Dehydrogenation of Isobutane to Isobutene with Carbon Dioxide over SBA-15-Supported Chromia-Ceria Catalysts

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A series of SBA-15-supported chromia-ceria catalysts with 3% Cr and 1%-5% Ce (3Cr-Ce/SBA) were prepared using an incipient wetness impregnation method. The catalysts were characterized by XRD, N₂ adsorption, SEM, TEM-EDX, Raman spectroscopy, UV-vis spectroscopy, XPS and H₂-TPR, and their catalytic performance for isobutane dehydrogenation with CO₂ was tested. The addition of ceria to SBA-15-supported chromia improves the dispersion of chromium species. 3Cr-Ce/SBA catalysts are more active than SBA-15-supported chromia (3Cr/SBA), which is due to a higher concentration of Cr⁶⁺ species present on the former catalysts. The 3Cr-3Ce/SBA catalyst shows the highest activity, which gives 35.4% isobutane conversion and 89.6% isobutene selectivity at 570 °C after 10 min of the reaction.

Keywords isobutane dehydrogenation, carbon dioxide, chromia-ceria, SBA-15, supported catalyst

Introduction

Because C_2-C_4 small alkenes are important building blocks in chemical industry, attention has been paid remarkably to the catalytic dehydrogenation of small alkanes over the last few decades.^[1,2] Nowadays, the industrial uses of isobutene comprise production of polyisobutene, methyl *tert*-butyl ether (MTBE), butyl rubber, methyl acrylates and so on. Naphtha steam cracking and fluidized catalytic cracking, which are the main two methods to obtain isobutene, can not meet the requirements for the expanding isobutene market. Hence, catalytic dehydrogenation of isobutane to isobutene has received considerable attention.^[3]

There are some disadvantages for direct isobutane dehydrogenation, such as equilibrium limitations regarding isobutane conversion, large energy consumption due to endothermic reaction and high temperature operation, and fast catalyst deactivation due to coke formation. Alternatively, the oxidative dehydrogenation of isobutane with O₂ can overcome the above drawbacks.^[1] Nevertheless, this process suffers from a significant loss of selectivity toward isobutene owing to the deep oxidation of isobutene.^[4,5] Moreover, it is difficult to deal with the oxygen-containing mixture with potential explosion and remove heat.

Recently, the utilization of CO_2 as a mild oxidant for the selective dehydrogenation of light alkanes to their respective alkenes has received much attention. Deep oxidation of the desirable dehydrogenation product to CO and CO₂ can be avoided through employing CO₂ instead of O₂.^[6] In comparison with the direct dehydrogenation of small alkanes, CO₂ can act as a weak oxidant to improve the alkenes yields^[7-9] and/or enhance the dehydrogenation through reaction coupling between a simple dehydrogenation of light alkanes and the reverse water–gas shift reaction.^[10-13] On the other hand, this new dehydrogenation process opens a new attractive pathway for the utilization of CO₂ which is one of the major greenhouse gases, because CO₂ is reduced to CO which is more valuable in chemical industry. Hence, the CO₂-assisted dehydrogenation of light alkanes is believed to be an attractive alternative to the direct dehydrogenation.

Compared to the extensive studies on the CO₂-assisted dehydrogenation of ethane and propane,^[6,14-16] there is less work reported on the dehydrogenation of isobutane to isobutene in the presence of CO₂. The catalysts reported for this reaction mainly comprise of iron oxide,^[17] vanadium–magnesium oxide,^[18] V₂O₅,^[19,20] LaBaSm oxide^[21] and NiO.^[13] Nakagawa *et al.* reported that oxidized diamond-supported chromia is more active than supported vanadia for propane dehydrogenation in the presence of CO₂, but the former catalyst is less active than the latter one for isobutane dehydrogenation in

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the presence of CO_2 .^[19] Thus, it is interesting and a challenge to improve the catalytic activity of supported chromia for the dehydrogenation of isobutane with CO_2 . Silica mesoporous molecular sieves such as MCM-41 and SBA-15 are widely employed as catalyst supports due to their very high surface areas and pore volumes. In this work, a detailed investigation of isobutane dehydrogenation with CO_2 over SBA-15-supported chromiaceria catalysts was studied. To the best of our knowledge, there has been no work reported on it. These catalysts were found to be more active than SBA-15-supported chromia. The catalysts were characterized in detail, and the reasons for the superior activities of SBA-15-supported chromia-ceria were elucidated.

