

Oxidative Dehydrogenation of Ethane with CO₂ over Novel Cr/SBA-15/Al₂O₃/FeCrAl Monolithic Catalysts

Xuejun Shi, Shengfu Ji,* Kai Wang, and Chengyue Li

State Key Laboratory of Chemical Resource Engineering, Beijing University of Chemical Technology, 15 Beisanhuan Dong Road, Post Office Box 425, Beijing 100029, China

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The oxidative dehydrogenation (ODH) of ethane with CO₂ was successfully carried out over the Cr-based monolithic catalysts, which were prepared using FeCrAl alloy foil as support. High catalytic activity and stability can be drawn on these monolithic catalysts. For example, 66.5% ethane conversion and 99.5% ethylene selectivity can be achieved on the 5.0% Cr loading monolithic catalyst at 750 °C. After 1130 h of stability reaction, the hexagonal mesoporous structure of SBA-15 was still present and the pore walls of SBA-15 prevented the aggregation of Cr species. It was proposed that the Cr⁶⁺ species were responsible for the high catalytic activity of monolithic catalysts. During the reaction, the reduction–oxidation cycle between Cr⁶⁺ and Cr³⁺ species can be carried out via the dehydrogenation of ethane and oxidation by CO₂ processes. Interactions between Cr, SBA-15, and the Al₂O₃/FeCrAl support modify the redox properties of the Cr/SBA-15/Al₂O₃/FeCrAl catalysts.

1. Introduction

The processes of catalytic conversion of ethane and other light alkanes to corresponding alkenes are currently being extensively studied as a new energy-saving method for producing light olefins. Ethane is an abundant component in natural gas; one important way to use ethane is to convert it into ethylene, which has a well-established chemistry in the petrochemical industry. Thus far, the thermal cracking of hydrocarbons in the presence of steam is the main commercial method used for ethylene production, and this process involves endothermic reactions carried out at very high temperatures. The catalytic oxidative dehydrogenation of ethane is a promising route for ethylene production.¹ The oxidative dehydrogenation (ODH) of ethane by oxygen into ethylene has been proposed as an alternative to the process of thermal cracking of ethane because it provides several advantages, such as lower reaction temperature operation and less catalyst deactivation because of coking.^{2–5} However, because of the exothermic characteristic of this reaction in the presence of oxygen, it is necessary to remove heat and avoid deep oxidation of ethylene to give high selectivity of ethylene.

Carbon dioxide is a promising oxidant for dehydrogenation of ethane. In the dehydrogenation reaction, CO₂ can offer several advantages in catalysis, such as service as a medium for supplying heat, alleviation of thermodynamic equilibrium limitations, and holding catalyst life by removing coke formed

on the catalyst.⁶ Nakagawa et al.⁷ studied the dehydrogenation of ethane by carbon dioxide over several oxides and found that gallium oxide was an effective catalyst for this reaction, giving 18.6% ethylene yield with a selectivity of 94.5% at 650 °C. Takahara et al.⁸ reported the promoting effect of carbon dioxide on the dehydrogenation of propane over supported Cr₂O₃ catalysts. They found that carbon dioxide exerted a promoting effect only on SiO₂-supported Cr₂O₃ catalysts. Wang et al.⁹ investigated the effect of support, such as Al₂O₃, SiO₂, TiO₂, and ZrO₂, on the ODH of ethane to ethylene by CO₂ over several supported Cr₂O₃ catalysts. In addition, 8 wt % Cr₂O₃/SiO₂ catalyst could produce a 61% ethane conversion and 55.5% ethylene yield. The distribution of Cr₂O₃ on the supports and surface chromium species structure, which determine the activity of catalysts, are influenced by the nature of supports. In view of this fact, the support plays a decisive role in determining the dispersion of the active phase, and in certain occasions, salt support interaction enhances the catalytic activity of the active phase enormously.¹⁰

The newly discovered SBA-15 mesoporous silica material has a lot of scope to develop as a versatile new support, because of its unique surface and pore structure and, in particular, its tunable uniform hexagonal channels ranging from 5 to 30 nm and thick pore walls in the range of 3.1–6.4 nm.¹¹ In addition, SBA-15 has successfully been applied as a support for various catalytically active phases, such as Cr₂O₃, V₂O₅, TiO₂, ZrO₂,

* To whom correspondence should be addressed. Telephone: +86-10-64412054. Fax: +86-10-64419619. E-mail: jisf_buct@live.cn.

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MoO₃, etc.^{12–14} Supported Cr-based catalysts are well-known to be active catalysts for dehydrogenation of alkanes.¹⁵ In previous work, we prepared Cr-based catalysts using SBA-15 mesoporous silica as support, which exhibited high selectivity (89%) to propylene at high propane conversion (25%) in the ODH of propane at 675 °C.¹⁶ The enhanced catalytic activity of Cr-based catalysts using SBA-15 as a support had been attributed to the larger pore diameters and the stronger interaction between the active species and the support, which could provide more favorable conditions for mass transfer, thereby leading to an enhanced performance for ODH of propane.

Recently, monolithic catalysts and reactors are becoming increasingly significant as catalyzed gas–solid or multiphase reactors. Such catalysts and reactors can provide many advantages in comparison to conventionally used packed beds and trickle beds for a host of processes. These advantages, generally speaking, include low-pressure drop, high heat- and mass-transfer rates, and minimum axial dispersion stemming from the uniquely structured multichannel configuration of monoliths.^{17,18} Although ceramic substrates still predominate in the production of monolithic catalysts, metal substrates are being increasingly widely used because thin sheets of a metal can be rolled into concentric cylinders with longitudinal channels. The thin sheets of metal allow for the creation of a high density of active sites; this can be further increased if a stack of alternate flat and corrugated sheets are rolled into a cylinder. An FeCrAl alloy has been shown to be particularly suitable for the preparation of monolithic catalysts because heat treatment in air at temperatures above 900 °C results in the formation of a thin layer of α -alumina, which facilitates the deposition of other oxide phases on the surface.^{19,20} For example, Yin et al.^{21–23} prepared monolithic catalysts using the FeCrAl alloy as supports, and they showed good catalytic activity for the methane combustion reaction, whereas the catalyst using FeCrAl as a support has not been reported in the ODH of ethane with CO₂. Here, Cr-based metal monolithic catalysts with different Cr loadings were prepared using FeCrAl foils with honeycomb structure as supports and SBA-15/Al₂O₃ as washcoat, and their catalytic activity and stability for the ODH of ethane with CO₂ were investigated. The aim of this work is to assess the properties of the monolithic catalysts and their potential application in the ODH of ethane reactions.

