Catalysis Letters 63 (1999) 59–64

Oxidative dehydrogenation of ethane by carbon dioxide over sulfate-modified Cr_2O_3/SiO_2 catalysts

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Received 21 May 1999; accepted 2 September 1999

The oxidative dehydrogenation of ethane into ethylene by carbon dioxide over unsupported Cr_2O_3, Cr_2O_3/SiO_2 and a series of Cr_2O_3/SiO_2 catalysts modified by sulfate was investigated. The results show that Cr_2O_3/SiO_2 is an effective catalyst for dehydrogenation of ethane and CO_2 in the feed promotes the catalytic activity. Sulfation of silica will influence the catalytic behavior of Cr_2O_3/SiO_2 in dehydrogenation of ethane with carbon dioxide depending on the amount of sulfate. Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 catalysts exhibit an excellent performance for this reaction, giving an ethylene yield of 55% at 67% ethane conversion at 650 °C. Characterizations indicate that addition of sulfate changes the bulk and surface properties of Cr_2O_3/SiO_2, promoting the reduction of Cr^{6+} to Cr^{3+} and favoring the catalytic conversion.

Keywords: ethane dehydrogenation, ethylene, CO_2, Cr_2O_3, sulfated silica

1. Introduction

The oxidative dehydrogenation of ethane by oxygen into ethylene has been proposed as an alternative to the process of thermal cracking of ethane. In the last decade, a great variety of catalysts have been developed for this reaction [1–3]. However, due to the exothermic characteristic of this reaction, it is necessary to remove heat and avoid overoxidation of ethylene to carbon oxides so as to give high selectivity towards ethylene. Therefore, it is required to develop more selective catalysts which can depress the deep oxidation or to explore weak oxidants replacing oxygen in this process.

Carbon dioxide as one of the major greenhouse gases has been recently considered as a source of carbon. Catalytic hydrogenation of carbon dioxide into several organic compounds has been intensively studied. Carbon dioxide can also act as a mild oxidant. Utilization of carbon dioxide in some partial oxidation reactions, such as CO_2 reforming of methane [4], oxidative coupling of methane [5], and oxidative dehydrogenation of ethane [6] and propane [7], has been reported. Wang et al. [8] investigated the effect of CO_2 on the selectivities in partial oxidation of methane and ethane over Li/MgO catalysts and reported that CO_2 either formed during reaction or added to the system increased the selectivity for the desired hydrocarbon products in the two reactions. CO_2 has a poisonous effect on the secondary reactions of alkyl radicals with the surface thus inhibiting deep oxidation. Nakagawa et al. [6] studied the dehydrogenation of ethane by carbon dioxide over several metal oxides and found that gallium oxide is an effective catalyst for this reaction, giving 18.6% ethylene yield with a selectivity of 94.5% at 650 °C. Takahara and Saito [7] investigated the effect of CO_2 on the hydrogenation of propane over supported Cr_2O_3 catalysts. They found that carbon dioxide exerted a promoting effect only on the SiO_2-supported Cr_2O_3 catalyst. Zhaorigetu et al. [9] also reported the promoting effect by carbon dioxide over rare earth vanadates in the oxidative dehydrogenation of propane.

Cr_2O_3-based catalysts have been proved active for the dehydrogenation of alkanes. Ashmawy [10] studied ethane dehydrogenation over Cr_2O_3/Al_2O_3 catalysts. Lugo and Lunsford [11] also investigated the dehydrogenation of ethane over Cr_2O_3/SiO_2. Recently, El-Idrissi et al. [12] investigated the effect of phosphorus introduction in Cr_2O_3/TiO_2 for the oxidative dehydrogenation of ethane with oxygen and found that addition of phosphorus improved the global conversion and ethylene selectivity. We have found that sulfation of zirconia enhanced the catalytic activities of ZrO_2 supported catalysts in the oxidative dehydrogenations of ethane [13] and propane [14]. We also studied several supported chromium catalysts in the oxidative dehydrogenation of ethane in the presence of CO_2 and found that Cr_2O_3/SiO_2 catalysts exhibited excellent performance for this reaction [15]. It is well known that catalytic properties of supported chromium catalysts are strongly influenced by the acidity/basicity of the oxide support. Modification of support will probably promote the catalytic conversion. In this work, we studied the effect of sulfation of silica on the activity of supported Cr_2O_3 catalysts in the oxidative dehydrogenation of ethane with carbon dioxide.

