# Dehydrogenation of Propane to Propylene over $Ga_2O_3$ Supported on Mesoporous HZSM-5 in the Presence of $CO_2^{\dagger}$

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Dehydrogenation of propane to propylene over mesoporous HZSM-5 supported  $Ga_2O_3$  catalysts in the presence of  $CO_2$  has been investigated, and compared with that of conventional HZSM-5 supported one. The initial activity of the catalysts descends while the stability and selectivity to propylene improve with increasing the Si/Al ratios of the support. The optimal Si/Al ratio is 240 for the propylene yield reaching 21.7% after reaction for 50 h. The introduction of the mesopores improves the activity as well as the stability of the catalyst, due to the better transport of the reactant and product molecules caused by its hierarchical structure. The selectivity for bulky products such as aromatics is also increased. The promoting effect of  $CO_2$  on the dehydrogenation reaction is observed.

Keywords dehydrogenation, gallium, supported catalysis, mesoporous HZSM-5

## Introduction

Propylene is an important raw material for producing polypropylene, acrolein, acrylic acid and other useful chemical products. The catalytic dehydrogenation of propane to propylene has drawn intense attention due to the growing demand for propylene. The present industrial process using Cr<sub>2</sub>O<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub> or Pt/Al<sub>2</sub>O<sub>3</sub> as catalysts is not optimal because of the quick deactivation of the catalysts during the reaction.<sup>1,2</sup> The oxidative dehydrogenation of propane by oxygen has been proposed as an alternative process. However, the over-oxidation of propane to carbon dioxide can not be avoided during the reaction, leading to low selectivity to propylene.<sup>3,4</sup> Carbon dioxide is a mild oxidant for many oxidation reactions. Previous researches show that carbon dioxide can also promote dehydrogenation of propane to propylene by the reversed water-gas shift reaction over some supported  $Cr_2O_3$ , ZnO and  $Ga_2O_3$  catalysts.<sup>5-9</sup> Since carbon dioxide is one of the major greenhouse gases, the utilization of carbon dioxide is attractive not only economically but also ecologically.

It is well known that Ga-loaded ZSM-5 is a good catalyst for aromatization of ethane and propane. The process is regarded as a bifunctional mechanism. Gallium oxide is responsible for catalyzing the dehydrogenation step while Bronsted acid sites for the oligomerization step.<sup>10-15</sup> Our recent work shows that high Si/Al ratio HZSM-5 supported Ga<sub>2</sub>O<sub>3</sub> is highly active and stable in dehydrogenation of propane to propylene in the

presence of CO<sub>2</sub>.<sup>16-19</sup> The propylene yield can stabilize at about 22% in 100 h without obvious deactivation. The superb stability can be explained by the decrease in the amount of acid sites with medium to strong strength, which can suppress the side reactions such as oligomerization, cyclization, cracking and aromatization.<sup>17</sup> Further study shows that the stability can also be enhanced by the introduction of mesopores through steaming, due to the promotion of desorption and diffusion of the propylene.<sup>18</sup>

Mesoporous ZSM-5 is a kind of zeolite containing both wormhole-like mesopores as well as micropores of MFI structure. It was synthesized by adding an amphiphilic organosilane as surfactant during the formation of MFI units.<sup>20</sup> This novel zeolite has been proved to exhibit better activity and higher resistance to deactivation as compared with conventional ZSM-5 in some reactions due to its hierarchical structure, which improves the mass transfer process during the reactions.<sup>20-28</sup> This advantage may also play a part in dehydrogenation of propane.

In this work,  $Ga_2O_3$  supported on mesoporous HZSM-5 with different Si/Al ratios were prepared. Their catalytic performance in dehydrogenation of propane to propylene in the presence of  $CO_2$  was investigated and compared with that of conventional ZSM-5 supported ones. The effects of Si/Al ratio,  $Ga_2O_3$  content, the introduction of mesopore and  $CO_2$  were also studied.



