Effect of promoters on catalytic performance of Cr/SiO_2 catalysts in oxidative dehydrogenation of ethane with carbon dioxide

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Several acidic and basic oxide promoted Cr/SiO_2 catalysts were prepared and investigated in oxidative dehydrogenation of ethane in the presence of carbon dioxide. The effects of SO_4^{2-}, WO_3 and alkali metal oxides (Li_2O, Na_2O, and K_2O) on the catalytic activity were studied. It is found that sulfation of silica produces a positive effect on ethane conversion and ethylene yield while tungstation and addition of strong basic promoters (alkali metal oxides) suppress the catalytic activity. Characterization indicates that the varying activity of the promoted catalysts can be attributed to the difference in acid/base property and redox potential.

KEY WORDS: oxidative dehydrogenation; Cr_2O_3/SiO_2; sulfation; tungstation; alkali metals

1. Introduction

Carbon dioxide is one of the major greenhouse gases. Emission control and efficient utilisation of carbon dioxide have attracted an intensive attention in academia and industry. Various reactions have been tried to transform carbon dioxide into valuable products by catalytic methods. Most of them are concentrated on the utilisation of carbon dioxide as a source of carbon in catalytic reduction processes. However, carbon dioxide can also play a role as an oxygen source or oxidant and can be employed for some oxidative conversions of hydrocarbons [1–3].

Ethylene is an important raw material in petrochemical industry. Up to now, ethylene is generally produced by the conventional steam cracking process. Oxidative dehydrogenation of ethane by oxygen

$$C_2H_6 + \tfrac{1}{2}O_2 \rightarrow C_2H_4 + H_2O \qquad (1)$$

has been proposed as an alternative to the above process because it has advantage of no thermodynamic limitations and lower temperature reaction. However, due to the strong oxidation ability of O_2, deep oxidation of ethylene to carbon oxides will cause the reduction in selectivity towards ethylene. Therefore, it is expected that using a weak oxidant, CO_2, replacing oxygen in this reaction will suppress the deep oxidation and enhance the ethylene selectivity:

$$C_2H_6 + CO_2 \rightarrow C_2H_4 + CO + H_2O \qquad (2)$$

Several researchers have investigated the dehydrogenation of lower hydrocarbons in the presence of carbon dioxide [4–6]. We have found that chromium oxide supported on silica and zirconia catalysts exhibit highly effective activity for the oxidative dehydrogenation of ethane by carbon dioxide [7] and sulfate will promote the catalytic activity [8]. In this paper, we report a further investigation of the effect of the modification of silica by some acidic or basic oxides on their catalytic behavior in carbon dioxide dehydrogenation of ethane.

2. Experimental

A commercial silica gel, obtained from Wako Chemicals, was used as the primary support. The sulfated silica and tungstated silica samples were prepared by wet impregnation on the amorphous silica with ammonium sulfate and ammonium tungstate hydrate salts at an appropriate concentration to maintain the loading of sulfate and WO_3 at 6 wt%, followed by drying at 105 °C and calcination at 700 °C for 3 h. Cr_2O_3-based catalysts were then prepared by the similar method using chromium nitrate (Wako Chemicals). Alkali metal oxide promoted catalysts were prepared by simultaneously mixing alkali metal nitrate salts (Wako Chemicals) at various concentrations and chromium nitrate with the sulfated silica, evaporation under constant stirring and then calcination at 700 °C for 3 h. The contents of Cr_2O_3 and alkali metal oxide were kept at 5 and 0.2 wt%, respectively.

Specific surface area (S_{BET}) of the support and catalysts was measured by nitrogen adsorption at $-196\,°C$ on a Micromeritics volumetric equipment provided by Shimadzu. XRD patterns of the catalysts were determined on a Philips PW 1800 X-ray diffractometer at 40 kV and 40 mA. The radiation source was Cu Kα with a Ni filter. XPS measurements were carried out on a PHI 5500 ESCA system (Perkin–Elmer) with Mg Kα as radiation source. Data were acquired at 14 kV, 30 mA under the vacuum of 9.4×10^{-10} Torr. 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

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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 a heating rate of 5 °C/min and then further heat-treated under the same temperature for 30 min. The hydrogen concentrations were determined by a GC-8A equipped with TCD.