2. Experimental Section

2.1. Catalyst Preparation. SBA-15 was synthesized according to the method described in the literature.¹¹ The Cr/SBA-15 samples

with different Cr content used in preparation of metal monolithic catalysts were prepared by the impregnation method using an aqueous solution of chromium nitrate (Cr(NO₃)₃·9H₂O). The catalyst samples were dried at room temperature and then calcined at 600 °C for 4 h in air. The above prepared Cr/SBA-15 samples powder were mixed with a sol made from boehmite.²⁰ The weight ratio of the Cr/SBA-15/Al₂O₃ was 1:1. The nitrate solution was added into the mixture; then the mixture was vigorously stirred for ca. 10 h; and finally, the Cr/SBA-15 slurry was obtained.

The monolithic supports (Al₂O₃/FeCrAl) were prepared according to the method described in the literature.²⁰ The monolithic supports were dipped into the above Cr/SBA-15 slurry, withdrawn at a constant speed of 3 cm/min, dried in air and thereafter at 120 °C for 3 h, and then calcined at 500 °C for 4 h. Finally, the Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts were obtained. If a higher loading is required, the coating procedure should be repeated. For the monolithic catalysts, the weight of SBA-15/Al₂O₃ washcoat layers is ca. 11.0 wt % in terms of the catalyst weight including the FeCrAl support and the loadings of Cr/SBA-15 is ca. 6.1 wt % in terms of the catalyst weight not including the FeCrAl support.

2.2. Characterization of the Catalysts. X-ray powder diffraction (XRD) patterns of the fresh and used catalysts were performed with a Bruker D8 diffractometer using Cu K α radiation at the following operation conditions: 40 kV and 30 mA in the 2θ range of 0.5–5° for the verification of SBA-15 structural ordering and 40 kV and 40 mA in the 2θ range of 10–80° for the study of structure phase behavior. N₂ sorption isotherms were obtained at liquid nitrogen temperature with a Thermo Electron Corporation Sorptomatic 1990 instrument. The samples were pretreated at 200 °C for 5 h, and the specific surface area of the samples was determined using the Brunauer–Emmett–Teller (BET) method. The pore volume and pore size distribution were derived from the desorption profiles of the isotherms using the Barrett–Joyner–Halanda (BJH) method. XPS experiments were carried out on an Escalab 250 instrument (Thermo Electron Corporation), using Al K α as the exciting radiation at constant pass energy of 50 eV. Binding energies were calibrated using the carbon present as a contaminant (C1s = 285.0 eV). The surface atomic compositions of all samples were calculated from photoelectron peak areas for each element after correcting for instrument parameters. Temperature-programmed reduction (TPR) experiments were performed using a Thermo Electron Corporation TPD/D/R/O 1100 series catalytic surfaces analyzer equipped with a thermal conductivity detector (TCD). Fresh catalysts were preheated using a 10% O₂/He mixture, with a temperature rate of 10 °C/min up to 600 °C and hold for 120 min, then cooled in flowing N₂ down to room temperature, and thereafter reduced with 5% H₂/N₂ mixture, heating 10 °C/min up to 900 °C. For the used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl catalyst, the TPR experiment was performed without being pretreated in the 10% O₂/He atmosphere. Water produced by the sample reduction was condensed in a cold trap before reaching the detectors. Only H₂ was detected in the outlet gas, confirming the effectiveness of the cold trap.

2.3. Catalytic Activity and Stability Tests. In the catalytic activity test, the ethane dehydrogenation experiments were performed in CO₂ or Ar atmosphere. The ethane dehydrogenation reactions were carried out using a fixed bed flow-type quartz reactor (inner diameter, 6 mm; length, 300 mm) under atmospheric pressure in the temperature range of 500–750 °C. The test was performed with cylindrical monolithic catalysts, which were made up of several cylinders with different diameters and 50 mm in length. Prior to the test, the catalysts were pretreated at 600 °C in a flow of oxygen (O₂, 5 mL/min) for 1 h and then cooling in flowing argon down to room temperature. No diluted reactant gas stream comprising C₂H₆ (99.99% purity) and carbon dioxide (99.99% purity) was introduced into the reactor with a gas hourly space velocity (GHSV) range of 3600–10 800 mL g^{−1} h^{−1}. The mole ratio of V_{CO₂}/V_{C₂H₆} was 2.0. The velocities of reactant gases were controlled by two mass flow controllers (Seven Star D07). The reaction temperature was controlled with a thermocouple attached to the outer wall of the reactor at a position corresponding to the center of the catalytic

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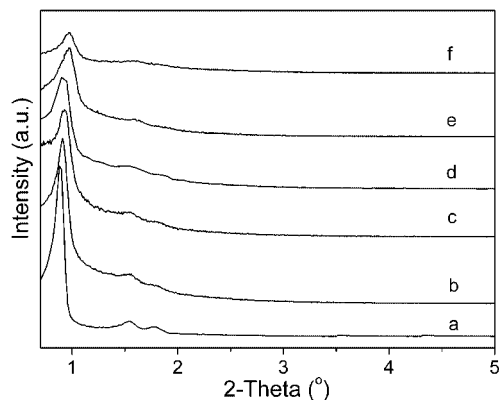


Figure 1. XRD patterns of the samples (a) SBA-15, (b) SBA-15/Al₂O₃/FeCrAl, (c) 2.5% Cr/SBA-15/Al₂O₃/FeCrAl, (d) 5.0% Cr/SBA-15/Al₂O₃/FeCrAl, (e) 7.5% Cr/SBA-15/Al₂O₃/FeCrAl, and (f) 10% Cr/SBA-15/Al₂O₃/FeCrAl.