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## Experimental

#### **Catalyst preparation**

Mesoporous ZSM-5 with different Si/Al ratios were prepared following the procedures in the literature.<sup>20</sup> In a typical procedure, 0.0209 g sodium aluminate, 1.1 g tetrapropylammonium bromide (TPABr), and 0.8 g NaOH were dissolved in 135 g H<sub>2</sub>O. Then a mixture of 8.57 g tetraethylorthosilicate (TEOS) and 1.19 g [3-(trimethoxysilyl)propyl]octcyldimethylammonium chloride (TPOAC) was slowly dripped into this solution. After stirring at room temperature for 2 h, the mixture gel was transferred into a stainless steel autoclave lined with Teflon and crystallized at 170  $^{\circ}$ C for 2 d. The products were filtered and washed, then dried at 100 °C, finally calcinated at 550 °C for 6 h in air. These mesoporous ZSM-5 were exchanged with 1 mol•L<sup>-1</sup> NH<sub>4</sub>NO<sub>3</sub> solution for three times and finally calcinated in air at 600 °C for 3 h into the H-form. The attained mesoporous HZSM-5 were impregnated by Ga(NO<sub>3</sub>)<sub>2</sub> solution using an incipient wetness method. The impregnated samples were dried at 100  $\,^\circ\!C$  and calcined at 600  $\,^\circ\!C$  for 6 h in air. The obtained catalysts were denoted as Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(x), in which x represents the bulk molar ratio of Si/Al. The content of Ga<sub>2</sub>O<sub>3</sub> in all the catalysts was 5 wt%, unless otherwise noted.

Conventional HZSM-5 supported  $Ga_2O_3$  catalysts were prepared according to the procedures in another literature<sup>18</sup> and denoted as  $Ga_2O_3/HZSM-5(x)$ .

#### **Catalyst characterization**

X-ray diffraction (XRD) of the catalysts was carried out on a Bruker D8-Advanced X-ray diffractometer using nickel-filtered Cu-K $\alpha$  radiation at 40 kV and 40 mA. The bulk Si/Al ratio of the mesoporous ZSM-5 was measured by X-ray fluorescence spectrum (XRF) on Bruker-AXS S4 Explorer.

The  $N_2$  adsorption/desorption isotherms were measured on a Micromeritics ASAP2000 instrument at liquid  $N_2$  temperature. Specific surface areas of the samples were calculated from the adsorption isotherms by BET method, and pore size distributions from the adsorption isotherms by BJH method.

 $^{27}$ Al MAS NMR measurements were performed on a Bruker DSX-300 spectrometer at a resonance frequency of 78.2 MHz. Spectra were recorded at a spinning rate of 12 kHz, a pulse length of 0.31  $\mu$ s and a delay time of 0.5 s. All the samples were hydrated in a desiccator over a saturated NaCl solution for 3 d prior to the measurements.

The surface acidity was measured by temperature-programmed desorption of NH<sub>3</sub> (NH<sub>3</sub>-TPD) in a flow-type fixed-bed reactor at ambient pressure. A 100-mg sample was preheated at 550  $^{\circ}$ C for 2 h, and then cooled to 120  $^{\circ}$ C in flowing helium. At this temperature, sufficient pulses of ammonia were injected until adsorption saturation occurred, followed by purging with helium for 2 h. The temperature was then raised from 120 to 600  $^{\circ}$ C at a rate of 10  $^{\circ}$ C/min, and the ammonia desorbed was collected in a liquid nitrogen trap and detected by an on-line gas chromatograph (GC) equipped with a TCD.

Thermal gravimetric analysis (TGA) was conducted in flowing air on a Perkin Elmer TGA 7 to determine the amount of coke deposited on the catalyst after reaction.

#### Catalytic activity tests

The activities of the samples toward cumene cracking were tested in a pulse microreactor. The catalyst load for the tests was 20 mg, and the catalyst was preheated at 350 °C for 2 h before reaction. Hydrogen with a flow rate of 40 mL/min was used as the carrier gas. The reactions were conducted at 250 °C, and 1  $\mu$ L cumene was injected for each test. The products were analyzed by an on-line GC equipped with a TCD.