The selective oxidative dehydrogenation of ethane with CO_2 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 was introduced into the reactor at a flow rate of 60 ml/min. The reaction temperature ranged between 500 and 650 °C. 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.

3. Results and discussion

Table 1 gives the results of catalytic activity and selectivity of the support, Cr/SiO_2 and modified Cr/SiO_2 catalysts at the temperatures of 500–650 °C. One can see that, for all catalysts, ethane conversion increases as temperature increases and ethylene selectivity decreases with the increasing ethane conversion. The SiO_2 support shows little activity for this reaction. Cr/SiO_2 is an effective and selective catalyst, giving ethane conversion of 56 and 93% ethylene selectivity at 650 °C. Addition of WO_3 in Cr/SiO_2 slightly decreases the ethane conversion and ethylene selectivity, resulting in a reduction of ethylene yield. In contrast, sulfation of Cr/SiO_2 significantly increases the ethane conversion but decreases the ethylene selectivity. However, the ethylene yield still gets an enhancment compared with the values of the unpromoted Cr/SiO_2 catalysts. Ethane conversion and ethylene yield can be achieved at 67 and 55% at 650 °C, respectively.

It is generally believed that the acid–base property is an important factor influencing the catalytic activity. Acid–base pairs are important for the activation of hydrocarbons. In consideration of the balance of acidity/basicity of catalysts, some basic promoters were added in the $Cr/SO_4–SiO_2$ catalyst. Table 2 presents the catalytic activity of the alkali metal oxide promoted $Cr/SO_4–SiO_2$ catalysts at various temperatures. It is seen that addition of alkali metal oxides generally decreases the catalytic activity and the reduction extent depends on the nature of the alkali metal. $CrLi/SO_4–SiO_2$ exhibits the greatest reductions in ethane conversion and ethylene yield. The ethane conversion and ethylene yield at 650 °C are only 16.7 and 16.3%, similar to the values of $Cr/SO_4–SiO_2$ at 500 °C. $CrNa/SO_4–SiO_2$ and $CrK/SO_4–SiO_2$ show lower catalytic activities than $Cr/SO_4–SiO_2$. The activity follows an order of $Cr/SO_4–SiO_2 > CrK/SO_4–SiO_2 > CrNa/SO_4–SiO_2 > CrLi/SO_4–SiO_2$.

As a follow-on of the results in table 2, the effect of K_2O loading on the catalytic activity of $CrK/SO_4–SiO_2$ was investigated and their activities at 650 °C are shown in figure 1. As seen, the catalytic activity varies with K_2O content. Trace amount of K_2O (0.1 wt%) can improve the ethane conversion and slightly increase ethylene selectivity. Higher amount of K_2O loading on $CrK/SO_4–SiO_2$ will result in a significant reduction in ethane conversion but an enhancement in ethylene selectivity. However, ethylene yield shows a greater reduction due to the low ethane conversion. CO_2 conversion always shows a decreasing trend, which is probably due to the strong adsorption of CO_2 on the basic sites.

The catalytic stability of Cr/SiO_2, $Cr/SO_4–SiO_2$, and $CrK/SO_4–SiO_2$ at 650 °C was further investigated and the results are presented in figure 2. Three catalysts exhibit somewhat deactivation but at slow rates. Ethylene selectivity generally shows an increasing trend with the decreasing ethane conversion. After 6 h, ethane conversions over

Table 1
Catalytic activity and product selectivity over various chromium oxide based catalysts at 500–650 °C.

