important effect on the dehydrogenation activity. The results are presented in Fig. 6 and Table 2. It is evident that there is only one reduction peak at $370\text{ }^\circ\text{C}$, with a shoulder at $270\text{ }^\circ\text{C}$, that can be attributed to the reduction of Cr^{6+} to Cr^{3+} (and/or Cr^{2+}) [30–32]. H_2 consumption is higher over the NaZSM-5-supported catalysts as compared with HZSM-5 material, and increases as the Si/Al ratio is increased, indicating increasing quantities of reducible surface Cr^{6+} . All these findings are consistent with the data obtained from laser Raman studies, showing that high Si/Al ratios and the Na-form are favorable for CrO_x dispersion.

3.3. Catalytic activity

The prepared Cr/ZSM-5 catalysts were evaluated during ethane dehydrogenation in the presence of CO_2 , and the results are shown in Table 3. For each catalyst, the ethane conversion drops with reaction time while the selectivity for ethylene increases. There are only minimal differences in the initial activities as well as the initial ethylene yields among the Cr/NaZSM-5 catalysts, although the stability is improved with increasing Si/Al ratios in the ZSM-5 support, resulting in a slight increase in the plateau value for the yield of ethylene. While all the submicron particle-supported catalysts exhibit superior performance, the 3Cr/NaZSM-5-160 shows higher activity than the 3Cr/HZSM-5-160.

Cr-based catalysts have been reported to represent one of the most promising catalysts for light alkane dehydrogenation reactions because of their high catalytic efficiency both in the absence and presence of CO_2 . There are two types of coordinatively-unsaturated $Cr(III)$ in chromium species, $Cr(III)$ ions formed from the reduction of $Cr(VI)$ and dispersed on fresh catalysts. Both are generally considered as active sites during

Table 3

Reaction data for ZSM-5-supported chromium oxide catalysts obtained at 10 min and 6 h.

Catalyst	Conversion (%)		Selectivity (%)						Yield (%)	
			CH ₄		C ₂ H ₄		C ₃ H ₆			
	10 min	6 h	10 min	6 h	10 min	6 h	10 min	6 h	10 min	6 h
3Cr/NaZSM-5-60	64.1	57.9	24.1	18.0	75.7	81.8	0.2	0.2	48.5	47.4
3Cr/NaZSM-5-100	65.9	60.5	25.6	19.9	74.2	79.9	0.1	0.1	48.9	48.3
3Cr/NaZSM-5-160	65.5	61.3	24.3	20.9	75.4	78.9	0.3	0.2	49.4	48.4
3Cr/HZSM-5-160	59.1	57.2	26.3	23.2	73.4	76.2	0.3	0.3	43.4	43.7

non-oxidative dehydrogenation and oxidative dehydrogenation reaction processes. However, several groups have reported that coordinatively unsaturated Cr(III) formed from the reduction of higher-valence states (*i.e.* Cr(VI)) is more active, whether applied to the non-oxidative dehydrogenation reaction or oxidative dehydrogenation with CO₂. As a result, the amount of reducible Cr(VI) on the calcined samples is crucial for the dehydrogenation reaction [17,32]. H₂ consumption results allow one to estimate the amount of redox-active Cr(VI) species, and it can be seen from Table 2 that the amount of reducible Cr(VI) on the freshly calcined samples increases with the Si/Al ratio, which is in agreement with their increasing dehydrogenation activity. These results confirm that the reducible Cr(VI) makes an important contribution to the dehydrogenation reaction. This is also the reason why the activity of the 3Cr/NaZSM-5 is higher than that of the 3Cr/HZSM-5.

The type of Cr(VI) species is considered to be another possible factor in the dehydrogenation reaction. Kumar et al. [34] reported that isolated chromium species are more active for the dehydrogenation reaction than crystalline α -Cr₂O₃, whereas oligomeric chromium species are more active than isolated chromium species. We can see from Fig. 5 that dispersed Cr(VI) species are present in the form of polymeric chromates and monochromates on the surface of Cr/NaZSM-5 while crystalline Cr₂O₃ was formed on the Cr/HZSM-5. This may be the reason why 3Cr/HZSM-5-160 exhibits relatively low activity even though it has a higher amount of reducible Cr(VI) as compared with 3Cr/NaZSM-5-60.

The effect of the Cr loading on the dehydrogenation activity was also investigated. The ethane conversion was found to increase with increasing extents of Cr loading and then decreased as the Cr content was further increased, such that mass fraction of 3% Cr₂O₃ is optimal.