Experimental

Catalyst preparation

SBA-15 (BET surface area=555 $\text{m}^2 \cdot \text{g}^{-1}$, total pore volume=0.875 $\text{cm}^3 \cdot \text{g}^{-1}$) was purchased from Nanjing Pioneer Nanomaterials Science and Technology Co., Ltd. in Nanjing, China. The SBA-15-supported chromia-ceria catalysts were prepared by impregnating a mixed aqueous solution of Cr(NO₃)₃•9H₂O and Ce(NO₃)₃•6H₂O on SBA-15 using the incipient wetness impregnation method. The impregnated samples were dried at 100 °C and calcined at 600 °C for 4 h in static air. The resulting catalysts were labelled as mCr-nCe/ SBA, where *m* and *n* represent the weight percentage of Cr and Ce in the catalysts, respectively. The weight content of Cr is 3%, and the weight contents of Ce are 1%, 3% and 5%, respectively. For comparison, a 3Cr/SBA catalyst with a Cr weight content of 3% was prepared in the same way using Cr(NO₃)₃•9H₂O as the precursor.

Catalyst characterization

X-ray diffraction (XRD) patterns were collected on an MSAL XD2 X-ray diffractometer using Cu Ka radiation at 40 kV and 30 mA. The BET specific surface areas and pore volumes of the catalysts were determined by the adsorption-desorption of nitrogen at liquid N₂ temperature with a Micromeritics Tristar 3000 instrument. The pore sizes of the catalysts were obtained from the peak positions of the distribution curves determined from the adsorption branches of the isotherms. Fieldemission SEM images were recorded on Nova Nano-SEM 450. TEM images and 2-D atomic mapping were recorded on an FEI Tecnai G² F20 S-TWIN instrument. Thermogravimetric (TG) analysis was performed in air flow on a Perkin-Elmer 7 Series Thermal Analyzer apparatus to determine the amount of coke deposited on the catalyst after reaction.

Laser Raman spectra were recorded on a HORIBA Jobin Yvon XploRA spectrometer. The wavelength of exciting light was selected as 532 nm. The laser power was 25 mW, and the spectral resolution was $1-2 \text{ cm}^{-1}$. The Raman spectra were obtained at room temperature

and under ambient conditions. UV-vis spectra were recorded at ambient temperature on a Perkin-Elmer Lambda 650S spectrometer equipped with a diffuse reflectance accessory. The spectra were measured in reflectance mode and converted with the Kubelka-Munk function $F(R_{\infty})$. X-ray photoelectron spectroscopy (XPS) measurements were carried out on 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.

Temperature-programmed reduction (TPR) profiles were obtained on a Micromeritics AutoChem II apparatus loaded with 0.1 g of catalyst. The samples were pretreated at 500 °C for 1 h in Ar flow, and then the samples were cooled to 100 °C in Ar flow. The samples were subsequently contacted with a 10% H₂/Ar mixture flowing at 30 mL•min⁻¹, then heated to 650 °C with a ramping rate of 10 °C •min⁻¹. H₂ consumption was monitored using a TCD.

Activity measurement

The oxidative dehydrogenation of isobutane with CO_2 was carried out in a homemade flow-type fixed-bed microreactor at 570 °C under atmospheric pressure. 0.5 g of catalyst (40–60 mesh) was first pretreated at 570 °C in N₂ flow for 1 h. Then, a gas mixture of isobutane and CO_2 (1 : 5 molar ratio) flowed through the catalyst at a flow rate of 19.3 mL•min⁻¹. The hydrocarbon products were analyzed using an on-line gas chromatograph (GC) equipped with a FID and an HP-AL/S capillary column (50 m×0.32 mm×8.0 µm). CO and CO_2 were analyzed on-line by another GC equipped with a TCD and a 6 m long stainless steel column packed with Porapak Q. The conversion, selectivity and yield were calculated as follows:

$$i-C_{4}H_{10} \text{ conversion} = \frac{i-C_{4}H_{10 \text{ in}} - i-C_{4}H_{10 \text{ out}}}{i-C_{4}H_{10 \text{ in}}} \times 100\%$$
$$i-C_{4}H_{8} \text{ selectivity} = \frac{i-C_{4}H_{8 \text{ out}}}{i-C_{4}H_{10 \text{ in}} - i-C_{4}H_{10 \text{ out}}} \times 100\%$$
$$i-C_{4}H_{8} \text{ yield} = \frac{i-C_{4}H_{8 \text{ out}}}{i-C_{4}H_{10 \text{ in}}} \times 100\%$$

Results and Discussion

Structure and physicochemical properties

The low-angle XRD patterns of SBA-15-supported chromia-ceria samples with 3% Cr and different Ce content (3Cr-Ce/SBA) are displayed in Figure 1. An intense diffraction peak and two other weak peaks, which correspond to (100), (110) and (200) reflections of the hexagonal regularity of SBA-15, were observed for all samples. This result indicates that the hexagonal array of mesopores in SBA-15 is retained after the introduction of chromia-ceria. Figure 2 shows the wide-angle XRD patterns of SBA-15-supported chromia-ceria

Dehydrogenation of Isobutane to Isobutene with Carbon Dioxide

samples. Distinct diffraction peaks corresponding to Cr_2O_3 crystallites can be observed for all samples. The 3Cr-Ce/SBA samples display weaker diffraction peaks assigned to crystalline Cr_2O_3 than 3Cr/SBA, suggesting that the dispersion of chromia is better in the former samples than in the latte one. When the content of Ce is 3% or higher, diffraction peaks of crystalline CeO₂ were also observed.