2. Experimental

A commercial silica gel obtained from Wako Chemicals was used as a support and raw material for the preparation of sulfated silica. Sulfated silica samples were prepared by wetness impregnation of ammonium sulfate solution, drying at 105 °C and then calcination at 700 °C for 3 h. Cr_2O_3-based catalysts were prepared by impregnating chromium nitrate (Wako Chemicals) on the silica and sulfated silica supports, drying under constant stirring and calcination at 700 °C for 3 h. The loading of Cr_2O_3 was kept at 5 wt%. A pure Cr_2O_3 sample obtained from Soekawa Chemicals was also used as a catalyst for a reference.

BET surface areas of the support and catalysts were determined by nitrogen adsorption at −196 °C on a Micromeritics volumetric equipment provided by Shimadzu. XRD patterns of catalysts were obtained on a Philips PW 1800 X-ray diffractometer at 40 kV and 40 mA. XPS measurements were carried out in a PHI 5500 ESCA system (Perkin–Elmer) with Mg Kα as radiation source. Temperature-programmed reduction (TPR) experiments were conducted in a fixed-bed reactor loaded with 0.5 g samples. The samples were reduced in 10% H_2/Ar flow at a rate of 30 ml/min from ambient temperature to 700 °C at a heating rate of 3 °C/min. Before TPR the samples were treated under Ar gas flow of 30 ml/min to 700 °C at the heating rate of 5 °C/min and then further treated at the same temperature for 30 min.

The selective oxidative dehydrogenation of ethane was performed at atmospheric pressure in a fixed-bed vertical-flow reactor constructed from a high-purity alumina tube (i.d. = 6 mm) packed with 1 g catalysts and 2 g quartz sand and mounted inside a tube furnace. The reactant stream consisting of 10% ethane, 50% carbon dioxide and 40% nitrogen (or $C_2H_6 : He : N_2 = 10 : 50 : 40$) was introduced into the reactor at the flow rate of 60 ml/min. The reaction temperature ranged between 500 and 650 °C. Samples were taken for analysis after 10 min flow at each temperature. The products were analyzed by two gas chromatographs (Shimadzu, GC-8A) equipped with a Porapak Q column using FID for hydrocarbons and a 5A molecular sieve column for CO, CO_2, CH_4, O_2, N_2, and H_2 using TCD. Water produced in the reaction was collected using a cold-trap.

3. Results

3.1. Dehydrogenation of ethane over Cr_2O_3/SiO_2 in the absence or in the presence of CO_2

The dehydrogenations of ethane in the absence and presence of carbon dioxide over Cr_2O_3/SiO_2 were firstly investigated under similar conditions. Figure 1 presents the results of catalytic performance as a function of temperature in the two processes. It is shown that Cr_2O_3/SiO_2 exhibits high ethane conversion and ethylene selectivity in the dehydrogenation of ethane and ethane conversion increases with increasing temperature. As the conversion increases, ethylene selectivity shows a decreasing trend. At 650 °C, 50% ethane conversion with 90% ethylene selectivity can be obtained. Addition of CO_2 in the feed enhances not only the ethane conversion but also the ethylene selectivity. In this reaction Cr_2O_3/SiO_2 exhibits 93% ethylene selectivity at 56% ethane conversion with 52% ethylene yield at 650 °C. In the two processes, however, it was found that there were carbon deposits formed on the used catalysts in the process of dehydrogenation of ethane without carbon dioxide. No carbon was deposited on catalysts when CO_2 was present in the flow. This suggests that CO_2 favors the dehydrogenation of ethane and inhibits carbon deposition.