To investigate the stability of the 3Cr/NaZSM-5-160 catalyst, the dehydrogenation reaction was run continuously for 50 h, with the results shown in Fig. 7. The catalyst is relatively stable; the ethylene yield over the catalyst is maintained at about 46% without any obvious deactivation over the 50 h,

Fig. 7. (1) Ethane conversion, (2) ethylene selectivity and (3) ethylene yield over 3Cr/NaZSM-5-160 as functions of reaction time.

although the activity does drop slowly. This is quite different from the behavior of other commonly studied Cr-containing catalysts, over which the ethylene yields are reported to have dropped quickly within 6 h.

3.4. Effect of CO₂ partial pressure

The effect of CO₂ partial pressure on the dehydrogenation of ethane was also investigated, and the results are summarized in Table 4. The promotional effect of CO₂ on the reaction is quite evident. The initial ethane conversion increases quickly from 20.4% with increasing CO₂/C₂H₆ ratios until it reaches its peak at 65.5% when the CO₂/C₂H₆ ratio equals 5, after which the conversion decreases slightly with further increases in the CO₂/C₂H₆ ratio. The effect of CO₂ can be attributed to the reverse water-gas shift reaction, which accelerates the formation of the dehydrogenation products by transforming H₂ and CO₂ into CO and H₂O. This is demonstrated by the results of the H₂/CO₂ reaction over 3Cr/NaZSM-5-160. Obviously, the catalyst is very active for the reverse water-gas shift reaction, with a CO₂ conversion of 22.6% at 650 °C.

Table 4Reaction data for 3Cr/NaZSM-5-160 under different CO₂ partial pressures obtained at 10 min and 6 h.

C ₂ H ₆ /CO ₂ ratio	Conversion (%)		Selectivity (%)						Yield (%)	
			CH ₄		C ₂ H ₄		C ₃ H ₆			
	10 min	6 h	10 min	6 h	10 min	6 h	10 min	6 h	10 min	6 h
∞	20.4	12.5	3.1	2.4	95.6	96.8	1.3	0.8	19.5	12.1
1/1	55.2	52.6	15.4	14.2	84.3	85.5	0.3	0.3	46.5	45.0
1/3	60.5	57.8	18.7	17.3	81.1	82.5	0.2	0.2	49.1	47.7
1/5	65.5	61.3	24.3	20.9	75.4	78.9	0.3	0.2	49.4	48.4
1/7	64.9	60.3	23.7	20.3	76.2	79.5	0.2	0.2	49.4	48.0

The stability of the catalysts was also improved greatly by the addition of CO₂. About 40% of the initial activity was lost within 6 h in the absence of CO₂. However, when 15% CO₂ was introduced, only 5% loss was observed during the same period. The enhanced stability can be explained primarily by two effects: (1) CO₂ promotes the Cr⁶⁺/Cr³⁺ reaction through the oxidation of reduced Cr species, $\text{Cr(III)O}_{x-1} + \text{CO}_2 \rightarrow \text{Cr(VI)O}_x + \text{CO}$, and regenerates the active species [6,7,17,35–37], and (2) CO₂ eliminates the formation of coke by the Boudouard reaction, $\text{CO}_2 + \text{C} \rightarrow 2\text{CO}$, and thus exposes more active sites to the reactants [6,7,17,35–37]. This can be confirmed by thermogravimetric tests that show that the amount of coke deposited on the catalyst after 6 h is 3.4% in the absence of CO₂, a value that is higher than the 3.0% amount obtained in the presence of CO₂. The fact that the Boudouard reaction proceeds is also evident from the observation that the molar ratio of CO formed to CO₂ converted is approximately 1.4 during the reaction, since this ratio should be equal to unity if the Boudouard reaction does not occur.

4. Conclusions

Catalysts composed of submicron ZSM-5-supported chromium oxide particles were prepared by an incipient wetness method, and their catalytic performance for ethane dehydrogenation in the presence of CO₂ was compared. The results show that chromium oxide supported on submicron Na-type ZSM-5 with a high Si/Al ratio is an excellent catalyst for the oxidative dehydrogenation of ethane with CO₂. High activity as well as high stability can be obtained over this catalyst. The promotional effect of CO₂ on dehydrogenation can also be observed on this catalyst and is attributed to the reverse water-gas shift reaction. Characterization by laser Raman, UV-Vis DRS, XPS and H₂-TPR revealed that improved dispersion of Cr species can be achieved in submicron catalysts, resulting in a greater quantity of the reducible Cr(VI) species that play a key

role in the ethane dehydrogenation reaction. The type of Cr(VI) species present is another possible factor affecting the dehydrogenation reaction.

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Graphical Abstract

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Oxidative dehydrogenation of ethane with CO₂ over Cr supported on submicron ZSM-5 zeolite

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Submicron ZSM-5 supported chromium oxide catalysts were prepared and exhibit both high activity and stability, with an ethane conversion of ~65% and ethylene yield of ~49% without any obvious trend of deactivation in 50 h.

