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Effects of CO_2 addition on the aromatization of propane over metal-loaded ZSM-5 catalysts†

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The catalytic reduction of CO_2 accompanying the aromatization of propane is a new type of catalytic reaction for the utilization of CO_2. CO_2 is reduced into CO by hydrocarbon, and hydrocarbon (propane) is converted into more valuable products. This type of reaction is more economical than the hydrogenation of CO_2, since propane is much cheaper than hydrogen. The combined conversion of propane and CO_2 was investigated by using metal-loaded ZSM-5 catalysts, which were characterized by temperature-programmed desorption, X-ray diffraction, thermogravimetric analysis and BET analysis. Reduction of CO_2 by propane resulted in higher conversion of CO_2 and higher CO yield than that by hydrogen. The incorporation of metal ions, such as Zn^{2+}, Cr^{3+}, Fe^{3+} and Ni^{2+}, into HZSM-5 enhanced the catalytic activity for CO_2 reduction. The addition of CO_2 was found to suppress the coke deposition during the aromatization of propane. Copyright © 2000 John Wiley & Sons, Ltd.

Keywords: CO_2; propane; aromatization; ZSM-5; Zn

INTRODUCTION

CO_2, are cause of the greenhouse effect, is one of the most abundant carbon resources and its concentration in the atmosphere has steadily increased. In order to improve climate conditions, as well as to solve the carbon resource problem, hydrocarbon synthesis through CO_2 hydrogenation is desirable to develop techniques whereby CO_2 can be converted into valuable materials such as methanol or hydrocarbons. Copper-based catalysts and zeolites were mostly used for this synthesis and CO_2 catalytic reduction.[1–3]

On the other hand, much attention has been paid to the transformation of lower alkanes, such as propane and butanes, into aromatic hydrocarbons. The aromatic hydrocarbons can be utilized as a booster for high octane number gasoline and are fundamental raw chemicals in the petroleum chemistry. HZSM-5 and various metal-loaded ZSM-5 materials are known to be active catalysts for the production of aromatics from lower alkanes and alkenes.[4–9]

The catalytic reduction of CO_2 accompanying the aromatization of propane was proposed as a new type of catalytic reaction for the utilization of carbon dioxide.[10] CO_2 can be reduced into CO by hydrocarbons and the hydrocarbon (propane) can be converted into more valuable products. In this work, the reduction of CO_2 by propane was compared with that by hydrogen over the metal-loaded ZSM-5 catalysts, and the effect of metal incorporation into ZSM-5 on the activity and selectivity was discussed. Also, the effect of CO_2 addition on the propane aromatization was investigated.

EXPERIMENTAL

Metal-loaded HZSM-5 catalysts were prepared by the ion-exchange method. HZSM-5 (Si/Al ratio = 25) powders were mixed with an aqueous solution of metal nitrate for 24 h, and followed by drying and calcination at 823 K.

The structures of ZSM-5 catalysts were confirmed by their powder X-ray diffraction (XRD) pattern using Cu Kα radiation. The crystallinity was estimated through the intensity of characteristic

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Table 1 Conversion of CO_2 and yield of CO over various metals loaded HZSM-5

	Reduction of CO_2 by H_2		Reduction of CO_2 by C_3H_8	
Catalyst	Conv. (%)	CO yield	Conv. (%)	CO yield
HZSM-5	0.6	—	7.3	2.2
Cr–ZSM-5	0.7	—	9.2	0.2
Fe–ZSM-5	10.8	6.3	13.7	14.5
Ni–ZSM-5	6.0	4.2	10.7	3.1
Zn–ZSM-5	16.6	16.9	40.2	60.3

Reaction conditions: temp. = 873 K, W/F = 5.0 g·h mol^{-1}, H_2/CO_2 or C_3H_8/CO_2 = 2.25, 1 h reacted.

peaks. The surface area was measured by the nitrogen BET method using a Micromeritics ASAP 2000. Thermogravimetric analysis (TGA) was performed using a Cahn micro-balance to measure the coke amount after reaction. Temperature-programmed desorption (TPD) measurements were carried out to determine the acid properties of zeolites by using ammonia as an adsorbate. In a typical run, 0.3 g of a calcined sample was placed in a quartz tubular reactor and heated at 500 °C under a helium flow of 45 ml min^{-1} for 1 h. The reactor was then cooled to 100 °C and adsorption was conducted at that temperature by exposing the sample to an ammonia flow of 23 ml min^{-1} for 1 h. Physically adsorbed ammonia was removed by purging the sample with a helium stream flowing at 45 ml min^{-1} for 30 min at 100 °C.