bed. Kinetic studies were conducted with significantly low conversion, which were usually controlled to be significantly lower than those defined by thermodynamic equilibrium by adjusting GHSV (10 800 mL g⁻¹ h⁻¹). Rate limitation by external and/or internal mass transfer under differential conditions proved to be eliminated by applying suitable experimental criteria. The outlet products were analyzed after the reaction for 30 min by an online gas chromatograph (Beijing East and West Electronics Institute, GC-4000A) using a TCD. The conversion, selectivity, and TOF were calculated as follows:

$$\text{C}_2\text{H}_6 \text{ conversion} = 1 - \frac{2n_{\text{C}_2\text{H}_6}}{2n_{\text{C}_2\text{H}_6} + 2n_{\text{C}_2\text{H}_4} + n_{\text{CH}_4}}$$

$$\text{CO}_2 \text{ conversion} = 1 - \frac{n_{\text{CO}_2}}{(n_{\text{CO}_2} + n_{\text{CO}})}$$

$$\text{C}_2\text{H}_4 \text{ selectivity} = \frac{2n_{\text{C}_2\text{H}_4}}{2n_{\text{C}_2\text{H}_4} + n_{\text{CH}_4}}$$

$$\text{TOF (mol s}^{-1} \text{ mol}_{\text{Cr-atom}}^{-1}) = C_{\text{product}} F_{\text{total}} / M_{\text{Cr-atom}}$$

where C_{product} is the concentration of products in the outlet gas observed by GC analysis (%), F_{total} is the flow rate of feed gas (mol/s), and $M_{\text{Cr-atom}}$ is the amount of Cr atoms in the catalyst (mol). The calculations do not consider the conversion of ethane to coke, because its instantaneous formation is time-dependent and difficult to estimate. Moreover, the reaction data in the work were reproducible with a precision of less than 3.0%.

3. Results and Discussion

3.1. XRD of the Catalysts. The small-angle XRD patterns of the fresh samples are shown in Figure 1. The SBA-15 support (Figure 1a) shows three well-resolved diffraction peaks in the 2θ range of 0.7–2°, corresponding to the diffraction of (100), (110), and (200) planes and being characteristic of the hexagonally ordered structure of SBA-15.¹¹ When SBA-15/Al₂O₃ washcoat is coated on the surface of the FeCrAl support (Figure 1b), the d_{100} peak shifts to a higher angle and attenuates in intensity, suggesting that Al₂O₃ and FeCrAl affect the particles of SBA-15. When Cr is loaded on the support (Figure 1c), the d_{100} peak still shifts to a higher angle relative to that of SBA-15/Al₂O₃/FeCrAl, which may be attributed to the blockage the

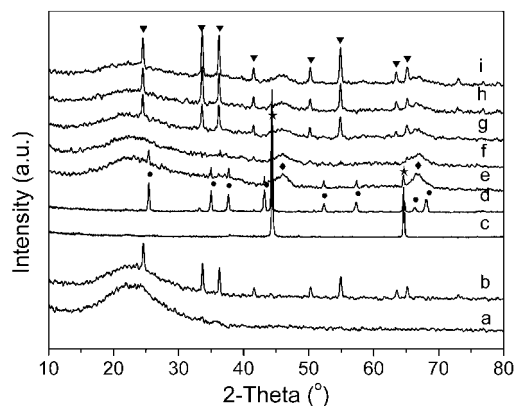


Figure 2. XRD patterns of the samples (a) SBA-15, (b) 5.0% Cr/SBA-15, (c) FeCrAl, (d) FeCrAl pre-oxidized at 950 °C, (e) SBA-15/Al₂O₃/FeCrAl, (f) 2.5% Cr/SBA-15/Al₂O₃/FeCrAl, (g) 5.0% Cr/SBA-15/Al₂O₃/FeCrAl, (h) 7.5% Cr/SBA-15/Al₂O₃/FeCrAl, and (i) 10% Cr/SBA-15/Al₂O₃/FeCrAl. (●) α-Al₂O₃, (◆) γ-Al₂O₃, (★) FeCr, and (▼) Cr₂O₃.

frameworks of SBA-15 with the introduction of Cr species.²⁴ Additionally, the d_{100} , d_{110} , and d_{200} peaks attenuate further in intensity, with an increasing Cr content from 2.5 to 10%, and may attribute to the constriction of their frameworks with further Cr loading during the calcination procedure. This phenomenon was also observed by Liu et al.¹⁴ on the V/SBA-15 sample.

The wide-angle XRD patterns of cleaned FeCrAl foil, pre-oxidized FeCrAl foil, SBA-15/Al₂O₃/FeCrAl, and fresh Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts are presented in Figure 2. To better understand the structure of the samples, the phase structures of SBA-15 and Cr/SBA-15 powder are also measured by XRD and the patterns of SBA-15 and 5.0% Cr/SBA-15 samples are shown in curves a and b of Figure 2. The characteristic peaks of FeCr are observed at $2\theta = 44.3^\circ$ and 64.6° (Figure 2c). After the heat treatment at 950 °C for 15 h, besides the characteristic peaks of FeCr, the peaks assigned to α-Al₂O₃, which appear at $2\theta = 25.5^\circ, 35.0^\circ, 37.6^\circ, 43.2^\circ, 52.4^\circ, 57.3^\circ, 66.3^\circ$, and 68.0° , are found on the surface (Figure 2d). This is consistent with the reports in the literature.^{19,23} As seen, after the heat treatment, the segregation of an alumina layer on the FeCrAl surface, α-Al₂O₃ phase, is present. The formation of the α-Al₂O₃ can improve the combination between the washcoat and the FeCrAl support.^{20,26} After the heat-treated support was coated with SBA-15/Al₂O₃ washcoat, besides the characteristic peaks of FeCrAl and α-Al₂O₃, those of γ-Al₂O₃ appearing at ca. 46.1° and 66.7° are also found, respectively (Figure 2e).

For the Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts with over 2.5% Cr content, the characteristic peaks for Cr₂O₃(012), Cr₂O₃(104), Cr₂O₃(110), Cr₂O₃(113), Cr₂O₃(024), Cr₂O₃(116), Cr₂O₃(214), and Cr₂O₃(300) can be clearly seen at $2\theta = 24.5^\circ, 33.6^\circ, 36.2^\circ, 41.6^\circ, 50.2^\circ, 54.9^\circ, 63.5^\circ$, and 65.1° , respectively (curves g–i of Figure 2). Furthermore, the intensity of Cr₂O₃ peaks increases gradually with increasing Cr content in the Cr/SBA-15/Al₂O₃/FeCrAl series monolithic catalysts, whereas no characteristic peaks for the Cr₂O₃ phase can be observed with the 2.5% Cr content sample (Figure 2f). Additionally, the color of catalysts changes from yellow to green with the growing Cr content, in accordance with above phenomenon, indicating the