Catalytic tests for propane dehydrogenation were performed at 600 °C in a fixed-bed flow microreactor at atmospheric pressure. The catalyst load was 200 mg, and it was activated at 600 °C for 1 h in nitrogen flow prior to the reaction. The gas reactant contained 2.5 vol% propane, 5 vol% carbon dioxide and balancing nitrogen. For dehydrogenation of propane in the absence of CO<sub>2</sub>, the gas reactant contained 2.5 vol% propane and balancing nitrogen. The total flow rate of the gas reactant is 20 mL/min. The hydrocarbon reaction products were analyzed using an on-line GC equipped with a 6-m packed column of Porapak Q and a FID. The gas products, including CO and CO<sub>2</sub>, were analyzed on-line by another GC equipped with a 2-m packed column of carbon molecular sieve 601 and a TCD.

### **Results and discussion**

#### Catalyst preparation and characterization

The mesoporous HZSM-5 with different Si/Al ratios were synthesized using TPOAC as a template. Their XRD patterns were measured and shown in Figure 1. Five diffraction peaks characteristic of MFI structure at  $2\theta = 8.0^{\circ}, 8.9^{\circ}, 23.1^{\circ}, 23.3^{\circ}$  and  $24.0^{\circ}$  were observed on the patterns of all the samples. The relative crystallinity of MFI sample was determined by comparing the sum of the intensities of its peaks at d=3.851, 3.823, 3.798,3.732 and 3.711 nm with that of the reference sample. The result shows that all those materials have similar degrees of crystallization except for the one with a Si/Al ratio of 78, whose crystallinity is a bit higher than that of the others. No peaks corresponding to gallium oxide are observed on the XRD patterns of supported catalysts (not shown here), indicating that gallium oxide is well dispersed on all the supports.

The  $N_2$  adsorption/desorption isotherms of the catalysts were measured. All are typical type IV isotherms except for the one with a Si/Al ratio of 78, as shown in Figure 2A, which shows that most catalysts have very regular mesoporous channels after the gallium oxide



**Figure 1** XRD patterns of mesoporous HZSM-5 with different Si/Al ratios: (a) M-HZSM-5(78), (b) M-HZSM-5(144), (c) M-HZSM-5(173), (d) M-HZSM-5(240), (e) M-HZSM-5(307).

supporting. This was proved by the pore size distributions shown in Figure 2B.

The bulk Si/Al ratio of the HZSM-5 support measured by XRF was presented in Table 1. The bulk Si/Al ratio is generally much smaller than that of the initial gel, showing that Al is probably much easier to be incorporated into the framework than Si during the synthesis of mesoporous ZSM-5 with high Si/Al ratio. The specific surface area, pore volume and the most probable



**Figure 2** N<sub>2</sub> adsorption isotherms (A) and pore size distribution (B) of the catalysts: (a)  $Ga_2O_3/M$ -HZSM-5(78), (b)  $Ga_2O_3/M$ -HZSM-5(144), (c)  $Ga_2O_3/M$ -HZSM-5(173), (d)  $Ga_2O_3/M$ -HZSM-5(240), (e)  $Ga_2O_3/M$ -HZSM-5(307). The isotherms (b), (c), (d) and (e) were vertically offset by 50, 100, 150 and 200 cm<sup>3</sup>/g, respectively.

pore diameter of the catalysts were also summarized in Table 1. The BET specific surface areas of mesoporous HZSM-5 supported catalysts are in the range of 363 to 385 m<sup>2</sup>/g, the pore volumes are in the range of 0.20 to 0.27 cm<sup>3</sup>/g, showing that the channels in the mesoporous HZSM-5 supports are not blocked by supported Ga<sub>2</sub>O<sub>3</sub>.

Figure 3 depicts the <sup>27</sup>Al MAS NMR spectra of the samples. An intense line at  $\delta$  55 from 4-coordinate aluminum in the ZSM-5 framework and a very weak line at  $\delta$  0 from extra-framework 6-coordinate aluminum were observed in all the samples, indicating that the majority of the Al species have been incorporated into the framework of ZSM-5, which is exactly the same as that in conventional ZSM-5.



**Figure 3** <sup>27</sup>Al MAS NMR spectra of mesoporous HZSM-5 with different Si/Al ratios: (a) M-HZSM-5(78), (b) M-HZSM-5(144), (c) M-HZSM-5(173), (d) M-HZSM-5(240), (e) M-HZSM-5(307).