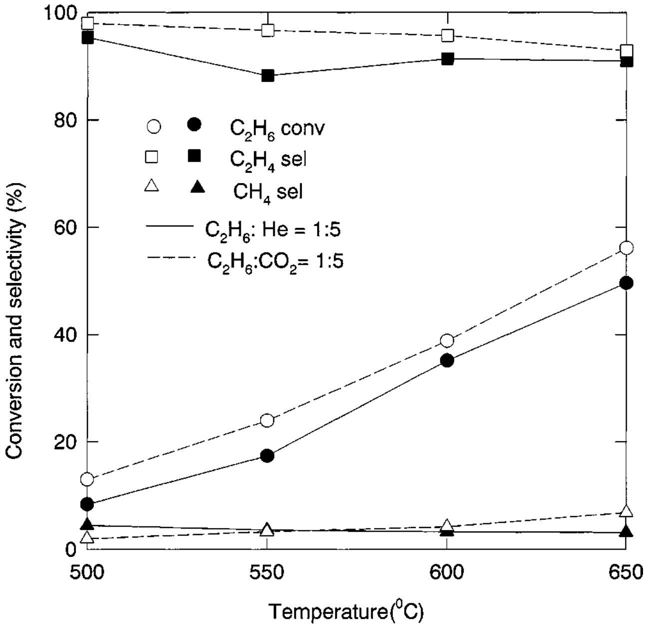

Figure 1. Catalytic performance of Cr_2O_3/SiO_2 catalysts as a function of temperature in dehydrogenation of ethane in absence or presence of carbon dioxide. Reaction conditions: 1 g catalyst, $C_2H_6 : He(CO_2) = 1 : 5$, flow rate = 60 ml/min.

3.2. Catalytic performance over various sulfate-modified supported Cr_2O_3/SiO_2 catalysts

Table 1 lists the catalytic conversion and product distributions in the oxidative dehydrogenation of ethane with carbon dioxide over silica, Cr_2O_3, unmodified Cr_2O_3/SiO_2, and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 catalysts at various temperatures. It is seen that catalytic conversion increases with increasing temperature for all catalysts. Silica gel shows little activity in CO_2 oxidative dehydrogenation of ethane below 600 °C. It exhibits only 2% ethane conversion at 650 °C, indicating that the homogeneous reaction and the support will not make significant contributions to the activity of the supported Cr_2O_3/SiO_2 catalysts in this heterogeneous reaction. The products are only ethylene, methane and hydrogen. No CO and water formed in the reaction. Cr_2O_3 is an active and selective catalyst in the oxidative dehydrogenation of ethane by CO_2, presenting ethane conversion as high as 22% with 87% ethylene selectivity at 650 °C. It is noted that CO_2 conversions are higher than ethane conversions at all temperatures, suggesting that Cr_2O_3 is very active for CO_2 activation. The Cr_2O_3/SiO_2 catalyst shows high activity and selectivity to ethylene. C_3H_8 and ethanol

Table 1
Catalytic activities of various supported Cr_2O_3 catalysts at 650 °C.

Catalyst	T	Conversion (%)		Selectivity (%)					C_2H_4 yield
	(°C)	C_2H_6	CO_2	C_2H_4	CH_4	C_3H_8	EtOH	CO/H_2	(%)
SiO_2	500	0.03	0.01	92.3	7.7	0	0	0	0.03
	550	0.09	0.02	94.5	5.5	0	0	0	0.08
	600	0.3	0.05	96.2	3.8	0	0	0	0.29
	650	2.2	0.8	97.2	2.8	0	0	0	2.1
Cr_2O_3	500	1.1	4.5	94.4	5.6	0	0	19.2	1.0
	550	6.2	9.5	97.7	2.3	0	0	9.9	6.0
	600	12.1	16.8	95.4	4.6	0.03	0	4.8	11.6
	650	22.5	29.4	87.0	12.9	0.06	0	3.2	19.6
Cr_2O_3/SiO_2	500	13.0	3.2	98.0	1.95	0.05	0	1.1	12.7
	550	23.9	5.9	96.7	3.3	0.07	0	1.2	23.1
	600	38.8	9.6	95.7	4.2	0.1	0	1.4	37.1
	650	56.1	14.6	92.9	6.8	0.2	0.08	1.8	52.1
Cr_2O_3/6 wt% SO_4^{2-}–SiO_2	500	16.8	7.5	95.8	4.1	0.06	0	1.9	16.1
	550	30.4	11.0	93.2	6.6	0.11	0.09	2.1	28.3
	600	48.6	15.8	88.7	11.0	0.17	0.13	2.6	43.1
	650	67.2	21.9	81.8	17.8	0.26	0.14	2.9	55.0

can be produced over Cr_2O_3/SiO_2 catalysts besides ethylene and methane. Although ethylene selectivity decreases as ethane conversion increases, ethylene selectivities are still over 92% at all temperatures. Ethane conversion can reach 56% and 52% ethylene yield can be attained at 650 °C. As seen from the table, ethane and CO_2 conversions as well as ethylene yield are all enhanced when Cr_2O_3/SiO_2 catalysts are modified by sulfation. However, methane selectivity is also increased, suggesting that sulfation favors the dissociation of ethane because of the increase in acidity. When ethane conversion increases, ethylene selectivity decreases. As compared with Cr_2O_3/SiO_2, Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 exhibits 67% ethane conversion and 55% ethylene yield, respectively, at 650 °C.