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Table 1. Activity of Cr/SBA-15/Al₂O₃/FeCrAl Catalysts for the Dehydrogenation of C₂H₆^a

catalyst	in the presence of CO ₂				yield (%)	in the presence of Ar				E _p (kJ/mol)	
	conversion (%)		selectivity (%)			yield (%)	conversion (%)		selectivity (%)		
	C ₂ H ₆	CO ₂	C ₂ H ₄	CH ₄			C ₂ H ₆	C ₂ H ₄	CH ₄		C ₂ H ₄
SBA-15/Al ₂ O ₃ /FeCrAl	4.31	0.05	93.9	6.1	4.05	3.29	94.3	5.7	3.10		
2.5% Cr/SBA-15/Al ₂ O ₃ /FeCrAl	60.3	15.7	95.8	4.2	57.8	41.6	91.2	8.8	37.9	104.25	
5.0% Cr/SBA-15/Al ₂ O ₃ /FeCrAl	66.5	17.3	95.5	4.5	63.5	47.4	86.9	13.1	41.2	90.53	
7.5% Cr/SBA-15/Al ₂ O ₃ /FeCrAl	63.5	16.4	95.3	4.7	60.5	46.1	82.1	17.9	37.9	97.44	
10% Cr/SBA-15/Al ₂ O ₃ /FeCrAl	63.7	16.5	95.2	4.8	60.6	45.2	80.9	19.1	36.6	94.12	

^a Reaction conditions: GHSV, 5400 mL g⁻¹ h⁻¹; V_{CO₂} or Ar/V_{C₂H₆}, 2.0; T, 750 °C.

formation of Cr^{III} at high Cr species loading.²⁷ When patterns of 5.0% Cr/SBA-15 and 5.0% Cr/SBA-15/Al₂O₃/FeCrAl samples are compared, it can be found that the Cr₂O₃ peaks of the former are sharper and intenser than that of the latter. This result indicates that the dispersion of chromium is enhanced remarkably when the Cr/SBA-15 powders are deposited onto the surface of the FeCrAl support.

3.2. Activity and Stability of the Catalysts. **3.2.1. Activity of the Catalysts.** Dehydrogenation of C₂H₆ over Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts with different Cr content in the absence or presence of CO₂ was investigated at 750 °C. The results are given in Table 1. The formation rate (TOF) of ethylene is calculated using the ethylene yield data of the turnover frequency, defined in terms of ethylene mole formation per chromium atom per unit time. The SBA-15/Al₂O₃/FeCrAl support shows negligible C₂H₆ and CO₂ conversion. Over the Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts, the major reaction product is C₂H₄ and the minor products are CH₄, CO, H₂, and H₂O in the presence of a CO₂ atmosphere. After CO₂ was replaced with Ar, the above products are also detected, except for CO and H₂O products. In addition, the catalytic performances of the Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts in the absence of CO₂ are obviously lower than that in the presence of CO₂, indicating the promoting effects of CO₂ for the ODH of ethane in the CO₂ atmosphere. In the presence of CO₂, considerable amounts of CO and H₂O are formed during the reaction, demonstrating the occurrence of a reaction between CO₂ and H₂ (water–gas shift reaction). Removal of deposited carbon through the Boudouard reaction is another plausible cause. The water–gas shift reaction can shift the dehydrogenation of ethane to the product side, thus leading to the higher C₂H₆ conversion over these catalysts. Moreover, CO₂ also has the function maintaining chromium oxide in higher oxidation states.^{28–30}

A redox mechanism is suggested in the presence of CO₂. Mimura et al.²⁸ used Fourier transform infrared spectroscopy (FTIR) and X-ray absorption fine structure (XAFS) to probe the active species and role of CO₂ for the ODH of ethane over Cr/H-ZSM-5 catalyst. They found that there existed a redox cycle involving Cr⁶⁺/Cr³⁺ species, in which a Cr⁶⁺ species was reduced to Cr³⁺ by ethane treatment and CO₂ treatment led to re-oxidation to Cr⁶⁺ species. In fact, a Cr redox cycle can be observed at 500–550 °C, which is lower than the temperature of ethane dehydrogenation (650 °C³¹). On the basis of the current results, we believe that a high-oxidation-state Cr species is effective for the oxidative dehydrogenation. Indeed, the reduction of Cr⁶⁺ to Cr³⁺ was demonstrated by the TPR analysis.

That means the reduced Cr species was re-oxygenated by CO₂. As a result, the high dehydrogenation activity Cr⁶⁺ species can be obtained by the Cr redox cycle during the ODH of ethane in the presence of CO₂. That result again indicates the promoting effects of CO₂ for the ODH of ethane in the CO₂ atmosphere.

It has been generally recognized that the surface chromium species strongly depends upon the surface density of chromium oxide.³² From Table 1, it can be seen that the C₂H₆ conversion and C₂H₄ yield increase and reach a maximum level at the Cr loading up to 5%. Further increasing Cr content caused a slight decrease in conversion. This indicates that a 5% Cr loading on the Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalyst is sufficient for obtaining high C₂H₆ conversion and C₂H₄ yield. The change of catalytic activity with the variance of Cr loading is related to not only the amount of active sites provided by Cr species but also chromium oxide species.^{32,33} When Cr loading is 5.0%, the diffraction peaks of crystalline Cr₂O₃ appear in the XRD patterns (Figure 2g). The color of catalysts changes from yellow to green with the growing Cr content. This indicates the formation of Cr^{III} at high Cr loadings.²⁷ This is similar to the discovery of Hakuli that CrO_x was inclined to form clusters rather than a well-dispersed phase with the increase of Cr content on the CrO_x/SiO₂ catalyst.³⁴ Yim et al.³² confirmed that mono-, di-, tri-, and tetrachromate species of Cr^{VI} and crystalline Cr₂O₃ were gradually formed on the surface of Al₂O₃ with an increase in the Cr content from 1 to 17 wt %. In this study, the formation of crystalline Cr₂O₃ correlates well to our results.

The influence of temperature on the catalytic performance of the 5.0% Cr content monolithic catalyst is shown in Figure 3. The conversion of C₂H₆ and CO₂ increases with raising the temperature (Figure 3a). With a higher reaction temperature, the C₂H₄ selectivity has a bit of a decrease but is still above 95%. On the other hand, selectivity to methane increases little by little with a higher reaction temperature, which indicates that the elevation of the reaction temperature favors hydrocracking of ethane. The result suggests that the rates of secondary reaction increase with a higher reaction temperature. As a result, more CH₄ is formed in the products. Moreover, in the products, the CO concentration also increases gradually with a higher reaction temperature in the ODH reaction. CO mainly comes from the reduction of CO₂ (CO₂ + H₂ → H₂O + CO, where H₂ comes from C₂H₆). The increase of the CO concentration in the products indicates that the high temperature benefits the activation of CO₂. Similar trends on the variation of conversion and selectivity can be obtained over the other Cr/SBA-15/Al₂O₃/FeCrAl catalysts.