#### Acidity measurements

The acidity of the catalysts was measured by NH<sub>3</sub>-TPD and results were summarized in Table 2, together with that of Ga<sub>2</sub>O<sub>3</sub>/HZSM-5(180) for comparison. There is a broad asymmetric NH<sub>3</sub> desorption peak on the TPD profiles of all Ga<sub>2</sub>O<sub>3</sub> supported catalysts. The acidity of the mesoporous ZSM-5 supported catalysts decreases with increasing the Si/Al ratio of the support. Not only the total amount of acid sites but also that of medium to strong acid sites (expressed as the amount of NH<sub>3</sub> desorbed within the temperature zone of 350–600  $^{\circ}$ C) decrease sharply, quite similar to those of Ga<sub>2</sub>O<sub>3</sub> catalysts supported on the conventional HZSM-5. Meanwhile, the total amounts of acid sites as well as that of medium to strong acid sites on Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5 catalyst are much lower than that on  $Ga_2O_3$ catalyst supported on the conventional HZSM-5 with similar Si/Al ratio. Since the Si/Al ratio of the support is so high that the acid sites of the support itself is very low, the above acidity difference comes from the dispersed gallium oxides, caused by the different interaction between the gallium oxide and the supports after the introduction of mesoporous channels. Similar results were observed before.<sup>16,17</sup>

The catalytic activities of these supported gallium

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 Table 1
 Composition and textural properties of the catalysts prepared

Catalyst	Si/A	l ratio	Surface area/	Pore volume/	Mesopore volume/	Mesopore diameter/ nm		
	Gel <sup>a</sup>	Bulk <sup>b</sup>	$(m^2 \bullet g^{-1})$	$(\mathrm{cm}^3 \cdot \mathrm{g}^{-1})$	$(\mathrm{cm}^{3} \cdot \mathrm{g}^{-1})$			
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(78)	200	78	363	0.20	0.12	2.3		
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(144)	300	144	336	0.23	0.19	2.2		
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(173)	400	173	344	0.24	0.21	2.1		
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(240)	500	240	385	0.22	0.18	2.1		
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(307)	600	307	385	0.27	0.23	2.1		

<sup>a</sup> Calculated from the amount of NaAlO<sub>2</sub> and TEOS added in the reactant gel. <sup>b</sup> Determined by XRF.

oxide catalysts toward cumene cracking, a typical strong acid catalyzed reaction, have been investigated. The results are given in Table 2. The activity of these mesoporous ZSM-5 supported catalysts decreases with the increase of the Si/Al ratio, and is lower than that of conventional HZSM-5 supported one with similar Si/Al ratio, which is consistent with NH<sub>3</sub>-TPD results.

 Table 2
 NH<sub>3</sub>-TPD data and cumene cracking results of various catalysts

Catalyst	Amount o	Conversion of cumene/		
	120—350 ℃	) 350—600 ℃	Total	%
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(78)	0.15	0.19	0.34	27.6
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(144)	0.08	0.11	0.18	22.2
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(173)	0.05	0.09	0.14	21.2
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(240)	0.04	0.07	0.11	20.5
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(307)	0.03	0.06	0.09	19.0
Ga <sub>2</sub> O <sub>3</sub> /HZSM-5(180)	0.10	0.15	0.25	24.6

### **Catalytic activity**

The dehydrogenation of propane in the presence of CO<sub>2</sub> was carried out at 600 °C over various mesoporous HZSM-5 supported gallium oxide catalysts. The variation of propane conversion versus time on stream for these catalysts was illustrated in Figure 4A. The initial propane conversion decreases as the Si/Al ratio increases, due to the decrease of the acid sites on the catalysts, quite similar to the results over Ga<sub>2</sub>O<sub>3</sub>/HZSM-5 catalysts.<sup>16</sup> Meanwhile, the selectivity to propylene increases with the increase of Si/Al ratio. Thus, the propylene initial yield has the sequence of  $Ga_2O_3/M-HZSM-5(240) > Ga_2O_3/-HZSM-5(173) \approx$  $Ga_2O_3/M-HZSM-5(144) > Ga_2O_3/M-HZSM-5(307) \approx$ Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(78) as displayed in Figure 4B.

