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Catalytic Reduction of Carbon Dioxide with Simultaneous Aromatization of Propane on Metal-loaded HZSM-5 Catalysts

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For the purpose of examining the possibility of performing reduction of carbon dioxide, and concurrently producing more value-added products from hydrocarbon, as a reducing agent, a reaction of carbon dioxide and propane on HZSM-5 catalysts containing Ga, Zn and Pt was conducted by using a continuous flow reaction apparatus. The catalytic test demonstrated the possibility of conducting the reduction of carbon dioxide with simultaneous aromatization of propane on metal-loaded HZSM-5. Thus, carbon dioxide was reduced to carbon monoxide, and propane was converted into aromatics, mainly composed of benzene, toluene and xylene isomers, and lower alkenes generating by-products, such as methane and ethane. Among the catalysts examined in the present study, Zn-loaded HZSM-5 was most effective for the reduction of carbon dioxide by propane. It was also found that the introduction of carbon dioxide had some favorable effects on the aromatization of propane. Carbon dioxide suppressed catalyst deactivation caused by coke deposition and formation of by-product, ethane, to improve the selectivity of lower alkenes, such as ethene and propene.

1. Introduction

Catalytic reduction of carbon dioxide draws considerable attention as a possible technology for chemical fixation of carbon dioxide. It should, however, be taken into consideration that carbon dioxide is quite stable, and its reduction requires much energy. Utilization of hydrocarbons, as reducing reagent, might be one of the approaches to the problem. If valuable products could be formed from the hydrocarbon as a reducing reagent, the reaction would be more attractive. The merit of the combination of reduction of carbon dioxide and conversion of reducing reagents into value-added products would depend on whether or not carbon dioxide would favorably influence the conversion of reducing reagents.

We have reported the preliminary results of the catalytic reduction of carbon dioxide by propane with simultaneous dehydrogenation of propane into propene on oxide catalysts¹⁾. Present study aims to examine the possibility of conducting catalytic reduction of carbon dioxide with simultaneous aromatization of propane²⁾ by using Ga-, Zn-, and Pt-loaded HZSM-5 catalysts, which

are typical catalysts for the aromatization of propane^{3),4)} and the effect of carbon dioxide on aromatization of propane.

2. Experimental

HZSM-5 was prepared by ion-exchange of Na-ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3$ molar ratio=23.3, supplied from TOSOH Co.) with NH_4NO_3 followed by drying and calcination in flowing air for 4 h at 823 K. Metal-loaded HZSM-5 catalysts were prepared by refluxing aqueous solutions of $\text{Ga}(\text{NO}_3)_3$, $\text{Zn}(\text{NO}_3)_2$ and $\text{Pt}(\text{NH}_3)_4\text{Cl}_2 \cdot \text{H}_2\text{O}$ containing $\text{NH}_4\text{-ZSM-5}$ powders for 24 h, followed by evaporation-to-dryness. Metal content was 10 wt% for Ga and Zn and 1 wt% for Pt. Ga- and Zn-HZSM-5 thus obtained were calcined in the same way as cited above. Pt-HZSM-5 was calcined in flowing air for 3 h at 773 K, followed by reduction in flowing hydrogen for 3 h at 773 K.

Propane and carbon dioxide were used as-received. Nitrogen and hydrogen were used after being purified by passing them through columns of Molecular Sieve 5A for desiccation.

The catalytic test was conducted by using a continuous flow reaction apparatus at atmospheric pressure. A small amount of catalyst (0.3 g) was

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placed in a quartz tube with an inside diameter of 10 mm. The catalyst, excepting Pt-HZSM-5, was pretreated in flowing oxygen diluted with nitrogen ($O_2/N_2=1/5$) for 1 h at 823 K. Hydrogen was used instead of oxygen-nitrogen mixture for the pretreatment of Pt-HZSM-5. Partial pressures of propane and carbon dioxide in the reaction of propane and carbon dioxide were 18 and 43 kPa, respectively, with nitrogen balance, and that of propane in the reaction of propane alone was 18 kPa with nitrogen balance. Total feed rate was $0.15 \text{ mol} \cdot \text{h}^{-1}$ in both cases. The reaction temperature was raised every 50 K from 673 K to 873 K, and at each temperature the catalytic run was conducted for 45 minutes, at the end of which reaction products were analyzed with gas chromatography. The reverse water gas shift conversion was also conducted by using the same apparatus described above. The partial pressures of carbon dioxide and hydrogen were 18 kPa, respectively, with nitrogen balance.