The influence of the space velocity on the C₂H₆ conversion and C₂H₄ and CH₄ selectivity was tested over the 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalyst at 750 °C under

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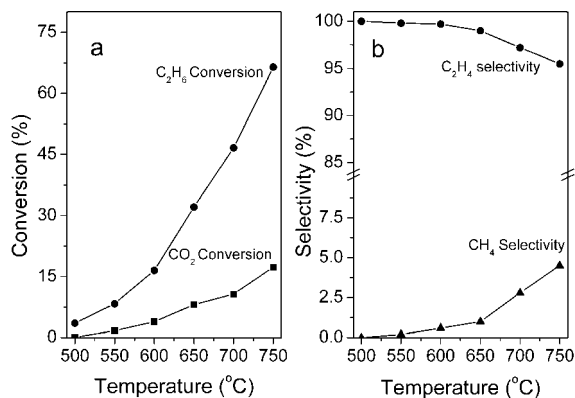


Figure 3. Conversion and selectivity versus reaction temperature during the ODH of ethane with CO₂ over 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts. Reaction conditions: GHSV, 5400 mL g⁻¹ h⁻¹; V_{CO₂}/V_{C₂H₆}, 2.0.

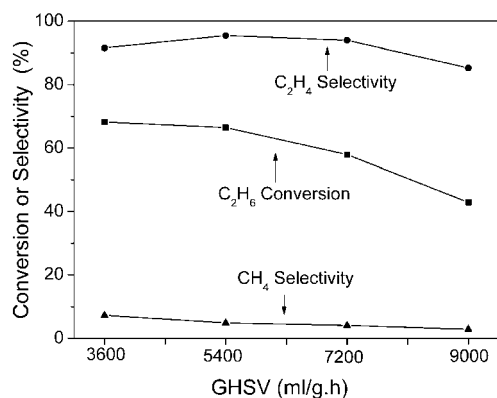


Figure 4. Effect of space velocity on the performance of the 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalyst. Reaction conditions V_{CO₂}/V_{C₂H₆}, 2.0; T, 750 °C.

atmospheric pressure, with a V_{CO₂}/V_{C₂H₆} = 2.0. From Figure 4, it can be seen that, with increasing space velocity from 3600 to 9000 mL g⁻¹ h⁻¹, the C₂H₆ conversion and the CH₄ selectivity decrease gradually. This might be a result of the decrease in the contact time of the reactants and the surface activity sites of the catalyst; that is, the reaction of the reactants on the surface of the catalyst is not complete, and therefore, catalytic activity decreases with higher space velocity. In addition, the decrease of CH₄ selectivity indicates that high space velocity is unfavored with the occurrence of the secondary reaction, which causes more CH₄ selectivity in the ODH of ethane with CO₂. The C₂H₄ selectivity first increases when the space velocity increases to 5400 mL g⁻¹ h⁻¹ and then decreases with higher space velocity. The results indicate that the appropriate GHSV is necessary to obtain a maximum C₂H₄ yield in the ODH reaction. The best C₂H₆ conversion and C₂H₄ selectivity, which are 66.5 and 95.5%, respectively, can be obtained at the GHSV = 5400 mL g⁻¹ h⁻¹ reaction condition.

Figure 5 shows the Arrhenius plots of the formation rate of ethylene over Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts with different Cr content, and the activation energies (*E_p*) are also shown in Table 1. It can be seen that the activation energy of the Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts is in the range of 90.53–104.25 kJ/mol and the 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalyst has the lowest activation energy, which is 90.53 kJ/mol. The results are in agreement with the results of dehydrogenation activity of the catalysts. Mimura et al.²⁸ reported the similar activation energy, which is in the range of 86.1–143.9 kJ/mol on the Cr/H-ZSM-5 catalysts. The difference in the activation energy for the Cr/SBA-15/Al₂O₃/

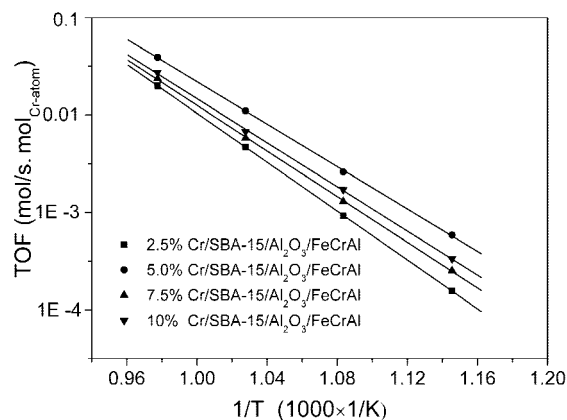


Figure 5. Arrhenius plots for ethylene over Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts. Feed gas: GHSV, 10 800 mL g⁻¹ h⁻¹; V_{CO₂}/V_{C₂H₆} = 2.0.

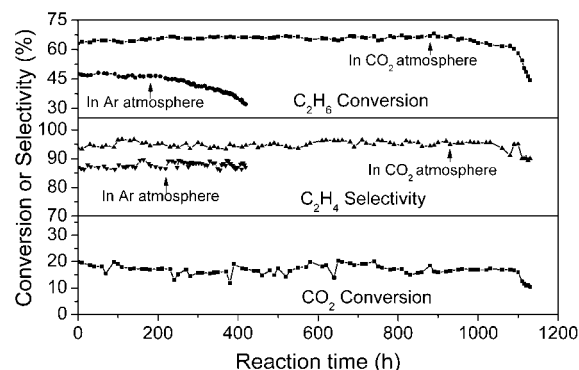


Figure 6. Stability of the 5.0% Cr/SBA-15/Al₂O₃/FeCrAl catalyst at GHSV, 5400 mL g⁻¹ h⁻¹; V_{CO₂} or Ar/V_{C₂H₆}, 2.0; and T, 750 °C.

FeCrAl monolithic catalysts with different Cr content in our study suggests that both the number and nature of active sites has changed by the interaction among the Cr, SBA-15, and Al₂O₃/FeCrAl support.