The effect of  $Ga_2O_3$  loading over  $Ga_2O_3/M$ -HZSM-5(240) was shown in Table 3. The activity of the catalyst increases sharply when the content is raised from 3% to 5%. However, only a little improvement can be observed when the loading amount is increased from 5% to 7%. In the same time, raising the  $Ga_2O_3$  loading also has a negative effect on the propylene selectivity, since too many active sites would enhance the side reac-



**Figure 4** Propane conversion (A) and propylene yield (B) on the catalysts as a function of reaction time: ( $\blacksquare$ ) Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(78), ( $\bullet$ ) Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(144), ( $\blacktriangle$ ) Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(173), ( $\blacktriangledown$ ) Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(240), ( $\blacktriangleleft$ ) Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(307).

tions besides the dehydrogenation to produce more by-products such as aromatics. Thus, 5% is an optimal content in our present work, which is similar to the result of conventional HZSM-5 supported  $Ga_2O_3$ .

#### The effect of CO<sub>2</sub>

The effect of  $CO_2$  addition on the dehydrogenation of propane over  $Ga_2O_3/M$ -HZSM-5(240) catalyst was also investigated, and the results were shown in Figure 5 and Table 4. The amount of coke determined by TG was also contained. The promoting effect of carbon dioxide on the reaction was observed. The initial propane conversion increases from 48.6% to 57.5% by the introduction of  $CO_2$ . Despite of the reduction in the propylene selectivity, an improvement in the initial propylene yield is also obtained. This enhancement can be attributed to the reverse water gas shift reaction, which accelerates

Dehvdrogenation	of Propane to	Propylene ove	er Ga <sub>2</sub> O <sub>3</sub> Supported	on HZSM-5
			2 5 1	

Table 3 Reaction data over Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(240) with different Ga<sub>2</sub>O<sub>3</sub> loadings

Loading/ wt%	C		Viold of $C \amalg \frac{a}{b}$				
	Conversion /%	$CH_4$	$C_2H_4$	$C_2H_6$	$C_3H_6$	Aromatics	There of $C_3 \Pi_6 / \%$
3	46.8 (43.2)	3.8 (3.4)	14.3 (15.0)	0.7 (0.5)	44.7 (48.3)	36.4 (32.8)	20.9 (20.9)
5	57.5 (53.0)	2.7 (2.4)	9.0 (9.8)	0.2 (0.2)	40.2 (42.7)	47.9 (44.8)	23.1 (22.6)
7	62.0 (56.6)	3.1 (2.4)	10.3 (9.5)	0.4 (0.4)	38.0 (39.6)	48.1 (48.2)	23.6 (22.4)

<sup>a</sup> The values outside and inside the parenthesis are the data obtained at 1 and 10 h, respectively.



**Figure 5** Propane conversion (A) and propylene yield (B) of  $Ga_2O_3/M$ -HZSM-5(240) ( $\circ$ ) in the presence of CO<sub>2</sub>, and (**n**) in the absence of CO<sub>2</sub>.

the formation of the dehydrogenation products by transforming  $H_2$  with CO<sub>2</sub> into CO and  $H_2O$ .

It can also be seen that the stability of the catalysts is improved after the addition of CO<sub>2</sub>. The initial activity of Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(240) catalyst dropped about 22.4% within 30 h in the absence of CO<sub>2</sub>, but when CO<sub>2</sub> was introduced, only 16.5% was dropped within the same period. This improvement can be attributed to the suppression of coke formation (Table 4) coming from two aspects:<sup>9,16</sup> elimination of coke by the Boudouard reaction and promotion of desorption of propylene from the catalyst surface.

#### The effect of mesoporosity

Figure 6 illustrated the difference of the catalytic behavior between the mesoporous ZSM-5 supported gallium oxide and conventional ZSM-5 supported one. The details were listed in Table 4. It can be seen that the conversion of propane over  $Ga_2O_3/M$ -HZSM-5(173) is higher than  $Ga_2O_3/HZSM$ -5(180) despite there is less acid sites on the former one. This indicates that the introduction of the mesoporous channel can promote the

reaction by better transport of the reactant or product molecules due to its hierarchical structure.