3. Results

3.1. HZSM-5 and Ga-HZSM-5

In the reaction of propane alone on HZSM-5, the conversion of propane occurred significantly above 723 K, but significant amount of aromatics, mainly consisting of benzene, toluene and xylene, was formed only above 823 K. In the reaction of propane and carbon dioxide, a noticeable amount of carbon monoxide was formed above 773 K, though the conversion of carbon dioxide was not significant. The introduction of carbon dioxide had only slight effect on the conversion of propane and the yield of aromatics, as shown in Table 1.

The addition of Ga to HZSM-5 resulted in remarkable improvement of the activity and selectivity for the aromatization of propane, as

reported in the literatures³⁾⁻⁷⁾. The conversion of propane and the yield of aromatics were remarkably improved (Table 1). The addition of Ga, however, considerably decreased the hydrocarbon balance, suggesting the deposition of coke. Actually, the catalyst appeared highly darkened after the catalytic run.

The catalytic activity for the reduction of carbon dioxide was not remarkably improved by the addition of Ga to HZSM-5. The yield of carbon monoxide and the conversion of carbon dioxide were significant only above 823 K, as shown in Fig. 1. Carbon dioxide had some effect on the aromatization of propane over Ga-HZSM-5. Both of the conversion of propane and the yield of aromatics were lower than those without carbon

●○, Conversion of propane; ■□, Yield of aromatics; △, Yield of carbon monoxide.

Fig. 1 Conversions and Yields in the Reaction of Propane Alone (●■) and in the Reaction of Propane and Carbon Dioxide (○□△) on 10%Ga-HZSM-5

Table 1 Reactions of C_3H_8 Alone and $C_3H_8+CO_2$ over Metal-loaded HZSM-5

Catalyst	Reaction Temperature [K]	HZSM-5		Ga-HZSM-5 ^{a)}		Zn-HZSM-5 ^{a)}		Pt-HZSM-5 ^{b)}	
		C_3H_8 823	$C_3H_8+CO_2$ 823	C_3H_8 823	$C_3H_8+CO_2$ 823	C_3H_8 823	$C_3H_8+CO_2$ 823	C_3H_8 773	$C_3H_8+CO_2$ 773
C_3H_8 conv.	[%]	36.5	39.8	63.4	69.1	57.4	71.4	72.1	50.6
CO_2 conv.	[%]	—	2.4	—	2.4	—	6.3	—	3.0
CO yield	[%]	—	1.1	—	2.7	—	12.1	—	1.1
H_2 yield	[%]	3.0	2.2	21.6	24.4	15.0	17.9	11.7	9.8
Hydrocarbon product distribution (C%)									
CH_4		26.3	25.8	7.3	10.2	13.5	14.6	7.9	6.0
C_2H_6		7.1	6.9	6.3	5.9	15.7	15.4	39.9	30.5
C_2H_4		30.0	30.5	9.7	9.0	10.4	6.1	0.7	6.1
C_3H_6		18.3	16.5	12.7	8.5	21.2	18.3	13.3	19.0
C_4^+		7.3	6.1	2.6	1.9	2.2	2.2	6.4	9.7
Aromatics		11.1	14.2	61.5	64.6	37.0	43.5	31.9	28.8
Balance									
Hydrocarbon		99.6	98.2	93.9	93.3	88.9	87.0	99.8	101.5
CO_x		—	98.8	—	100.3	—	105.9	—	98.1
Total carbon		99.6	98.6	93.9	98.3	88.9	100.5	99.8	99.1

a) Metal content, 10 wt%. b) Metal content, 1 wt%.

For the symbols, see Fig. 1.

Fig. 2 Conversions and Yields in the Reaction of Propane Alone and in the Reaction of Propane and Carbon Dioxide over 10%Zn-HZSM-5

dioxide at lower temperature, but higher above 823 K (Fig. 1).

3. 2. Zn-HZSM-5

Figure 2 shows that addition of Zn to HZSM-5 also improved the activity and selectivity for aromatization of propane in a manner similar to the case of Ga, though the effect of Zn on the activity and selectivity was slightly less than that of Ga. These results are in good agreement with the reported results^(4),8)~10). In the reaction of propane alone, the conversion of propane and the yield of aromatics at 873 K were lower than those at 823 K, which may be due to the catalyst deactivation by coke formation⁽¹¹⁾ at high temperature. A low hydrocarbon balance shown in Table 1 also suggests the deposition of coke.