Figure 1 XRD patterns of 3Cr-Ce/SBA samples with different Ce content in the small-angle region. (a) SBA, (b) 3Cr/SBA, (c) 3Cr-1Ce/SBA, (d) 3Cr-3Ce/SBA, (e) 3Cr-5Ce/SBA.



Figure 2 XRD patterns of 3Cr-Ce/SBA samples with different Ce content in the wide-angle region. (a) 3Cr/SBA, (b) 3Cr-1Ce/SBA, (c) 3Cr-3Ce/SBA, (d) 3Cr-5Ce/SBA.

Figure S1 illustrates the N₂ adsorption–desorption isotherms of SBA-15-supported chromia-ceria samples, and their textural properties are listed in Table 1. According to the IUPAC classification, all samples exhibit IV type adsorption isotherms and a clear H1 type hysteresis loop in the relative pressure range between 0.6 and 0.8, suggesting that these samples have regular mesoporous channels. The BET surface areas of these samples are $443-476 \text{ m}^2 \cdot \text{g}^{-1}$, and the total pore volumes are $0.706-0.753 \text{ cm}^3 \cdot \text{g}^{-1}$, which are lower than those of the parent SBA-15 (555 m² \cdot \text{g}^{-1} and 0.875 cm³ \cdot \text{g}^{-1}, respectively). This can be ascribed to the blocking of some mesopores in SBA-15 after the impregnation of chromia-ceria. Nevertheless, SBA-15-supported chromia-ceria samples still possess high surface areas and pore volumes, implying that the SBA-15 framework is

preserved after loading of chromia-ceria onto SBA-15. The N_2 adsorption result is consistent with that of XRD.

 Table 1
 Textural properties of the samples

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Sample	$S_{\rm BET}/({\rm m}^2 \cdot {\rm g}^{-1})$	$V_{t}^{a}/(cm^{3} \cdot g^{-1})$	D ^b /nm
3Cr/SBA	476	0.745	6.46
3Cr-1Ce/SBA	472	0.737	6.51
3Cr-3Ce/SBA	462	0.753	6.45
3Cr-5Ce/SBA	443	0.706	6.47

^{*a*} Total pore volume. ^{*b*} Pore diameter at the maximum of the pore size distribution.

Figure S2 presents the SEM images of 3Cr/SBA and 3Cr-3Ce/SBA samples. Both samples exhibit wheat-like macro-structures aggregated with rode-like domains of about 1 μ m length. Figure S3 shows the TEM images of 3Cr/SBA and 3Cr-3Ce/SBA samples. Both samples show well-ordered hexagonal arrays of mesopores. The TEM result indicates that the hexagonal pore structure of the parent SBA-15 is retained after loading of chromia and chromia-ceria, which is in accordance with the results obtained from XRD and N₂ adsorption measurements. An analytical HR-TEM with large angel detection was used for the 2-D atomic mapping. As shown in Figure 3, the distribution of chromium is more homogeneous in 3Cr-3Ce/SBA than in 3Cr/SBA. The 2-D mapping result is in line with that of XRD.

The dark-field TEM images of 3Cr/SBA and 3Cr-3Ce/SBA samples are shown in Figure S4. No chromia and ceria can be seen in the mesopores. We think that chromia and ceria are on the out surface of the mesopores in SBA-15.

Laser Raman is a useful technique to characterize chromium species dispersed on the SBA-15 support. Figure 4 shows the Raman spectra of SBA-15-supported chromia-ceria samples. An intense and sharp band at 547 cm⁻¹, which is commonly assigned to crystalline Cr_2O_3 ,^[22-25] was observed for all samples. The band at 985 cm⁻¹ can be attributed to Cr^{6+} species in the form of monochromate, while the band at 1012 cm^{-1} can be ascribed to Cr⁶⁺ species in the form of polychromate.^[24,26] Compared to the SBA-15-supported chromia sample (3Cr/SBA), SBA-15-supported chromia-ceria samples (3Cr-Ce/SBA) display weaker Raman band at 547 cm⁻¹ and higher intensity ratio of Raman band at 985 to 1012 cm^{-1} . The presented Raman data reveal that the addition of ceria to the 3Cr/SBA sample improves the dispersion of chromium species on the SBA-15 support. The Raman result is in agreement with the results measured by XRD and 2-D mapping. The broad and weak band at 457 cm⁻¹, which is assigned to CeO_2 with cubic fluorite structure,^[27] appears only in both 3Cr-3Ce/SBA and 3Cr-5Ce/SBA samples. The band at 607 cm⁻¹ observed in all samples can be attributed to the vibration of tri-siloxane ring of siliceous SBA-15.^[23,28]

3



Figure 3 2-D mapping images of (a) 3Cr/SBA and (b) 3Cr-3Ce/SBA.