Catalyst	S_{BET} (m^2/g)	Temp. (°C)	Conv. C_2H_6 (%)	Selectivity (%)				Yield C_2H_4 (%)
				C_2H_4	CH_4	C_3H_8	EtOH	
SiO_2	338	500	0.03	92.3	7.7	0	0	0.03
		550	0.09	94.5	5.5	0	0	0.08
		600	0.3	96.2	3.8	0	0	0.29
		650	2.2	97.2	2.8	0	0	2.1
Cr/SiO_2	334	500	13.0	98.0	1.9	0.05	0	12.7
		550	23.9	96.7	3.3	0.07	0	23.1
		600	38.8	95.7	4.2	0.11	0	37.1
		650	56.1	92.9	6.8	0.18	0.08	52.1
$Cr/WO_3–SiO_2$	310	500	10.8	97.9	2.0	0.05	0	10.6
		550	20.4	96.7	3.2	0.08	0	19.7
		600	35.6	94.6	5.2	0.13	0.06	33.7
		650	57.5	89.9	9.6	0.28	0.12	51.7
$Cr/SO_4–SiO_2$	337	500	16.8	95.8	4.1	0.06	0	16.1
		550	30.4	93.2	6.6	0.11	0.09	28.3
		600	48.6	88.7	11.0	0.17	0.13	43.1
		650	67.2	81.8	17.8	0.26	0.14	55.0

Table 2
Catalytic activity and product selectivity over alkali metal oxide promoted Cr-based catalysts at 500–650 °C.

Catalyst	S_{BET} (m^2/g)	Temp. (°C)	Conv. C_2H_6 (%)	Selectivity (%)				Yield C_2H_4 (%)
				C_2H_4	CH_4	C_3H_8	EtOH	
$Cr/SO_4–SiO_2$	337	500	16.8	95.8	4.1	0.06	0	16.1
		550	30.4	93.2	6.6	0.11	0.09	28.3
		600	48.6	88.7	11.0	0.17	0.13	43.1
		650	67.2	81.8	17.8	0.26	0.14	55.0
$CrLi/SO_4–SiO_2$	181	500	6.1	89.5	10.4	0.045	0	5.5
		550	10.8	97.2	2.8	0.025	0	10.5
		600	11.1	98.3	1.7	0.036	0	10.9
		650	16.7	98.0	1.9	0.10	0	16.3
$CrNa/SO_4–SiO_2$	301	500	12.0	95.7	4.3	0.032	0	11.5
		550	23.6	95.7	4.3	0.046	0	22.6
		600	37.4	94.5	5.5	0.068	0	35.3
		650	51.0	92.3	7.5	0.12	0.026	47.1
$CrK/SO_4–SiO_2$	306	500	14.6	95.8	4.2	0.038	0	14.0
		550	28.4	94.9	5.0	0.058	0	27.0
		600	44.4	92.5	7.4	0.091	0	41.0
		650	59.9	89.5	10.3	0.15	0.044	53.6

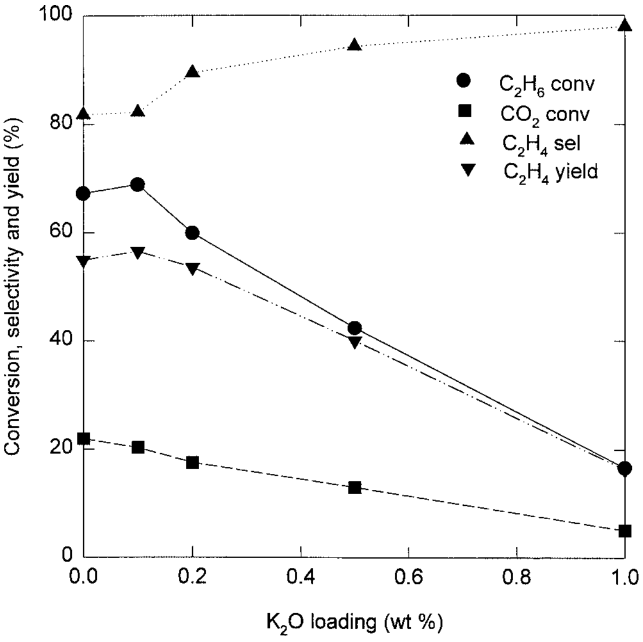

Figure 1. Effect of K_2O loading on activity of $CrK/SO_4–SiO_2$ catalysts.