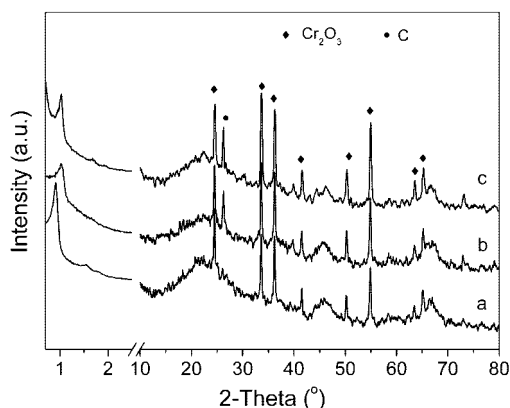
3.2.2. Stability of the Catalyst. From the above results, we can conclude that the 5% Cr/SBA-15/Al₂O₃/FeCrAl catalyst shows the best catalytic activity for ODH of ethane with CO₂. Thus, this catalyst is selected for study in the stability test. The relationship between the catalytic activity and stability of the 5% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalyst is shown in Figure 6. In the CO₂ atmosphere, the catalyst runs 1130 h and displays good activity under the reaction conditions (T, 750 °C; GHSV, 5400 mL g⁻¹ h⁻¹; V_{CO₂}/V_{C₂H₆}, 2.0). The conversions of C₂H₆ and CO₂ dropped from 66.5 and 17.3 to 42.3% and 10.6%, respectively. The selectivity for C₂H₄ decreased over the same period of time from 95.5 to 90.1%. To the best of our knowledge, this is the best stability Cr-based catalyst for ODH of ethane to ethylene. However, in the Ar atmosphere, the catalyst only runs 419 h, the C₂H₆ conversion decreased from 47.6 to 32.2%, and the C₂H₄ selectivity has a slight change.

In the ODH of ethane with the CO₂ reaction, the carbon deposition and the sintering and transformation of the active phase are key factors that cause the deactivation of the catalyst. Xu et al.³⁵ thought that the main factor for the coking reaction was from the C₂H₆ cracking reaction and the CO₂ took up the role of prohibiting carbon deposition by the Boudouard reaction (C + CO₂ → CO) during the ODH of ethane with the CO₂ reaction. Mimura et al.⁶ also reported that carbon dioxide maintained the activity of the catalyst by removing coke from

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Table 2. Physical Characteristics and the Coke Content of the Monolithic Catalysts

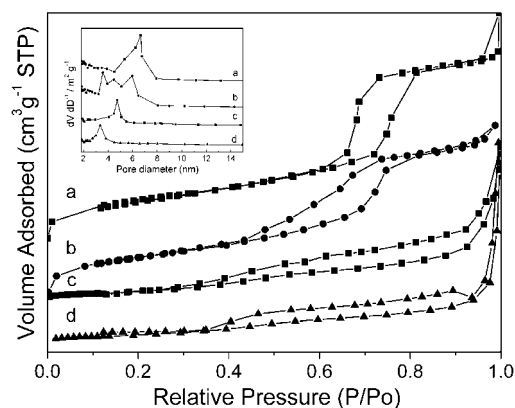
catalysts	A_{BET} (m^2/g)	V_{BJH} (cm^3/g)	D_{BJH} (nm)	coke content (wt %)
SBA-15/ Al_2O_3 /FeCrAl	45.1	0.075	6.65	
5% SBA-15/ Al_2O_3 /FeCrAl (fresh)	42.9	0.069	3.58; 5.96	
5% SBA-15/ Al_2O_3 /FeCrAl (used) ^a	12.0	0.047	3.36	7.9
5% SBA-15/ Al_2O_3 /FeCrAl (used) ^b	17.2	0.054	4.47	12.7

^a After the reaction at 750 °C for 1130 h in the CO_2 atmosphere.^b After the reaction at 750 °C for 419 h in the Ar atmosphere.**Figure 7.** XRD patterns for 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalyst: (a) fresh catalyst, (b) used catalyst in the CO_2 atmosphere, and (c) used catalyst in the Ar atmosphere.

the surface of the catalyst in the ODH of ethane with CO_2 . In the present study, the content of coke is 7.9 wt % (Table 2) as shown by the mass increment between the fresh catalyst and the used catalyst after the reaction for 1130 h. However, the content of coke is 12.7 wt % in the Ar atmosphere after 419 h of reaction. In the CO_2 atmosphere, efficient carbon elimination by the Boudouard reaction on the catalyst surface may contribute to the low carbon deposition and stable catalytic performance. In addition, the FeCrAl metal support has a high thermal conductivity. Therefore, the low-temperature gradient of the FeCrAl-based catalysts can be expected for the reactions occurring at a high-temperature reaction. This can avoid or decrease the sinter of activity phase (Cr species).

For good stability of the Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalysts, besides the main contribution of carbon elimination and the FeCrAl support, mesoporous SBA-15 also offers some advantageous characteristics compared to that of conventional silica and alumina supports. The dissolution of Cr species is confined in channels of SBA-15 material, which results in more difficulty for the sinter and agglomeration of Cr species. Consequentially, the Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalysts display excellent catalytic activity and stability in the ODH of ethane with CO_2 .

The XRD patterns of the fresh and used 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalysts in the CO_2 or Ar atmosphere are shown in Figure 7. For the three samples, one major characteristic peak of SBA-15 at about $0.9\text{--}1.1^\circ$ is observed. The result suggests that the pore structure of SBA-15 is retained in the used catalysts. However, the peak intensity of the two used catalysts decreases, and the position of the peak shifts to a higher 2θ value relative to that of the fresh catalyst. This indicates that the regularity of the hexagonal mesoporous structure of the used catalysts is partly changed after the stability test. When the XRD profiles of fresh and used catalysts are compared, the intensity of the Cr_2O_3 peak of the two used catalysts has a slight increase. This may be caused by the conglomeration of the Cr species after the stability test at 750

**Figure 8.** Nitrogen sorption isotherms of the sample: (a) SBA-15/ Al_2O_3 /FeCrAl, (b) 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl (fresh), (c) 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl (after 419 h of reaction in the Ar atmosphere), and (d) 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl (after 1130 h of reaction in the CO_2 atmosphere).**Table 3. Surface Concentration of the Cr Elements**

catalyst	Cr (%)	Cr ³⁺ BE (eV)	Cr ⁶⁺ BE (eV)	Cr ⁶⁺ / Cr ³⁺
5% Cr/SBA-15/ Al_2O_3 /FeCrAl (fresh)	1.23	576.4	578.6	0.36
5% Cr/SBA-15/ Al_2O_3 /FeCrAl (used) ^a	1.34	576.6	578.5	0.14
5% Cr/SBA-15/ Al_2O_3 /FeCrAl (used) ^b	1.32	576.5	578.5	0.13

^a After the reaction at 750 °C for 1130 h in the CO_2 atmosphere.^b After the reaction at 750 °C for 419 h in the Ar atmosphere.