Figure 4 Raman spectra of 3Cr-Ce/SBA samples with different Ce content. (a) 3Cr/SBA, (b) 3Cr-1Ce/SBA, (c) 3Cr-3Ce/SBA, (d) 3Cr-5Ce/SBA.

The oxidation state and coordination of chromium in SBA-15-supported chromia-ceria samples were investigated by UV-vis diffuse reflectance measurements, and the results are shown in Figure 5. Two intense bands at 273 and 358 nm are usually assigned to $O^{2-} \rightarrow Cr^{6+}$ charge transfer transition of chromate species with a tetrahedral symmetry.^[24,29-31] The bands at 453 and 603 nm are attributed to the $A_{2g} \rightarrow T_{1g}$ and $A_{2g} \rightarrow T_{2g}$ transitions of Cr^{3+} in crystalline Cr_2O_3 or CrO_x clusters with a octahedral symmetry, respectively.^[24,29-31] It can be concluded that the surface concentration of Cr^{6+} spe-

4

cies is higher over SBA-15-supported chromia-ceria samples (3Cr-Ce/SBA) than over the SBA-15-supported chromia sample (3Cr/SBA).



Figure 5 Diffuse reflectance UV-vis spectra of 3Cr-Ce/SBA samples with different Ce content. (a) 3Cr/SBA, (b) 3Cr-1Ce/SBA, (c) 3Cr-3Ce/SBA, (d) 3Cr-5Ce/SBA.

Figure S5 illustrates the XPS spectra of Cr 2p on the fresh and spent 3Cr-3Ce/SBA catalyst. There are two sets of Cr peaks at 570-583 eV and 583-593 eV, due to the splitting of the 3p orbit of Cr into Cr $3p_{3/2}$ and Cr $3p_{1/2}$. The following discussion will be focused on the Cr 3p_{3/2} peak due to its higher intensity. The XPS spectra were deconvoluted into two bands at ca. 576 and 580 eV which are attributed to Cr^{3+} and Cr^{6+} ions, respectively.^[32-36] The XPS data obtained by applying a peak-fitting program are listed in Table 2. After the dehydrogenation of isobutane with CO_2 at 570 °C for 250 min, the ratio of Cr^{6+} to Cr^{3+} declines significantly from 0.74 to 0.25, indicative of the reduction of most Cr^{6+} species to Cr^{3+} species in the reaction. This value is higher than that (0.14) after the dehydrogenation in the absence of CO₂ (*i.e.*, using N₂ instead of CO₂), confirming that a higher amount of chromium species were retained in a high oxidation state (Cr^{6+}) under a CO_2 atmosphere than under a N2 atomosphere during the dehydrogenation reaction. A subsequent treatment of the spent 3Cr-3Ce/SBA catalyst with CO₂ at 570 °C for 30

Table 2 XPS results of the fresh and spent 3Cr-3Ce/SBA catalyst after isobutane dehydrogenation at 570 $^{\circ}$ C in different atmospheres

Catalyst —	Binding energ	Binding energy of Cr 2p _{3/2} /eV		
	Cr ⁶⁺	Cr ³⁺		
Fresh	579.9	575.5	0.74	
Spent ^a	579.9	576.0	0.25	
Spent ^b	579.9	576.0	0.14	
Spent ^c	579.7	576.0	0.59	

^{*a*} Isobutane dehydrogenation in the presence of CO₂ for 250 min. ^{*b*} Isobutane dehydrogenation in the absence of CO₂ (*i.e.*, using N₂ instead of CO₂) for 250 min. ^{*c*} Isobutane dehydrogenation in the absence of CO₂ for 250 min, followed by treatment with CO₂ at 570 °C for 30 min. min brings about an increase of the Cr^{6^+} to Cr^{3^+} ratio from 0.14 to 0.59, but this value is still lower than that for the fresh catalyst (0.74). The XPS result reveals that CO_2 can act as a mild oxidant to oxidize the reduced Cr^{3^+} species to Cr^{6^+} species. Nevertheless, the complete recovery of the catalyst to its original state cannot be achieved. The XPS result demonstrates that the dehydrogenation of isobutane in the presence of CO_2 carried out mainly via a redox mechanism in which CO_2 reoxidized the catalyst which was reduced by isobutane, as shown in Figure S6.