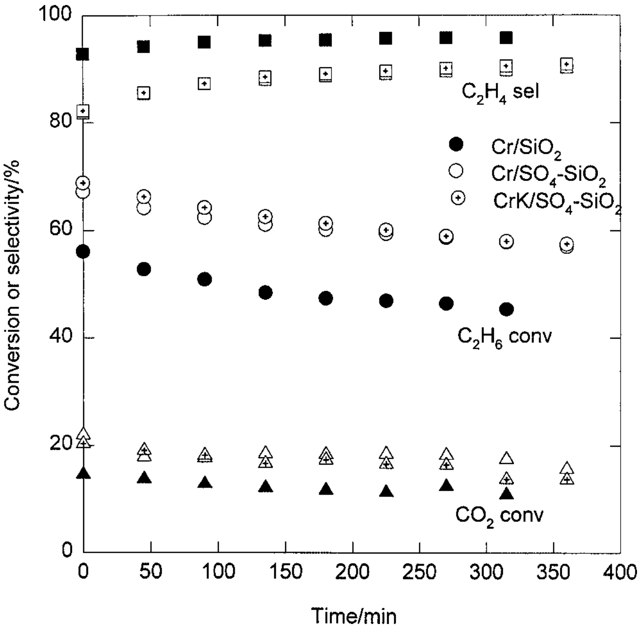

Figure 2. Catalytic performance of Cr/SiO_2, $Cr/SO_4–SiO_2$, and $CrK/SO_4–SiO_2$ catalysts as a function of time at 650 °C.

Cr/SiO_2, $Cr/SO_4–SiO_2$, and $CrK/SO_4–SiO_2$ decrease from 56, 67, and 69 to 45, 57, and 58%, respectively.

Figure 3 shows the XRD patterns of unpromoted Cr/SiO_2 and the various promoted Cr/SiO_2 catalysts. It can be seen that Cr/SiO_2, $Cr/SO_4–SiO_2$, and $CrK/SO_4–SiO_2$ display similar XRD patterns though different intensities of Cr_2O_3 diffraction peaks. Cr_2O_3 diffraction peaks on Cr/SiO_2 are stronger than those of $Cr/SO_4–SiO_2$ and $CrK/SO_4–SiO_2$, suggesting that the Cr_2O_3 dispersion is better on the surface of the latter two catalysts. For $Cr/WO_3–SiO_2$, the XRD pattern shows the coexistence of Cr_2O_3 and some SiO_2 quartz crystallites and more stronger Cr_2O_3 peaks.

Figure 4 shows the Cr 2p XPS spectra of the various Cr-based catalysts. One can see that two peaks occur for Cr 2p spectra over all catalysts: one appears around 576 eV and the other at 579 eV, which can be assigned to Cr^{3+} and Cr^{6+}, respectively. However, the binding energies for Cr^{3+} and Cr^{6+} differ between Cr/SiO_2 and the promoted Cr/SiO_2 catalysts, showing values ranging from 576.0 and 578.8 eV to 577.0 and 579.5 eV. For $Cr/SO_4–SiO_2$ and $CrK/SO_4–SiO_2$, the binding energies are more shifted to the lower values, suggesting the synergistic effect of Cr^{2+} and Cr^{3+}.