Figure 2 shows the effect of sulfate content in the Cr_2O_3/SO_4^{2-}–SiO_2 system on catalytic performance at 650 °C. It is seen that ethane and CO_2 conversions increase with increasing sulfate content and reach the highest levels at 6–10 wt% sulfate in Cr_2O_3/SO_4^{2-}–SiO_2 catalysts. However, ethylene selectivity decreases with the increasing ethane conversion. From the viewpoint of ethylene yield, 2–6 wt% sulfate will be the optimum at which catalysts can produce an ethylene yield around 55%.

The catalytic stabilities of the Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 catalysts at 650 °C are shown in figure 3. One can see that the two catalysts exhibit slight deactivations with similar variation patterns, however, the deactivation rates are all very low. With the decrease in ethane conversion, ethylene selectivity increases. After 6 h, ethane conversions over Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 decrease from 56 and 67% to 45 and 57%, respectively.

3.3. Catalyst characterization

BET surface areas of the support and supported Cr_2O_3 catalysts are listed in table 2. One can see that impregnation of Cr_2O_3 did not significantly reduce the surface area of the support SiO_2. Modification of Cr_2O_3/SiO_2 can affect its surface area depending on the sulfate content. Only at high sulfate loading, the surface area of Cr_2O_3/SiO_2 will be reduced but at low extent.

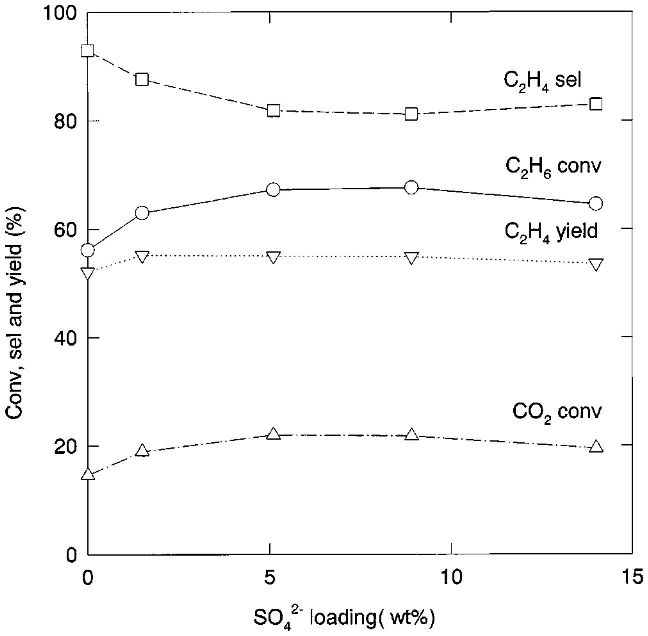

Figure 2. Effect of sulfate loading in Cr_2O_3/SiO_2 system on catalytic activity. Reaction conditions: 1 g catalyst, $C_2H_6:CO_2 = 1:5$, flow rate = 60 ml/min, $T = 650$ °C.

The XRD patterns of the SiO_2 support, and the Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 catalysts are shown in figure 4. SiO_2 gel is present as an amorphous phase. Cr_2O_3 reflectance peaks are appearing on the two Cr_2O_3-based catalysts. However, peak intensities of Cr_2O_3 are reduced and shifted on Cr_2O_3/6 wt% SO_4^{2-}–SiO_2, indicating a better dispersion and structure change occurring for Cr_2O_3 in SiO_2.