The redox properties of SBA-15-supported chromia-ceria samples were investigated by H₂-TPR, and the resulting profiles obtained between 100 and 650 $^{\circ}$ C are displayed in Figure 6. The 3Cr/SBA sample displays only one reduction peak at 395 °C, which corresponds to the reduction of Cr^{6+} to Cr^{3+} [34,35,37-39] In addition to the main reduction peak at ca. 400 °C, the weak peak at ca. 270 °C assigned to the reduction of surface cerium oxide and probably the active chromium species tightly interacted with ceria was observed for the 3Cr-Ce/SBA samples.^[7] The peak temperature of the Cr⁶⁺ to Cr³ reduction is equivalent for 3Cr/SBA, 3Cr-1Ce/SBA and 3Cr-3Ce/SBA samples (ca. 395 °C), but lower than that for the 3Cr-5Ce/SBA sample (414 °C). This result suggests that the oxygen is more strongly bound in chromium oxide on the latter sample. The amount of Cr^{6+} in the fresh catalysts determined by the TPR method is given in Table 3. It can be found that the incorporation of ceria to the 3Cr/SBA sample enhances the concentration of Cr⁶⁺ species in the catalysts, which could be related to the better dispersion of chromium species on SBA-15 after the doping of ceria, as revealed by the XRD, 2-D mapping and Raman results. This result is consistent with the data obtained from the UV-vis diffuse reflectance measurement.



Figure 6 H₂-TPR profiles of 3Cr-Ce/SBA samples with different Ce content. (a) 3Cr/SBA, (b) 3Cr-1Ce/SBA, (c) 3Cr-3Ce/SBA, (d) 3Cr-5Ce/SBA.

Catalytic performance

The dehydrogenation of isobutane to isobutene in the presence of CO_2 was investigated at 570 °C. The major hydrocarbon product formed in the reaction is isobutene,

and the minor hydrocarbon products are methane, ethane, ethylene, propane, propylene and butenes (except isobutene). Figure S7 shows the activities of SBA-15-supported chromia catalysts with different Cr content as a function of reaction time. It is seen that the supported chromia catalyst with a Cr content of 3% is the most active. Figure 7 displays the catalytic performance of SBA-15-supported chromia-ceria catalysts with 3% Cr and different Ce content (3Cr-Ce/SBA) as a function of reaction time. The SBA-15-supported chromia catalyst with 3% Cr (3Cr/SBA) gives a 26.9% conversion of isobutane after 10 min of the reaction and a 16.7% conversion of isobutane after 250 min of the reaction. The 3Cr-Ce/SBA catalysts are obviously more active than 3Cr/SBA. The highest activity was achieved on the 3Cr-3Ce/SBA catalyst with 3% Cr and 3% Ce, but the conversion of isobutane for 3Cr-Ce/SBA catalysts does not differ significantly. The 3Cr-3Ce/SBA catalyst gives a 35.4% conversion of isobutane after 10 min of the reaction and a 22.4% conversion of isobutane after 250 min of the reaction. The isobutane conversion is ca. 2% for 1Ce/SBA, 3Ce/SBA and 5Ce/SBA, which is similar to the value of the blank test (without catalyst) under the same reaction conditions. As shown in Figure 7b, the selectivity to isobutene is slightly higher for 3Cr-Ce/SBA catalysts than 3Cr/SBA. Therefore, as far as the isobutene yield is concerned, the 3Cr-Ce/SBA catalysts present higher isobutene yield than 3Cr/SBA (Table 3). The 3Cr-3Ce/SBA catalyst gives the highest isobutene yield of 31.7% after 10 min of the reaction. It can be also found in Table 3 that the 3Cr-Ce/SBA



Figure 7 Conversion of isobutane (a) and selectivity to isobutene (b) as a function of reaction time for 3Cr-Ce/SBA catalysts with different Ce content at 570 $^{\circ}$ C.

5

FULL PAPER

catalysts exhibit higher activity for CO₂ conversion to CO than 3Cr/SBA.

The reducibility of a catalyst plays a key role in the dehydrogenation reaction that involves a redox mechanism. It is generally suggested that Cr⁶⁺ species are responsible for the high catalytic activities of supported chromium oxide catalysts in the oxidative dehydrogenation of small alkanes with CO₂.^[7,30,40] Therefore, the evidently higher conversion of isobutane on the 3Cr-Ce/ SBA catalysts than 3Cr/SBA is due to the fact that the former catalysts possess higher content of Cr^{6+} species, as revealed by TPR and UV-vis diffuse reflectance results. On the other hand, the 3Cr-5Ce/SBA catalyst is a bit less active than 3Cr-3Ce/SBA, although the former catalyst possesses more Cr⁶⁺ species. This can be attributed to the lower reducibility of the former catalyst than the latter one, as suggested from the peak temperature of the Cr^{6+} to Cr^{3+} reduction (414 vs. 395 °C). Cerium oxide is a solid base.^[41] Thus, the desorption of dehydrogenation product isobutene is more favorable from SBA-15-supported chromia-ceria catalysts than SBA-15-supported chromia, which leads to the higher isobutene selectivity achieved on the former catalysts.

Figure 8 compares the isobutene yield on the 3Cr-3Ce/SBA catalyst at 570 °C as a function of reaction time in the presence of CO₂ and in the absence of CO₂ (*i.e.*, using N₂ instead of CO₂). The isobutene yield is obviously greater in the former case (31.7% after 10 min of the reaction) than in the latter one (23.7% after 10 min of the reaction). This result indicates that CO₂ has a promoting effect on the dehydrogenation of isobutane, which can be ascribed to the higher concentration of Cr⁶⁺ species kept under a CO₂ atmosphere than under a N₂ atomosphere as a consequence of weak oxidation ability of CO₂, as demonstrated by the XPS result.