TPR profiles of Cr/SiO_2, $Cr/WO_3–SiO_2$, $Cr/SO_4–SiO_2$ and $CrK/SO_4–SiO_2$ are presented in figure 5. There is one peak appearing at 350–550 °C in the TPR profiles of Cr/SiO_2 and $Cr/WO_3–SiO_2$ while two reduction peaks centered at 500 and 630 °C, respectively, in the TPR profiles of $Cr/SO_4–SiO_2$ and $CrK/SO_4–SiO_2$. The intensity of the first reduction

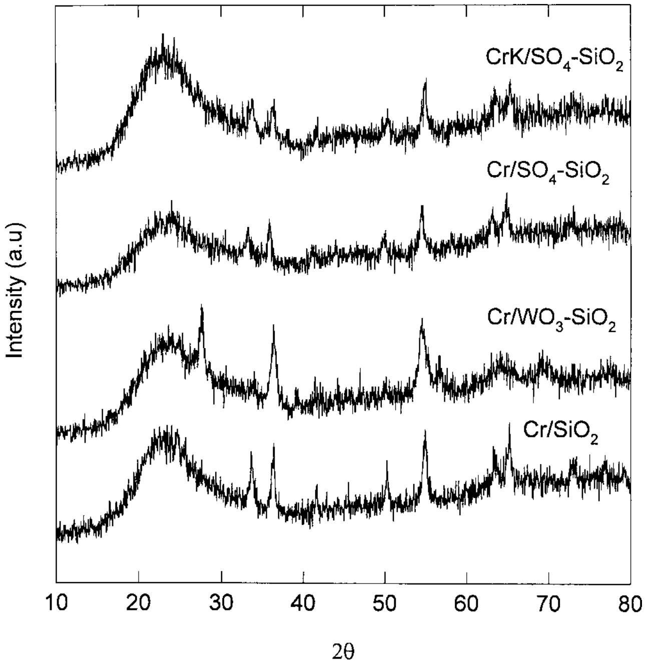

Figure 3. XRD patterns of various Cr-based catalysts.

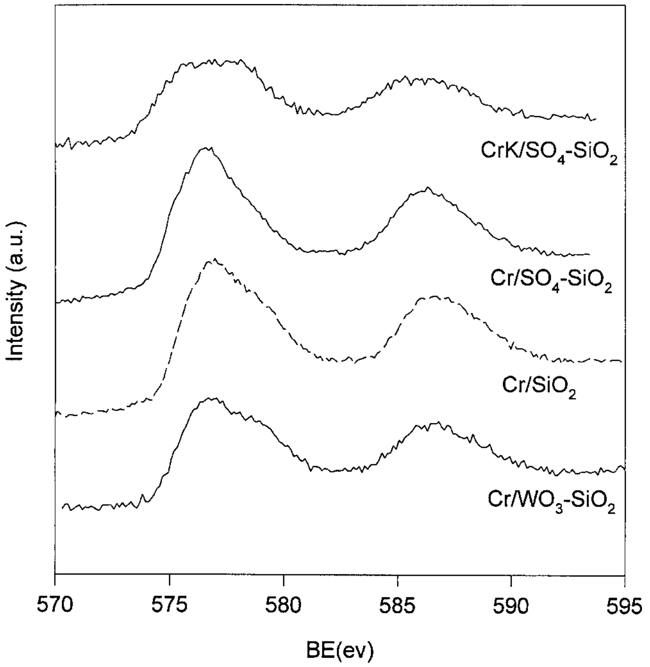

Figure 4. Cr 2p XPS spectra of various Cr-based catalysts.

peak of CrK/SO_4–SiO_2 is weaker than the corresponding one appearing on the other catalysts.