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**Figure 6** Propane conversion (A) and propylene yield (B) of  $(\blacksquare)$  Ga<sub>2</sub>O<sub>3</sub>/M-HZSM-5(173) and  $(\circ)$  Ga<sub>2</sub>O<sub>3</sub>/HZSM-5(180) as a function of reaction time.

However, the propylene selectivity on the mesoporous catalyst is relatively lower. Thus, no significant improvement in propylene yield was obtained after the introduction of the mesopores. Meanwhile, more aromatics were obtained on the mesoporous catalyst, indicating that the existence of mesoporous channel promoted the possibility of forming bulky products via side reactions such as oligomerization, cyclization and aromatization. GC-MS measurements show that the main component of the aromatic products is benzene, toluene and xylene, usually over 90%, which is also valuable in the chemical industry, as well as propylene.

The stability of the catalyst is also improved by the introduction of the mesopores. Thus, the steady propylene yield of  $Ga_2O_3/M$ -HZSM-5(173) is a bit higher than that over  $Ga_2O_3/HZSM$ -5(180). TG results show that less coke is formed on the mesoporous catalyst (see Table 4), which may also have something to do with the

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Table 4 Reaction data and coke amount over various catalysts in the presence or absence of CO<sub>2</sub>

Catalyst	C	Selectivity <sup><i>a</i></sup> /%					Viald of $C \amalg \frac{a}{b}$	Coke/
	Conversion /%	$CH_4$	$C_2H_4$	$C_2H_6$	$C_3H_6$	Aromatics	There of $C_3H_6^{-1}$ %	wt%
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(240) <sup>b</sup>	57.5 (48.0)	3.0 (2.2)	10.1 (8.7)	0.2 (0.1)	40.2 (45.2)	46.5 (43.7)	23.1 (21.7)	0.82
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(240) <sup>c</sup>	48.6 (37.7)	2.9 (2.5)	9.8 (10.1)	0.2 (0.2)	45.2 (53.3)	41.9 (33.9)	22.0 (20.1)	0.92
Ga <sub>2</sub> O <sub>3</sub> /M-HZSM-5(173) <sup>b</sup>	59.2 (52.8)	3.2 (3.5)	10.8 (14.5)	0.8 (0.5)	38.1 (41.3)	47.2 (40.2)	22.6 (21.8)	0.97
Ga <sub>2</sub> O <sub>3</sub> /HZSM-5(180) <sup>b</sup>	48.9 (37.5)	3.1 (2.7)	10.2 (10.8)	0.2 (0.2)	45.1 (53.5)	41.5 (32.8)	22.0 (20.1)	1.27

<sup>*a*</sup> The values outside and inside the parenthesis are the data obtained at 1 and 30 h, respectively; <sup>*b*</sup> in the presence of CO<sub>2</sub>; <sup>*c*</sup> in the absence of CO<sub>2</sub>.

better transport of the product molecules via mesoporous channels, besides the fact that there is less acid sites on  $Ga_2O_3/M$ -HZSM-5(173).

## Conclusion

Dehydrogenation of propane in the presence of CO<sub>2</sub> was investigated over a series of Ga2O3 catalysts supported on the mesoporous HZSM-5 with different Si/Al ratios. Their catalytic behavior has been compared with that on conventional HZSM-5 supported one. The initial activity of mesoporous HZSM-5 supported catalysts decreases with increasing the Si/Al ratio of the support, while the selectivity to propylene improves. The introduction of the mesoporous channels can promote the transport of the reactant and product molecules, leading to an enhancement in activity and stability of the catalysts. However, the selectivity to propylene decreases, since the existence of mesopores is more suitable for producing bulky products such as aromatics. Benzene, toluene and xylene are the main by-products, which are also valuable in chemical industry. The promoting effect of CO<sub>2</sub> on the dehydrogenation reaction is observed over these mesoporous catalysts by transforming  $H_2$ with CO<sub>2</sub> into CO and H<sub>2</sub>O through the reverse water-gas shift reaction. The catalytic stability is also enhanced by the addition of CO<sub>2</sub> to the feed gas due to the suppression of coke formation.