The catalytic performance of the best catalyst (3Cr-3Ce/SBA) in this work is compared with the performance of other catalysts reported in the literature. Table S1 lists the conversion, selectivity and space-time yield of isobutene, together with the reaction conditions. In fact, it is not appropriate to compare the catalytic activity because of the different reaction conditions. As far as the space-time yield of isobutene is concerned, the 3Cr-3Ce/SBA catalyst is less active than supported V-based and Fe-based catalysts, but more active than supported Cr-based catalyst.^[17-20,42]



Figure 8 Yield of isobutene in the presence and absence of CO_2 at 570 °C as a function of reaction time for the 3Cr-3Ce/SBA catalyst.

As shown in Figure 7a, isobutane conversion decreases relatively fast in the initial 50 min, followed by a slow diminishment with reaction time, which suggests a deactivation of the catalyst. The colour of the catalysts became black after the dehydrogenation of isobutane with CO₂, indicative of the coke formation. The amount of coke (determined by TG) deposited on the catalysts after 250 min of the reaction in the presence of CO_2 is listed in Table 3. It can be seen that the catalyst with higher activity has higher amount of coke. The amount of coke deposited on the 3Cr-3Ce/SBA catalyst after the dehydrogenation of isobutane in the presence of N₂ is 2.5%, less than that in the presence of CO₂. This result indicates that CO₂ can not suppress the coke deposition. Chen et al. observed similar phenomena for ethylbenzene dehydrogenation in the presence of CO₂ over alumina-supported vanadia catalysts.^[43] The Raman analysis on the spent 3Cr-3Ce/SBA catalyst reveals the nature of carbonaceous deposits. As presented in Figure S8, the G-band and D-band were observed for the spent catalyst at 1598 and 1347 cm⁻¹, respectively, which suggests the graphitic and amorphous carbon deposition on the catalyst.^[44,45]

On the other hand, the XPS data confirm that most Cr^{6^+} species present on the catalyst are reduced to Cr^{3^+} species during the dehydrogenation of isobutane with CO₂. In the oxidative dehydrogenation of hydrocarbons, both oxidized and reduced forms (Cr^{6^+}/Cr^{3^+}) are needed.^[46] Thus, the reduction of Cr^{6^+} to Cr^{3^+} will lead to a decrease in catalytic activity. To further demonstrate that the reduction of Cr^{6^+} to Cr^{3^+} is another cause for the

 Table 3
 Reaction data of SBA-15-supported chromia-ceria catalysts^a

Catalyst Cr^{6+} content/ (mmol•g ⁻¹)	Conversion/%		Selectivity/%				$i-C_4H_8$	Coke/				
	$(\text{mmol} \bullet \text{g}^{-1})$	i-C ₄ H ₁₀	CO_2	i-C ₄ H ₈	CH_4	C_2H_4	C_2H_6	C_3H_6	C_3H_8	$C_4 H_8{}^b$	yield/%	%
3Cr/SBA	0.044	26.9(16.7)	4.9(2.6)	89.7(89.9)	2.7(2.6)	0.2(0)	0(0)	6.0(6.6)	0.7(0.9)	0.7(0)	24.1(15.0)	2.5
3Cr-1Ce/SBA	0.054	33.0(20.6)	7.6(3.4)	90.1(91.5)	3.1(2.4)	0.2(0)	0(0)	5.3(5.5)	0.6(0.6)	0.7(0)	29.7(18.8)	3.2
3Cr-3Ce/SBA	0.060	35.4(22.4)	7.1(3.7)	89.6(91.6)	3.0(2.4)	0.3(0)	0.1(0)	5.7(5.4)	0.6(0.6)	0.7(0)	31.7(20.5)	3.2
3Cr-5Ce/SBA	0.080	34.6(21.2)	7.5(3.8)	89.8(91.6)	3.4(2.4)	0.3(0)	0.2(0)	5.1(5.4)	0.6(0.6)	0.6(0)	31.1(19.4)	3.2

^a The values outside and inside the bracket are the data obtained at 10 and 250 min, respectively. ^b Butenes except isobutene.



Figure 9 Variation of conversion and selectivity as a function of reaction time in consecutive cycles at 570 $^{\circ}$ C. (\blacksquare) conversion, (\Box) selectivity.

catalyst deactivation, the activity of the 3Cr-3Ce/SBA catalyst was investigated after the pretreatment with hydrogen (10 vol.% H₂/Ar, 400 °C and 1 h). As shown in Figure S9, the H₂-pretreated 3Cr-3Ce/SBA catalyst exhibits an obvious decrease in isobutane conversion than the fresh one at the initial stage of the reaction but a relatively small decline in isobutane conversion from 110 to 250 min. This result suggests that the reduction of Cr^{6+} to Cr^{3+} contributes more to the catalyst deactivation than to the coke formation during the dehydrogenation reaction.