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亚微米ZSM-5负载Cr催化剂上乙烷CO₂气氛下脱氢制乙烯

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摘要: 石油资源的日趋短缺使天然气和页岩气的开发利用受到重视, 因而低碳烷烃脱氢制取低碳烯烃也随之引起了人们越来越多的关注. 由于乙烷纯脱氢反应的平衡收率低, 能耗高, 而氧气氧化脱氢又易将乙烷深度氧化为CO₂或CO, 因此开发具有反应条件温和、装置投资和操作费用低等优势CO₂气氛下乙烷脱氢的技术路线日益得到重视. CrO_x是该反应理想的催化剂之一, CO₂的加入可使CrO_x对乙烷脱氢的催化活性提升3倍, 然而受困于CrO_x过小的比表面积, 通常将CrO_x制备成负载型催化剂使用. CrO_x的常见载体有Al₂O₃, ZrO₂和SiO₂等氧化物及MCM-41, SBA-15, SBA-1和MSU-x等介孔硅材料, ZSM-5作为载体负载CrO_x用于低碳烷烃脱氢的研究则较少, 所得结果也不甚理想. 我们采用亚微米尺寸的ZSM-5作为载体制备了负载型CrO_x催化剂, 研究了其在CO₂气氛下催化乙烷脱氢反应, 发现该催化剂具有非常优异的脱氢活性, 高硅铝比和Na型的ZSM-5作载体对反应更加有利, 而且在反应进行50 h后, 催化剂依然保持很好的活性和很高的乙烯收率, 这是在一般负载型CrO_x催化剂上所不能实现的.

X射线光电子能谱(XPS)表征发现, Na型ZSM-5载体制得的催化剂具有更高的Cr⁶⁺/Cr³⁺比. 一般认为, Cr⁶⁺是Cr系催化剂进行低碳烷烃脱氢反应时的活性位(或活性位前驱体), 因此可以初步判定, Na型载体具有很好催化效果的原因可能是由它制得的催化剂具有更多的反应活性位. 程序升温还原(H₂-TPR)表征结果证实了这一点, Na型载体明显具有更高的H₂消耗量; 也就是说, Na型载体制得的催化剂具有更多的可还原Cr物种, 即脱氢活性位. 进一步表征发现, 反应活性还与Cr物种存在形式有关. 文献报道, 低聚态的Cr物种和孤立态的Cr物种比Cr₂O₃有更好的催化活性. 通过漫反射紫外-可见光谱(UV-Vis)对Cr物种的存在形态进行表征后发现, Na型载体上Cr主要以四配位形式存在, 而在H型载体上出现了对应于六配位的Cr物种; 激光Raman表征结果表明, Na型载体上出现的都是低聚态Cr物种和孤立态Cr物种, 而H型载体上出现了明显的对应于α-Cr₂O₃的峰, 说明相较于H型载体, Na型载体更有利于Cr组分分散, 这也是Na型ZSM-5载体催化剂具有更高活性的原因之一.

CO₂引入后对乙烷脱氢反应具有明显的促进作用, 特别是在CO₂/C₂H₆ = 5时, 催化剂上C₂H₆转化率是非CO₂气氛下的3.2倍; 同时, CO₂的引入也提高了脱氢反应的稳定性. 在非CO₂气氛下, 反应进行6 h后, C₂H₆转化率降低到初活性的60%左右, 而在CO₂/C₂H₆ = 5时, 相同时间内催化剂活性下降仅有5%左右. 实验分析了CO₂对脱氢反应具有促进作用的原因. 在脱氢反应温度650 °C下, CO₂/H₂ = 1时进行了逆水煤气反应测试, 发现CO₂的转化率达到22.5%, 说明引入CO₂后可以通过逆水煤气反应有效地消耗掉乙烷脱氢反应生成的H₂, 从而促进反应向脱氢方向进行; CO₂的引入也可以促进Cr物种的CrO_x/CrO_{x-1}循环, 从而提高催化剂效率, 减缓催化剂失活; CO₂还可与反应中生成的积碳类物质发生Boudouard反应, 将反应活性位暴露出来, 从而提高催化剂的稳定性. CO₂气氛下反应6 h后催化剂的积碳量为3.0%, 低于非CO₂气氛下的3.4%, 同时在脱氢反应中生成的CO量与消耗掉的CO₂量的比值约为1.4, 也有力地说明Boudouard反应的存在.

关键词: 脱氢反应; 乙烷; ZSM-5分子筛; 亚微米; 二氧化碳

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