°C. Moreover, a peak corresponding to deposited carbon is observed, suggesting that deactivation of the Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalyst after the stability test could be caused by coking.

3.3. Textural and Structural Properties. Nitrogen adsorption–desorption isotherms of the SBA-15/ Al_2O_3 /FeCrAl and fresh and used 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalysts are displayed in Figure 8. The isotherm of the SBA-15/ Al_2O_3 /FeCrAl exhibits a type IV isotherm with H1-type hysteresis, which is typical of mesoporous materials with one-dimensional cylindrical channels.¹¹ The sharp inflection between the relative pressures $P/P_0 = 0.6$ and 0.8 observed in the isotherm corresponds to capillary condensation with uniform mesopores and is a function of the pore diameter. The SBA-15/ Al_2O_3 /FeCrAl support displays a pore diameter (D_{BJH}) of 6.65 nm, a total pore volume (V_{BJH}) of 0.075 cm^3/g , and a BET specific surface area (A_{BET}) of 45.1 m^2/g (see Table 2). The N_2 isotherms have some change in shape for the 5.0% Cr doped sample, where the hysteresis inflection is less sharp, indicating that the pore size of the material is less ordered and uniform compared to that of the SBA-15/ Al_2O_3 /FeCrAl support. The opening of the hysteresis loop at lower P/P_0 relative pressure is also observed with fresh 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl sample, witnessing the pore size diminution on the sample.³⁶ For the two used 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts, the hysteresis loop exhibits deformations and the adsorbed volume is clearly decreased as compared to the fresh catalyst. In addition, the A_{BET} and D_{BJH} also have an obvious decrease. This may be due to the fact that, during the reaction, the depositing coke blocks the mesochannels and causes some collapse of pore walls. However, the hexagonal mesoporous structure is still present in the used catalysts. The observed results are in good agreement with those obtained by XRD presented above.

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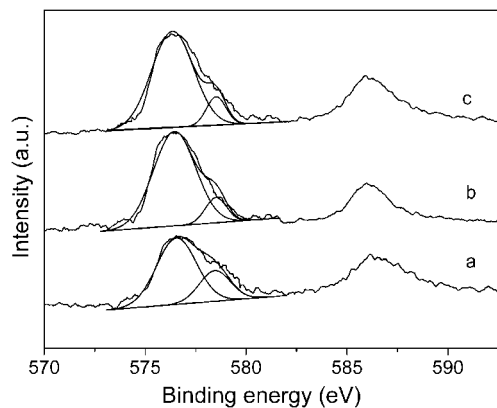


Figure 9. XPS spectra of Cr_{2p} over fresh and used 5% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts: (a) fresh catalyst, (b) used catalyst in the CO₂ atmosphere, and (c) used catalyst in the Ar atmosphere.

3.4. Characterization Results of XPS. Surface Cr species on the fresh and used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts are examined by XPS. The surface concentrations of Cr species are given in Table 3, and Cr_{2p} spectra are shown in Figure 9. It can be seen that the surface concentration of Cr on fresh and used catalysts show a small difference (Table 3). Two Cr species can be found by curve fitting, and they are assigned to Cr³⁺ (ca. 576.4 eV) and Cr⁶⁺ (ca. 578.6 eV).^{15,37,38} The peaks in the used catalyst spectrum slightly shift to lower binding energy. This may be caused by the carbon deposition, which changes the chemical environment of Cr species. Many researches have investigated the dehydrogenation of light alkanes over supported Cr-based catalysts. The chromium species with the high oxidation state were the key to higher catalytic activity during the dehydrogenation of light alkanes.^{6,39} Ge et al.⁴⁰ used electron spin resonance (ESR) and ultraviolet diffuse reflectance spectroscopy (UV-DRS) to probe the active site for the ODH of ethane with CO₂ over silica-supported chromium oxide catalyst and found that species with a high oxidation state (Cr⁵⁺ or Cr⁶⁺) are important for the reaction. In this investigation, it is found that two Cr species, Cr³⁺ and Cr⁶⁺, coexisted on the surface of the fresh and used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl catalysts and the Cr⁶⁺/Cr³⁺ ratios on the fresh catalyst are higher than that of the used catalyst. The decrease of the Cr⁶⁺/Cr³⁺ ratio on the catalyst surface may be the main reason for the decrease of the catalytic activity of the 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalyst. The following TPR of the fresh and used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts also show that the Cr⁶⁺ species is the main active species for ODH of ethane with CO₂. Thus, we believe that surface Cr⁶⁺ species and Cr⁶⁺/Cr³⁺ couples are the active sites for dehydrogenation of ethane based on XPS and TPR results. The catalytic activity is dependent upon the redox property of the monolithic catalysts. Therefore, it is believed that a redox mechanism will play an important role in the reaction. The dehydrogenation and oxidative dehydrogenation because of the introduction of CO₂ and its decomposition to produce surface oxygen species will be the parallel reaction paths in the dehydrogenation of ethane by CO₂.

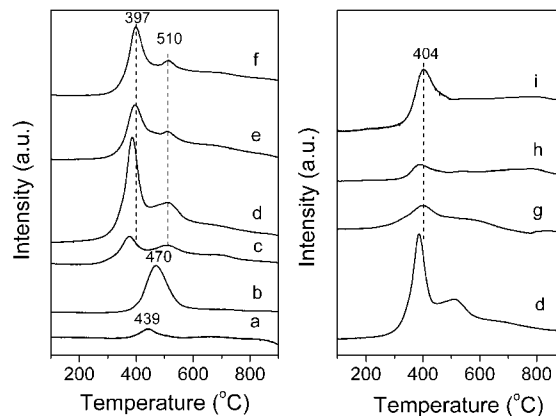


Figure 10. TPR profiles of the samples: (a) Cr₂O₃, (b) 5.0% Cr/SBA-15, (c) 2.5% Cr/SBA-15/Al₂O₃/FeCrAl, (d) 5.0% Cr/SBA-15/Al₂O₃/FeCrAl, (e) 7.5% Cr/SBA-15/Al₂O₃/FeCrAl, (f) 10% Cr/SBA-15/Al₂O₃/FeCrAl, (g) used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl (after 1130 h of reaction in the CO₂ atmosphere), (h) used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl (after 419 h of reaction in the Ar atmosphere), and (i) used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl (regenerated by CO₂ at 750 °C for 10 h).