## References

- 1 Barias, O. A.; Holmen, A.; Blekkan, E. A. J. Catal. 1996, 158, 1.
- 2 Gascon, J.; Tellez, C.; Herguido, J.; Menendez, M. Appl. Catal. A: Gen. 2003, 248, 105.
- 3 Sugiyama, S.; Hashimoto, T.; Tanabe, Y.; Shigemoto, N.; Hayashi, H. J. Mol. Catal. A: Chem. 2005, 227, 255.
- 4 Creaser, D. C.; Andersson, B.; Hudgins, R. R.; Silveston, P. L. *Cana. J. Chem. Eng.* 2000, 78, 182.
- 5 Takahara, I.; Saito, M. Chem. Lett. 1996, 973.
- 6 Michorczyk, P.; Ogonowski, J. Appl. Catal. A: Gen. 2003, 251, 425.

- 7 Liu, L.; Li, H.; Zhang, Y. Catal. Commun. 2007, 8, 565.
- 8 Ren, Y.; Zhang, F.; Hua, W.; Yue, Y.; Gao, Z. Catal. Today 2009, 148, 316.
- 9 Zheng, B.; Hua, W.; Yue, Y.; Gao, Z. J. Catal. 2006, 239, 470.
- 10 Guisnet, M.; Gnep, N. S.; Alario, F. Appl. Catal. A: Gen. 1992, 89, 1.
- 11 Himei, H.; Yamadaya, M.; Kubo, M.; Vetrivel, R.; Broclawik, E.; Miyamoto, A. J. Phys. Chem. **1995**, 99, 12461.
- 12 Guisnet, M.; Gnep, N. S. Catal. Today 1996, 31, 275.
- 13 Gonzales, N. O.; Chakraborty, A. K.; Bell, A. T. *Top. Catal.* 1999, 9, 207.
- 14 Frash, M. V.; van Santen, R. A. J. Phys. Chem. A 2000, 104, 2468.
- 15 Kazansky, V. B.; Subbotina, I. R.; Rane, N.; van Santen, R. A.; Hensen, E. J. M. *Phys. Chem. Chem. Phys.* **2005**, *7*, 3088.
- 16 Xu, B.; Zheng, B.; Hua, W.; Yue, Y.; Gao, Z. Stud. Surf. Sci. Catal. 2007, 170, 1072.
- 17 Xu, B.; Li, T.; Zheng, B.; Hua, W.; Yue, Y.; Gao, Z. Catal. Lett. 2007, 119, 283.
- 18 Ren, Y.; Hua, W.; Yue, Y.; Gao, Z. Chem. J. Chin. Univ. 2009, 30, 1162 (in Chinese).
- 19 Ren, Y.; Hua, W.; Yue, Y.; Gao, Z. React. Kinetics Catal. Lett. 2008, 95, 113.
- 20 Choi, M.; Cho, H. S.; Srivastava, R.; Venkatesan, C.; Choi, D.; Ryoo, R. *Nature Materials* 2006, *5*, 718.
- 21 Sun, Y. Y.; Prins, R. Appl. Catal. A 2008, 336, 11.
- 22 Sun, Y. Y.; Prins, R. Angew. Chem. Int. Ed. 2008, 47, 8478.
- 23 Kim, J.; Choi, M.; Ryoo, R. J. Catal. 2010, 269, 219.
- 24 Wang, Y.; Ma, L. R.; Zhu, N.; Chen, F. Q.; Zhan, X. L. Prog. Chem. 2009, 21, 1722.
- 25 Jin, M. J.; Taher, A.; Kang, H. J.; Choi, M.; Ryoo, R. Green Chem. 2009, 11, 309.
- 26 Zhao, Z. L.; Liu, Y. M.; Wu, H. H.; Li, X. H.; He, M. Y.; Wu, P. *Microporous Mesoporous Mater.* 2009, *123*, 324.
- 27 Srivastava, R.; Iwasa, N.; Fujita, S.; Arai, M. Chem. Eur. J. 2008, 14, 9507.
- 28 Perez-Ramirez, J.; Christensen, C. H.; Egeblad, K.; Christensen, C. H.; Groen, J. C. Chem. Soc. Rev. 2008, 37, 2530.

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