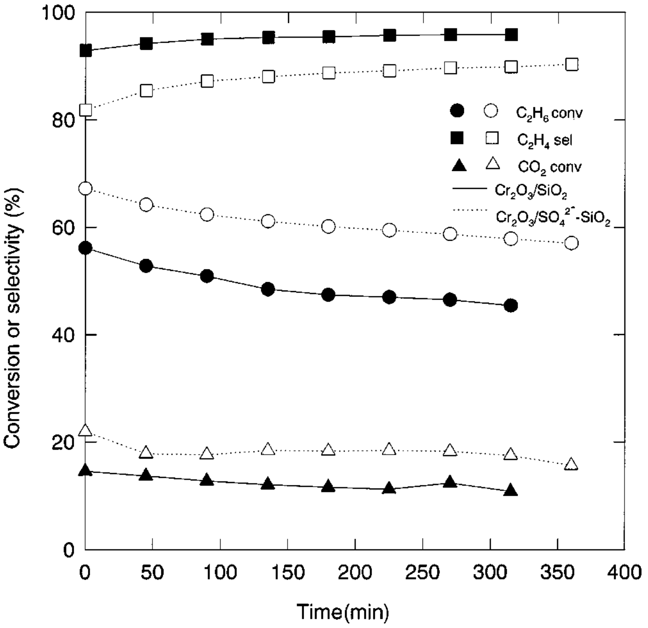

Figure 3. Stability of Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 catalysts at 650 °C. Reaction conditions: 1 g catalyst, $C_2H_6:CO_2 = 1:5$, flow rate = 60 ml/min.

Table 2
Surface areas of the support and various Cr_2O_3-based catalysts.

Catalyst	S_{BET} (m^2/g)
SiO_2	338
Cr_2O_3/SiO_2	334
Cr_2O_3/2 wt% SO_4^{2-}–SiO_2	333
Cr_2O_3/6 wt% SO_4^{2-}–SiO_2	337
Cr_2O_3/10 wt% SO_4^{2-}–SiO_2	314
Cr_2O_3/15 wt% SO_4^{2-}–SiO_2	303

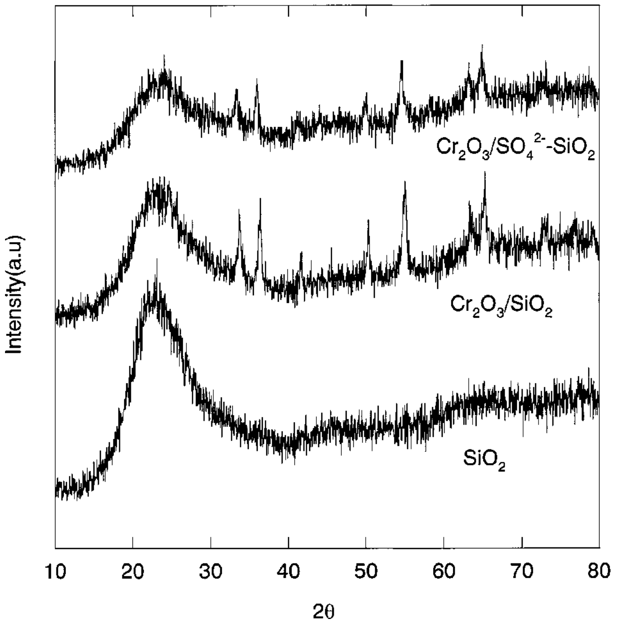

Figure 4. XRD patterns of the SiO_2 support and Cr_2O_3/SiO_2 catalysts.

Table 3
Surface concentration of chemical elements on Cr_2O_3-based catalysts.

Catalyst	Cr (%)	Cr^{3+} BE (eV)	Cr^{6+} BE (eV)	Cr^{6+}/Cr^{3+}
Cr_2O_3/SiO_2	3.59	576.8	579.3	0.54
Cr_2O_3/6 wt% SO_4^{2-}–SiO_2	3.16	576.2	578.2	0.61

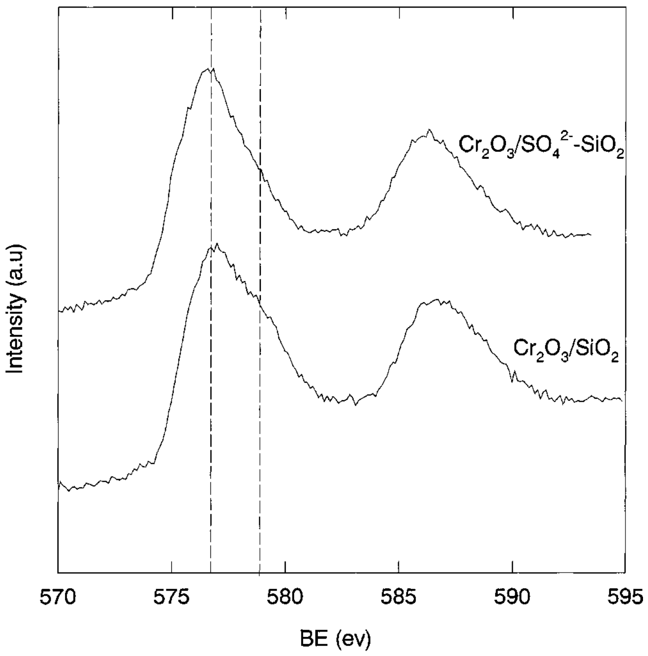

Figure 5. XPS spectra of Cr 2p over Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 catalysts.