Attempt was also carried out to regenerate the best performance catalyst of 3Cr-3Ce/SBA after isobutane dehydrogenation with CO₂ at 570 °C for 250 min, and the result is depicted in Figure 9. The conversion of isobutane diminishes from 35.4% to 22.4% after the dehydrogenation reaction for 250 min. The spent catalyst was regenerated by re-calcination in flowing air at 550 °C for 2 h, followed by subsequent purge with N₂ for another 1 h. The original activity of 3Cr-3Ce/SBA can be almost completely restored, with no noticeable deactivation being detected even after the third regeneration. This can be ascribed to the removal of deposited carbon on the catalyst and reoxidation of the reduced Cr^{3+} to Cr^{6+} after the catalyst regeneration.^[39]

Conclusions

The chromia-ceria catalysts supported on SBA-15 with 3%Cr and 1%-5% Ce (3Cr-Ce/SBA) were prepared using an incipient wetness impregnation method. Textural and XRD results demonstrate that the ordered hexagonal mesostructure of the SBA-15 support is retained after loading chromia-ceria. The addition of ceria to SBA-15-supported chromia improves the dispersion of chromium species. 3Cr-Ce/SBA catalysts are more active than the chromia catalyst supported on SBA-15 (3Cr/SBA with 3% Cr) in the dehydrogenation of isobutane with CO₂. This can be accounted for by a higher concentration of Cr^{6+} species on the former catalysts, as revealed by TPR and UV-vis diffuse reflectance results. In addition, the former catalysts display a bit higher selectivity to isobutene than the latter one. The highest activity was achieved on the 3Cr-3Ce/SBA catalyst with 3% Cr and 3% Ce, which affords 35.4% isobutane conversion and 89.6% isobutene selectivity at 570 °C after 10 min of the reaction. Both coke formation and reduction of Cr^{6+} to Cr^{3+} are responsible for the catalyst deactivation.

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References

- [1] Cavani, F.; Ballarini, N.; Cericola, A. Catal. Today 2007, 127, 113.
- [2] Caeiro, G; Carvalho, R. H.; Wang, X.; Lemos, M.; Lemos, F.; Guisnet, M.; Ribeiro, F. R. J. Mol. Catal. A 2006, 255, 131.
- [3] Sattler, J. J. H. B.; Ruiz-Martinez, J.; Santillan-Jimenez, E.; Weckhuysen, B. M. Chem. Rev. 2014, 114, 10613.
- [4] Al-zahrani, S. M.; Elbashir, N. O.; Abasaeed, A. E.; Abdulwahed, M. J. Mol. Catal. A 2004, 218, 17.
- [5] Cristina, R.; Zavoianu, R.; Portela, M. Catal. Commun. 2002, 3, 85.
- [6] Wang, S. B.; Zhu, Z. H. Energy Fuels 2004, 18, 1126.
- [7] Shi, X. J.; Ji, S. F.; Wang, K. Catal. Lett. 2008, 125, 331.
- [8] Takahara, I.; Chang, W. C.; Mimura, N.; Saito, M. Catal. Today 1998, 45, 55.
- [9] Wang, Y.; Ohishi, Y.; Shishido, T.; Zhang, Q. H.; Yang, W.; Guo, Q.; Wan, H. L.; Takehira, K. J. Catal. 2003, 220, 347.
- [10] Shen, Z. H.; Liu, J.; Xu, H. L.; Yue, Y. H.; Hua, W. M.; Shen, W. Appl. Catal. A 2009, 356, 148.
- [11] Michorczyk, P.; Ogonowski, J. Appl. Catal. A 2003, 251, 425.
- [12] Zheng, B.; Hua, W. M.; Yue, Y. H.; Gao, Z. J. Catal. 2005, 232, 143.
- [13] Ding, J. F.; Qin, Z. F.; Li, X. K.; Wang, G. F.; Wang, J. G. J. Mol. Catal. A 2010, 315, 221.
- [14] Yue, Y. H.; Hua, W. M. Petrochemical Technol. 2010, 39, 359.
- [15] Xie, Y. Q.; Hua, W. M.; Yue, Y. H.; Gao, Z. Chin. J. Chem. 2010, 28, 1559.
- [16] Zhang, F.; Miao, C. X.; Yue, Y. H.; Hua, W. M.; Gao, Z. Chin. J. Chem. 2012, 30, 929.
- [17] Shimada, H.; Akazawa, T.; Ikenaga, N.; Suzuki, T. Appl. Catal. A 1998, 168, 243.
- [18] Ogonowski, J.; Skrzńska, E. Catal. Lett. 2006, 111, 79.
- [19] Nakagawa, K.; Kajita, C.; Ikenaga, N.; Ando, T.; Suzuki, T. Catal. Today 2003, 84, 149.
- [20] Wei, C. L.; Xue, F. Q.; Miao, C. X.; Yue, Y. H.; Yang, W. M.; Hua,