The reaction was conducted by using a conventional continuous flow reaction apparatus using 0.3 g of catalyst. The catalyst was pretreated in a helium flow for 1 h at 823 K. In the aromatization reaction of C_3H_8 and CO_2, the ratio of partial pressures of CO_2/C_3H_8 was 2.25, with a balance of helium; the aromatization reaction of C_3H_8 alone was balanced by helium to maintain the total flow rate equal in both cases. CO_2 reduction by hydrogen was also carried out to compare the product distribution. The contact time (W/F) was 5.00 g h mol^{-1}.

RESULTS AND DISCUSSION

CO_2 is such a stable material that energy or a reducing agent must be used for its conversion. Table 1 shows the catalytic activities of the reduction of CO_2 using propane and hydrogen as a reducing agents. It shows that the conversion of CO_2 and the selectivity to CO are much higher in the CO_2 reduction by propane than by hydrogen. The introduction of metal ions, such as Zn^{2+}, Cr^{3+}, Fe^{3+} and Ni^{2+}, into HZSM-5 also enhanced the catalytic activity for CO_2 reduction. In particular, Zn^{2+} showed the highest activity.

Figures 1 and 2 show the effect of CO_2 addition on the activity of propane aromatization over HZSM-5 and Zn–ZSM-5 respectively. The aromatic compounds produced were benzene, toluene and xylene. For the HZSM-5 catalyst, the conver-

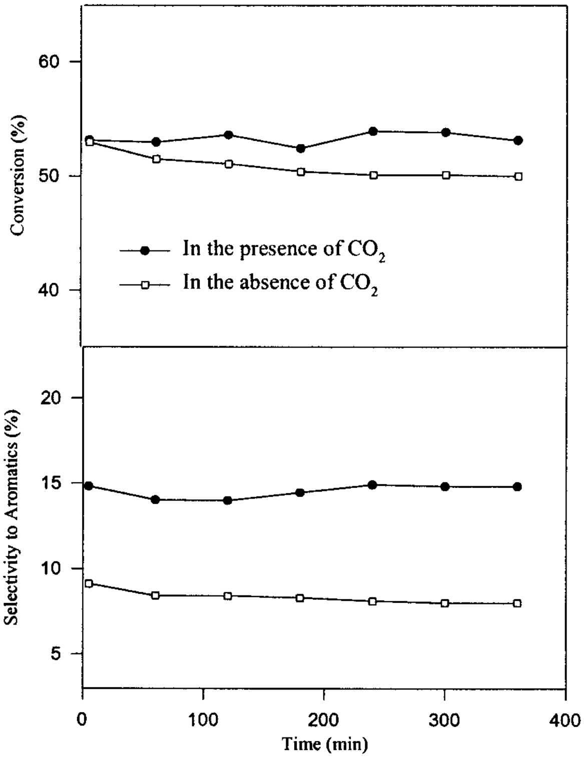

Figure 1 Conversion of C_3H_8 and selectivity to aromatics with time on stream over HZSM-5 (temp. = 873 K, H_2/CO_2 or C_3H_8/CO_2 = 2.25, W/F = 5.0 g·h mol^{-1}).

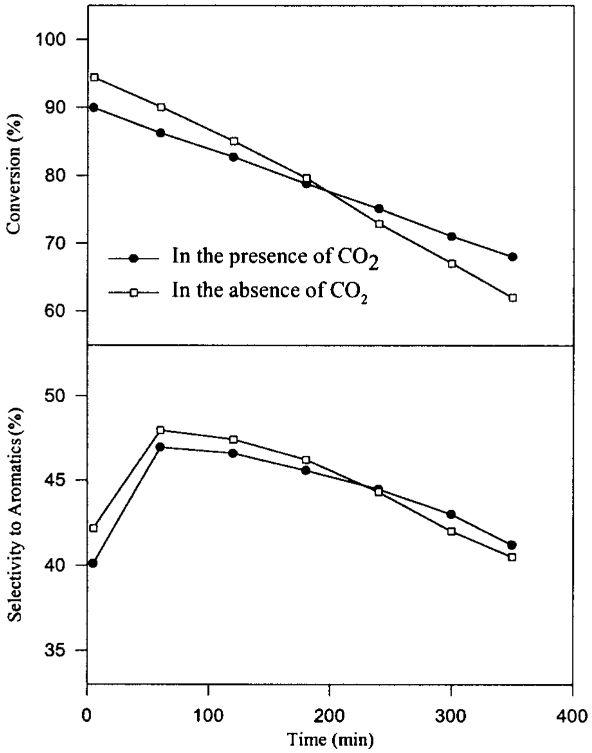

Figure 2 Conversion of C_3H_8 and selectivity to aromatics with time on stream over Zn–HZSM-5 (temp. = 873 K, H_2/CO_2 or $C_3H_8/CO_2 = 2.25$, W/F = 5.0 g h mol^{-1}).