The surface concentrations of Cr species determined by XPS measurements are given in table 3 and Cr 2p spectra are shown in figure 5. It is seen from the table that the surface concentrations of Cr on Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 are similar. However, their XPS spectra appear somewhat different. The peaks in Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 spectrum show a shift to lower binding energy. Two Cr species can be found by curve fitting and they are assigned to Cr^{3+} and Cr^{6+}, whose binding energies (BE) are given in table 3. The ratios of the two Cr species on the two catalysts also show different values. Sulfation of silica increases the ratio of high valence Cr species on the catalyst surface.

The TPR profiles of SiO_2, Cr_2O_3, Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 are presented in figure 6. No reduction peaks occur for the silica support while a weak reduction peak appears between 200 and 300 °C in the TPR profile of pure Cr_2O_3. There is one peak at 460 °C in the TPR profile of Cr_2O_3/SiO_2. Two peaks appear at 440 and 660 °C, respectively, for the sulfated-silica-supported Cr_2O_3. It is noted that a shoulder peak at 400 °C is also observed on Cr_2O_3/6 wt% SO_4^{2-}–SiO_2. This suggests that sulfation of silica decreased the interaction between support and metal oxide, resulting in the higher reducibility of Cr_2O_3. The comparison between the two TPR profiles also

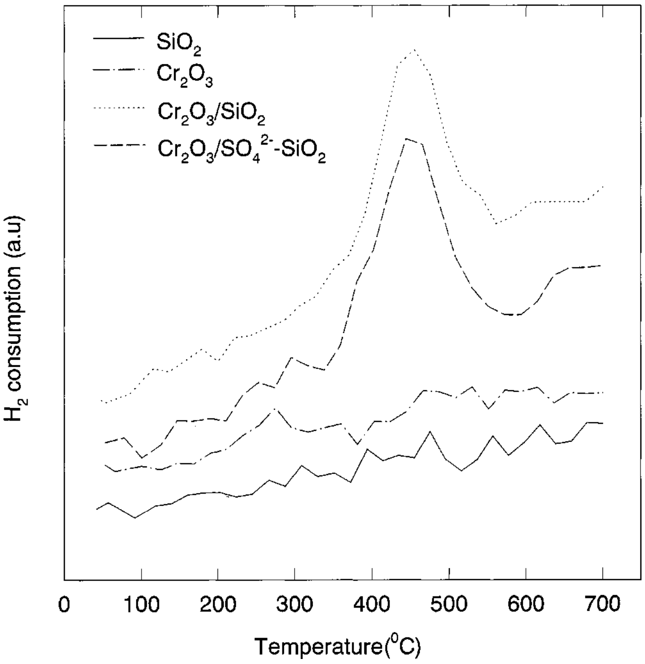

Figure 6. TPR profiles over the support SiO_2, Cr_2O_3, and Cr_2O_3/SiO_2 catalysts.

shows that there is a slight increase in the peak area on Cr_2O_3/6 wt% SO_4^{2-}–SiO_2, indicating that there is a higher amount of reducible oxygen species in this sample.