3.5. H₂-TPR of the Catalysts. H₂-TPR patterns of fresh Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts with different Cr loadings are shown in Figure 10. For comparison, the H₂-TPR of the bulk Cr₂O₃, 5.0% Cr/SBA-15, used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl samples, and the used 5.0% Cr/SBA-15/Al₂O₃/FeCrAl catalyst, which was regenerated by CO₂ at 750 °C for 10 h, are also measured. There are no obvious reduction peaks of the SBA-15/Al₂O₃/FeCrAl support in the temperature range of 25–900 °C. For bulk Cr₂O₃, only one weak reduction peak appears in the profile around 440 °C, corresponding to the reduction of Cr⁶⁺ species in the oxide.⁴¹ After Cr was deposited on the SBA-15/Al₂O₃/FeCrAl support, one intense peak in the range of 374–397 °C and a shoulder at about 510 °C are observed for each fresh Cr/SBA-15/Al₂O₃/FeCrAl monolithic catalysts. The two H₂ consumption peaks are also assigned to the reduction of Cr⁶⁺ → Cr³⁺.⁴² This indicates that there exist two kinds of Cr⁶⁺ species on the surface of the catalysts. On the basis of the study results of Cavani et al.,⁴³ two kinds of Cr⁶⁺ species, the grafted and the soluble Cr⁶⁺, are expected to form on the monolithic catalysts. The grafted Cr⁶⁺ species, which is anchored to the silica surface, has a greater interaction with the silica support and is harder to be reduced than the soluble Cr⁶⁺ species, which presents as isolated chromates on the surface of the catalyst. The study results of Kim et al.^{44,45} indicated that the isolated chromate species also predominate on silica support, in a distorted tetrahedral configuration. In addition, the nature of the silica support, mainly its surface hydroxyl chemistry, was found to affect the nature of the degree of oligomerization of chromium species, as well as the ability to stabilize Cr⁶⁺ at high temperature.⁴⁶ Therefore, the intense peak at lower temperature (ca. 374–397 °C) corresponds to reduction of soluble Cr⁶⁺ species, and the weak shoulder at higher temperature (ca. 510 °C) may result from reduction of the grafted Cr⁶⁺ species. From Figure 10, it can also be found

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that the corresponding temperatures for soluble Cr^{6+} move to high values with the increase of chromium loading. This behavior can be ascribed to the formation of more crystalline Cr_2O_3 phase, which would hinder the reduction of Cr^{6+} species.⁴² However, the grafted Cr^{6+} species has the same reduction temperature. This result can be explained as follows: the grafted Cr^{6+} species anchored to the catalyst surface has the similar interaction with the support, and as a result, they have the same reduction temperature. The 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalyst gives the biggest H_2 consumption. The H_2 consumption reduces gradually with higher Cr loading catalysts, suggesting that large numbers of Cr_2O_3 are formed, which replace Cr^{6+} species on the monolithic catalysts. The study results of Takehira *et al.*³⁰ indicated that the Cr^{6+} formed as an active species and reduced to Cr^{3+} as a less active species during the ODH of propane with CO_2 and this, as the main reason, led to the deactivation of Cr-MCM-41. In our study, the reduction of Cr^{6+} is also observed during the reaction and it also may play an important role for the deactivation of the Cr/SBA-15/ Al_2O_3 /FeCrAl monolithic catalyst.

Figure 10 also shows the H_2 -TPR profiles of 5.0% Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts, including before and after stability test and after regeneration with CO_2 . Before the reaction, the fresh catalyst shows two reduced peaks (ca. 385 and 510 °C), which are attributed to the reduction of Cr^{6+} species.⁴² After the stability test, the reduction peak became smaller, almost disappearing over the used monolithic catalysts (curves g and h of Figure 10), suggesting that most Cr^{6+} species were reduced to Cr^{3+} in the reaction. For the used catalyst in the CO_2 atmosphere, after regenerated by CO_2 at 750 °C for 10 h, Cr^{3+} species is re-oxidized to Cr^{6+} (Figure 10i) and the reduction peak appears again. Furthermore, the peak temperature shifts to a higher temperature (404 °C), and the H_2 consumption has some decrease compared to that of fresh catalyst. This indicates that the interaction among Cr species, SBA-15, and Al_2O_3 /FeCrAl support changed in the reaction and regeneration treatment. In addition, the C_2H_6 conversion recover from 42.3 to 54.7%. The study results of Takehira *et al.* revealed that Cr/ SiO_2 showed an insufficient recovery of the activity after treatment with O_2 for 5 h.³⁰ This result is similar to the present

study. Thus, the Cr^{6+} species is responsible for the initial high activity of the monolithic catalysts for the ODH of ethane with CO_2 . In the reaction, the Cr^{6+} species is reduced to Cr^{3+} by the dehydrogenated process. Simultaneously, the reduced Cr^{3+} species can be re-oxidized to Cr^{6+} species by CO_2 . Thus, the reduction–oxidation cycle between Cr^{6+} and Cr^{3+} species can be carried out in the ODH of ethane with the CO_2 reaction.

4. Conclusion

To summarize, the monolithic Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts were prepared. Their structures and properties were characterized, and their catalytic activity for the ODH of ethane with CO_2 was evaluated. It can be concluded from the present study and results that, in the Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts, the phase structures are Cr_2O_3 , α - Al_2O_3 , and γ - Al_2O_3 . After Cr species loading, the hexagonal mesoporous structure of SBA-15 is still present in the Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts and the framework of SBA-15 has some constriction with the increase of Cr content. The Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts show good catalytic activity and stability in ODH of ethane with CO_2 . After 1130 h of reaction, the ethane conversion and ethylene selectivity are 42.3 and 90.1%, respectively. An important role of CO_2 is removing carbon by the Boudouard reaction over the Cr/SBA-15/ Al_2O_3 /FeCrAl catalysts. In addition, in the ODH of ethane with the CO_2 reaction, the Cr^{6+} species as the active phase is reduced to Cr^{3+} , which has less active species by the dehydrogenated process. Simultaneously, the reduced Cr^{3+} species can be re-oxidized to Cr^{6+} species by CO_2 . Thus, the reduction–oxidation cycle between Cr^{6+} and Cr^{3+} species can be carried out and also plays an important role in the ODH of ethane with the CO_2 reaction over the monolithic catalysts.

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