FULL PAPER

W. M.; Gao, Z. Catalysts 2016, 6, 171.

- [21] Bi, Y. L.; Zhen, K. J.; Valenzuela, R. X.; Jia, M. J.; Corberán, V. C. Catal. Today 2000, 61, 369.
- [22] Zaki, M. I.; Fouad, N. E.; Leyrev, J.; Knözinger, H. Appl. Catal. 1986, 21, 359.
- [23] Hardcastle, F. D.; Wachs, I. E. J. Mol. Catal. 1988, 46, 173.
- [24] Weckhuysen, B. M.; Wachs, I. E.; Schoonheydt, R. A. Chem. Rev. 1996, 96, 3327.
- [25] Grzybowska, B.; Sloczynski, J.; Grabowski, R.; Wcislo, K.; Kozlowska, A.; Stoch, J.; Zielinski, J. J. Catal. 1998, 178, 687.
- [26] Baek, J.; Yun, H. J.; Yun, D.; Choi, Y.; Yi, J. ACS Catal. 2012, 2, 1893.
- [27] Li, X. H.; Feng, J.; Fan, H. X.; Wang, Q.; Li, W. Y. Catal. Commun. 2015, 59, 104.
- [28] Gao, X.; Bare, S. R.; Weckhuysen, B.; Wachs, I. E. J. Phys. Chem. B 1998, 102, 10842.
- [29] Subrahmanyam, C.; Louis, B.; Rainone, F.; Viswanathan, B.; Renken, A.; Varadarajan, T. K. *Catal. Commun.* 2002, *3*, 45.
- [30] Takehira, K.; Ohishi, Y.; Shishido, T.; Kawabata, T.; Takaki, K.; Zhang, Q. H.; Wang, Y. J. Catal. 2004, 224, 404.
- [31] Michorczyk, P.; Ogonowski, J.; Kuśtrowski, P.; Chmielarz, L. Appl. Catal. A 2008, 349, 62.
- [32] Kim, D. S.; Wachs, I. E. J. Catal. 1993, 142, 166.
- [33] Hakuli, A.; Kytökivi, A.; Krause, A. O. I. Appl. Catal. A 2000, 190, 219.
- [34] Yim, S. D.; Nam, I. S. J. Catal. 2004, 221, 601.

- [35] Zhu, Q. J.; Takiguchi, M.; Setoyama, T.; Yokoi, T.; Kondo, J. N.; Tatsumi, T. Catal. Lett. 2011, 141, 670.
- [36] Wu, R. X.; Xie, P. F.; Cheng, Y. H.; Yue, Y. H.; Gu, S. Y.; Yang, W. M.; Miao, C. X.; Hua, W. M.; Gao, Z. Catal. Commun. 2013, 39, 20.
- [37] Cherian, M.; Rao, M. S.; Yang, W. T.; Jehng, J. M.; Hirt, A. M.; Deo, G. Appl. Catal. A 2002, 233, 21.
- [38] Gaspar, A. B.; Brito, J. L. F.; Dieguez, L. C. J. Mol. Catal. A 2003, 203, 251.
- [39] Zhang, F.; Wu, R. X.; Yue, Y. H.; Yang, W. M.; Gu, S. Y.; Miao, C. X.; Hua, W. M.; Gao, Z. *Microporous Mesoporous Mater.* 2011, 145, 194.
- [40] Liu, L. C.; Li, H. Q.; Zhang, Y. Catal. Today 2006, 115, 235.
- [41] Zhang, H. X.; Chen, S. W.; Cui, X. Y.; Pan, D. H.; Qin, Z. F.; Wang, J. G. Acta Phys.-Chim. Sin. 2014, 30, 351.
- [42] Sun, G. S.; Huang, Q. Z.; Huang, S. Y.; Wang, Q. P.; Li, H. Q; Liu, H. T.; Wan, S. J.; Zhang, X. W.; Wang, J. S. *Catalysts* **2016**, *6*, 41.
- [43] Chen, S. W.; Qin, Z. F.; Xu, X. F.; Wang, J. G. Appl. Catal. A 2006, 302, 185.
- [44] De Morais Batista, A. H.; Ramos, F. S. O.; Braga, T. P.; Lima, C. L.; de Sousa, F. F.; Barros, E. B. D.; Filho, J. M.; de Oliveira, A. S.; de Sousa, J. R.; Valentini, A.; Oliveira, A. C. *Appl. Catal. A* **2010**, *382*, 148.
- [45] Nogueira, I. M.; Sabadia, G. Q.; Moreira, A. A.; Filho, J. M.; Oliveira, A. C. J. Mol. Catal. A 2011, 351, 81.
- [46] Michorczyk, P.; Ogonowski, J.; Niemczyk, M. Appl. Catal. A 2010, 374, 142.

(Zhao, X.)