sion of propane remained almost constant with time on stream, even if the conversion was improved slightly with CO_2 addition. On the other hand, the selectivity to aromatics increased significantly due to the presence of CO_2. For the Zn–ZSM-5 catalyst, the conversion and the selectivity were higher than those for HZSM-5. The propane conversion decreased monotonously and the selectivity to aromatics increased to the maximum and decreased with time on stream. The presence of CO_2 did not seem to affect the activity and selectivity, but the decreasing rate (or deactivation) was apparently retarded in the case of CO_2 addition. CO_2 must have retarded the deactivation of zeolite during the aromatization of propane. When other metal ions were incorporated into HZSM-5, their effects on the aromatization of propane were similar to that due to zinc.

In the case of CO_2 reduction with propane over Zn–HZSM-5, however, it was noted that the CO yield was much higher than CO_2 conversion. This implied that CO could be produced not only from CO_2 but also other sources such as propane.

The schematics of possible reaction routes can be described as follows:

$$C_3H_8 \rightarrow C_3H_6 + H_2 \qquad [1]$$

$$2C_3H_6 \rightarrow C_6H_6(\text{aromatics}) + 3H_2 \qquad [2]$$

$$CO_2 + H_2 \rightarrow CO + H_2O \qquad [3]$$

$$3CO_2 + C_3H_8 \rightarrow 6CO + 4H_2 \qquad [4]$$

Reactions [1] and [3] can then give

$$CO_2 + C_3H_8 \rightarrow C_3H_6 + CO + H_2O$$

Propane could be converted into aromatics

Table 2 Gibb's free energy of various reactions involved in the process at 1 atm

	ΔG (kJ mol^{-1})		
Temp. (°C)	Reaction [1]	Reaction [3]	Reaction [4]
25	86.67	28.62	383.55
550	13.09	7.53	−68.00
600	5.70	5.60	−113.39
650	−1.75	3.67	−159.08
700	−9.26	1.75	−205.05

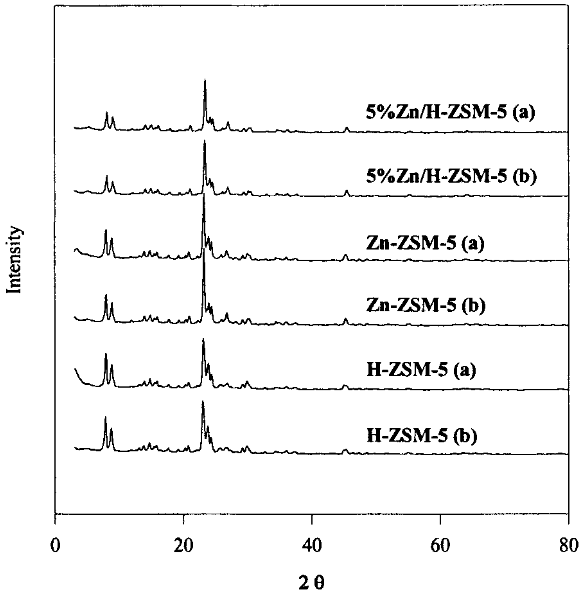

Figure 3 XRD patterns of deactivated catalysts: (a) aromatization reaction in the absence of CO_2; (b) aromatization reaction in the presence of CO_2.