4. Discussion

Both supported chromium and α-Cr_2O_3 are known to be active catalysts for the dehydrogenation of alkanes. However, there is a debate on the active sites. In the opinion of some authors the dehydrogenation active species is Cr^{3+} while others suggested both Cr^{2+} and Cr^{3+} or solely Cr^{2+} as active sites. Ashmawy [10] studied the dehydrogenation of ethane over Cr_2O_3/Al_2O_3 catalysts and proposed that both Cr^{2+} and Cr^{3+} are active for the reaction and Cr^{2+} is the more active ion. Lugo and Lunsford [11] investigated the oxidative dehydrogenation of ethane over α-Cr_2O_3, Cr_2O_3/Al_2O_3, Cr_2O_3/SiO_2 and Cr_2O_3/Y-zeolite and reported that Cr^{2+} ions acted as active sites. Konig and Tétényi [16] have explored the dehydrogenation of ethane on α-Cr_2O_3, and have identified coordinatively unsaturated Cr^{3+} ions as the active sites. El-Idrissi et al. [12] studied the oxidative dehydrogenation of ethane over Cr_2O_3/TiO_2 and found the catalytic activity could be attributed to the isolated Cr^{3+} species on the support. Loukah et al. also reported that the activity on layered zirconium phosphate exchanged with Cr^{3+} ions catalysts was to be attributed to Cr^{3+} ions in specific environments or/and to small Cr^{3+} clusters [17,18]. In this investigation it is found that two surface Cr species, Cr^{3+} and Cr^{6+}, exist on the Cr_2O_3-based catalysts. TPR experiments also show that reduction of Cr_2O_3-based catalysts will occur at lower temperatures, which can be the process of $Cr^{6+} \rightarrow Cr^{3+}$. Similar process can occur when ethane is introduced in the reactor. Thus it is proposed that Cr^{3+} ions will be the active sites for the dehydrogenation of ethane.

In this investigation it has been found that addition of carbon dioxide in the feed enhanced the catalytic activity of ethane dehydrogenation and a large amount of water and CO were formed. This suggests that CO_2 molecules could be dissociated into CO and surface oxygen species, which could abstract hydrogen from ethane and prevent the deposition of coke, and that the redox property of chromium species on catalysts will play an important role for the oxidative dehydrogenation. XPS results revealed the presence of Cr^{6+}/Cr^{3+} couples on the fresh Cr_2O_3-based catalysts. Measurements also show the existence of Cr^{6+} and Cr^{3+} species on catalysts after reaction. It is logical to assume that the reaction pathways involve the reduction of Cr^{6+} groups by ethane at the initial stage and H_2 produced thereafter and reoxidation of Cr^{3+} ions by surface oxygen species produced by CO_2 or CO_2 itself. Therefore, the reaction paths occurring in the dehydrogenation of ethane by carbon dioxide can be proceeded as follows:

$$C_2H_6 \rightarrow C_2H_4 + H_2 \tag{1}$$

$$H_2 + CO_2 \rightarrow CO + H_2O \tag{2}$$

$$3C_2H_6 + 2CrO_3 \rightarrow 3C_2H_4 + Cr_2O_3 + 3H_2O \tag{3}$$

$$Cr_2O_3 + 3CO_2 \rightarrow 3CO + 2CrO_3 \tag{4}$$

The different activity of Cr_2O_3-based catalysts can be attributed to the varying chromium structure and redox properties of the catalysts prepared. It has been reported that bulk Cr_2O_3 showed lower activity than those of supported Cr_2O_3 catalysts because crystalline Cr^{3+} species in Cr_2O_3 were less active than the amorphous Cr^{3+} in the supported Cr_2O_3 catalysts in the dehydrogenation of alkanes [11,19,20]. TPR has shown that a weak reduction can occur on unsupported Cr_2O_3. These probably account for the lower activity of unsupported Cr_2O_3. XPS results demonstrate that there is no significant difference of chromium content on Cr_2O_3/SiO_2 and Cr_2O_3/6 wt% SO_4^{2-}–SiO_2. However, $Cr^{6+}/Cr^{3+}$is higher on sulfated-silica-supported catalyst. This is believed to increase the redox potential and has been reflected in the TPR profile. Cr_2O_3/6 wt% SO_4^{2-}–SiO_2 exhibits three larger reduction peaks between 300 and 700 °C, indicating the high reducibility of the catalyst. In addition, XRD shows a higher Cr dispersion and a shift in diffraction peak suggesting the crystalline defect which can induce dehydrogenation reaction.

5. Conclusions

In this investigation it is found that Cr_2O_3/SiO_2 catalysts are effective and selective for ethane dehydrogenation into ethylene in the absence and presence of carbon dioxide. Addition of CO_2 promotes the ethylene yield and prevents carbon deposition. Addition of sulfate to Cr_2O_3/SiO_2 catalysts changes the surface properties of Cr_2O_3/SiO_2 and affects the redox property of Cr oxides, resulting in high activity and stability of the sulfated-silica-supported Cr_2O_3 catalysts. Cr^{3+} species and Cr^{6+}/Cr^{3+} couples are believed to be the active sites for the dehydrogenation reaction.

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