It is believed that the dehydrogenation of ethane by CO_2 is a combination of two consecutive coupling reactions, the coupling reaction of C_2H_6 dehydrogenation and CO_2 hydrogenation. The catalytic activity of dehydrogenation of ethane with carbon dioxide depends on catalyst surface and bulk properties. For Cr-based catalyst, dehydrogenation of hydrocarbons is greatly influenced by the Cr species and redox property [9]. XRD patterns show a better surface dispersion of Cr_2O_3 on Cr/SO_4–SiO_2. TPR profiles also show an improved redox potential on Cr/SO_4–SiO_2, which leads to a higher activity of Cr/SO_4–SiO_2 than Cr/SiO_2. The lower catalytic activity of Cr/WO_3–SiO_2 is probably due to the phase transformation and reduction of surface area as well as the low redox potential.

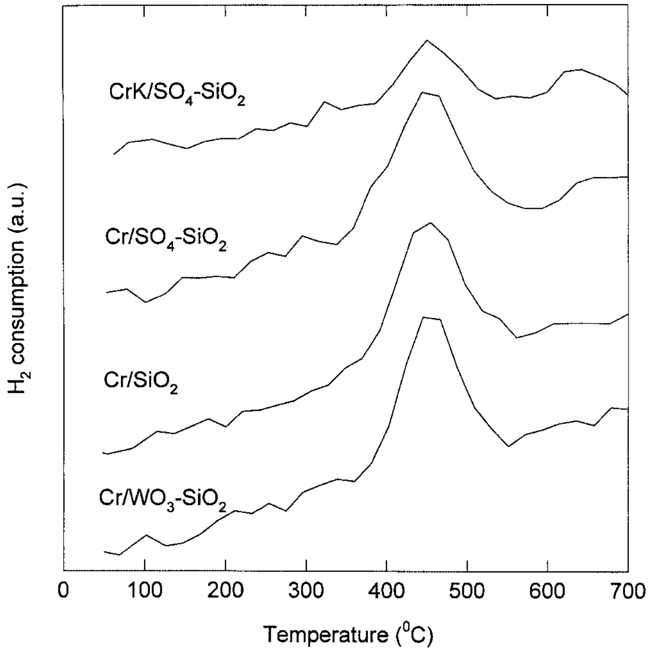

Figure 5. TPR profiles of various Cr-based catalysts.

For the alkali metal oxide promoted catalysts, the variation of BET surface area indicates that addition of alkali metal oxide results in the varying extent of decrease in S_{BET}. CrLi/SO_4–SiO_2 has the lowest surface area due to the occurrence of phase transformation. XRD measurements show that some quartz formed on CrLi/SO_4–SiO_2 except the Cr_2O_3 phase. The other two alkali metal oxide promoted Cr/SO_4–SiO_2 catalysts show a small reduction in S_{BET} and no significant phase transformation. In addition, Li_2O on the surface of catalyst can react with CO_2 and form Li_2CO_3 particles, which are difficult to be decomposed and could cover the active sites for ethane conversion. TPR measurements also show that alkali metal oxide promoted Cr/SO_4–SiO_2 catalysts have different redox potentials. CrLi/SO_4–SiO_2 displays no significant TPR peaks while CrNa/SO_4–SiO_2 shows a smaller reduction peak. CrK/SO_4–SiO_2 shows two reduction peaks as the behavior of Cr/SO_4–SiO_2. Those results indicate that addition of alkali metal oxide reduces the redox potential, which results in the lower catalytic activity. The order of redox potential displays the same order as the catalytic activity, e.g., Cr/SO_4–SiO_2 > CrK/SO_4–SiO_2 > CrNa/SO_4–SiO_2 > CrLi/SO_4–SiO_2.

4. Conclusion

The acidic and basic promoters will affect the catalytic activity of Cr/SiO_2 catalysts in the dehydrogenation of ethane with carbon dioxide. Sulfate will increase the redox potential while tungsten oxide decreases the surface area and redox potential, resulting in the lower activity. Addition of alkali metal oxide can also influence the catalyst surface properties and generally results in a decrease in catalytic activity. The effect depends on the nature of the alkali metal and its loading. For alkali metal oxides, the reduction shows an order of Li $>$ Na $>$ K.

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