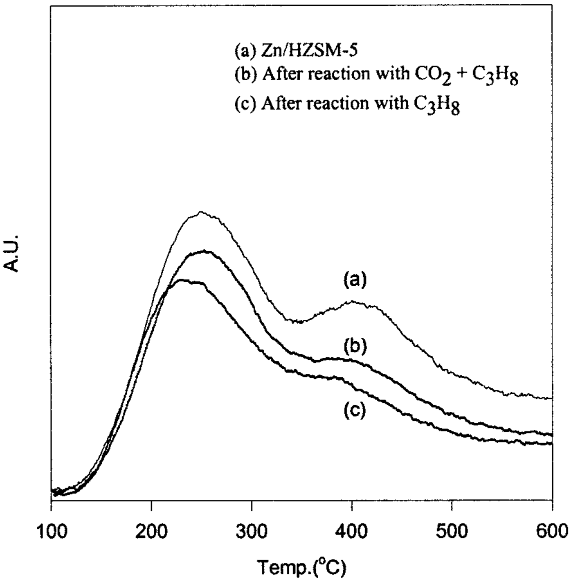

Figure 4 NH_3 TPD curves of Zn–ZSM-5.

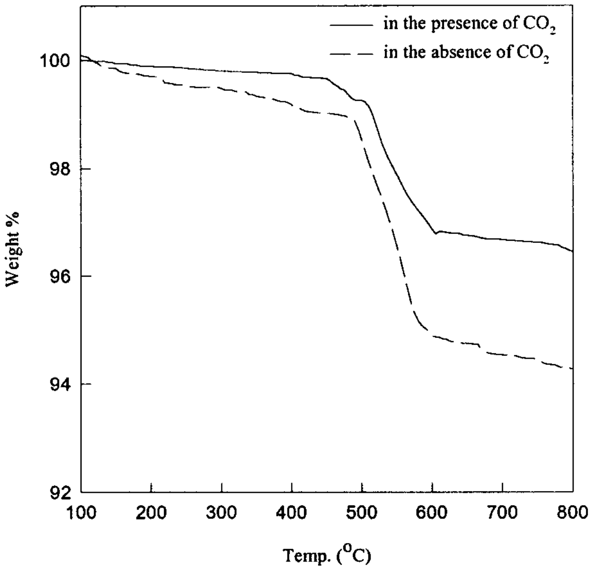

Figure 5 TGA results of deactivated Zn–ZSM-5.

through reactions [1] and [2]. CO_2 is consumed by reaction [3]. These reaction networks imply that propane aromatization and CO_2 reduction may occur consecutively. However, other reactions, such as [4], can also take place. CO_2 in reaction [4] reacted with propane directly. If CO_2 is converted into CO by reaction [4], the CO yield can be much higher than CO_2 conversion.

Table 2 shows the Gibb's free energy of various reactions involved in the process at 1 atm. At lower temperature, CO_2 can be converted into CO easily through reaction [3]. However, reaction [4] can occur more easily at higher temperature. In other words, CO_2 is more likely to react directly with propane at higher temperature and propane is a more effective reducing agent than hydrogen at high temperature.

XRD, NH_3 TPD, BET and TGA were carried out to investigate the effect of CO_2 addition on deactivation. The structure of the catalyst before and after the reaction remained almost unchanged, as shown in Fig. 3.

Figure 4 shows the NH_3 TPD of zeolites. Although the acidity was reduced for the deactivated Zn–ZSM-5 catalysts, the degree of reduction was smaller for the case of CO_2 addition. This might be ascribed to the role of CO_2 preventing deactivation of acid sites in HZSM-5 and Zn–ZSM-5.

Figure 5. shows the coking amount through TGA results of the catalysts after the aromatization reaction in the absence and in the presence of CO_2. The coke formation decreased when CO_2 was added into propane. The effect of CO_2 addition on the coke formation can also be evidenced by the change of surface area, as shown in Table 3.

SUMMARY

It was found that the reduction of CO_2 into CO and the conversion of propane into aromatics occurred simultaneously over Zn–ZSM-5 catalyst. The conversion of CO_2 and the selectivity to CO were

Table 3 BET surface areas of deactivated catalysts after the aromatization reaction in the absence of CO_2 and in the presence of CO_2

Catalyst	BET surface area (m^2 g^{-1})
HZSM-5 (no CO_2)	454
HZSM-5 (with CO_2)	517
Zn–ZSM-5 (no CO_2)	332
Zn–ZSM-5 (with CO_2)	387

much higher in the CO_2 reduction by propane than by hydrogen.

The introduction of metal ions, such as Zn^{2+}, Cr^{3+}, Fe^{3+} and Ni^{2+}, into HZSM-5 was found to enhance the catalytic activity for CO_2 reduction.

From the viewpoint of propane aromatization over Zn–ZSM-5 catalyst, the addition of CO_2 seemed to suppress coke deposition.

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