The effect of Zn on the reduction of carbon dioxide was more remarkable than that of Ga. The yield of carbon monoxide was higher than that on Ga-HZSM-5 over the whole temperature range, as can be seen by comparing Fig. 2 with Fig. 1. It should be noted that the yield of carbon monoxide on Zn-HZSM-5 was greater than the conversion of carbon dioxide, especially at higher temperature, as shown in Table 1.

The effect of carbon dioxide on the reaction of propane over Zn-HZSM-5 was similar to that over Ga-HZSM-5. The conversion of propane and the yield of aromatics were lower than those without carbon dioxide at lower temperature, but higher at above 823 K. As mentioned above, lower conversion of propane at 873 K than that at 823 K in the reaction of propane alone suggests the catalyst deactivation caused by coke deposition. Then, increase in conversion of propane with

For the symbols, see Fig. 1.

Fig. 3 Conversions and Yields in the Reaction of Propane Alone and in the Reaction of Propane and Carbon Dioxide over 1%Pt-HZSM-5

increasing temperature, in the presence of carbon dioxide, suggests that carbon dioxide suppresses coke deposition.

Carbon dioxide did not affect the hydrocarbon balance so much, which was very low at high temperature (Table 1). When carbon oxides were taken into account, however, the total carbon balance was complete within a reasonable error.

3. 3. Pt-HZSM-5

As shown in Fig. 3, Pt-HZSM-5 exhibited the highest activity for the conversion of propane at lower temperature, among the catalysts examined in the present study. Further increase in the temperature, however, led to drop in conversion. As for product distribution, the selectivity of ethane remarkably increased, at the expense of the selectivities of ethene and aromatics, in comparison with the results over Ga- and Zn-HZSM-5. These results agree well with those reported in the literatures^(3),4),12)~16).

When carbon dioxide was introduced, carbon monoxide was formed at above 723 K, but the yield of carbon monoxide and the conversion of carbon dioxide were not so great at below 773 K. The conversion of propane and the yield of aromatics dropped more seriously, by the introduction of carbon dioxide, than those on the other catalysts, especially at higher temperatures.

3. 4. Reverse Water Gas Shift Conversion

The results of the reverse water gas shift conversion are shown in Fig. 4. Over HZSM-5, carbon monoxide could not be detected even at 873 K. In the case of Ga-HZSM-5, the formation of carbon monoxide was confirmed at above 823 K, indicating that the addition of Ga to HZSM-5

Fig. 4 Reverse Water Gas Shift Conversion over Pt-HZSM-5 (●), Zn-HZSM-5 (○), Ga-HZSM-5 (■), and HZSM-5 (□)

●○, Conversion of propane; ■□, Yield of aromatics.

Fig. 5 Effect of Carbon Dioxide on the Deactivation of 10%Zn-HZSM-5 in the Reaction of Propane Alone (●■) and in the Reaction of Propane and Carbon Dioxide (○□) at 823 K

generates hydrogenation activity to some extent. Zn-HZSM-5 exhibited higher activity for the shift conversion of carbon dioxide. The highest conversion of carbon dioxide was obtained over Pt-HZSM-5. The yield of carbon monoxide over Pt-HZSM-5 was higher than those over the other catalysts, and further, some methane was also formed.

3.5. Deactivation of Catalysts

Figure 5 shows the effect of carbon dioxide on the deactivation of Zn-HZSM-5, in the aromatization of propane. In the reaction of propane alone, both the conversion of propane and the yield of aromatics decreased steeply, as shown

by closed symbols. The color of the catalyst was highly darkened after the reaction. On the other hand, when carbon dioxide was fed together with propane, the decreases in the conversion and yield were less pronounced, as shown by open symbols, indicating that the introduction of carbon dioxide suppressed the deactivation of the catalyst.

4. Discussion

4.1. Effect of Metal Species on the Reduction of Carbon Dioxide

It is well known that the aromatization of propane on HZSM-5 can be accelerated by the incorporation of metal species^{3),4)}. In the present study, the effect of Ga, Zn and Pt on the catalytic reduction of carbon dioxide with simultaneous aromatization of propane was examined. As shown in Table 1 and Figs. 1–3, the incorporations of these metals accelerated, not only the aromatization of propane, but also the reduction of carbon dioxide. The activity patterns for both reactions, however, did not agree with each other. The activity pattern for the reduction of carbon dioxide is Zn-HZSM-5>Pt-HZSM-5>Ga-HZSM-5>HZSM-5, but, in the reaction of propane alone, those for the conversion of propane and for the formation of aromatics are Pt-HZSM-5>Ga-HZSM-5>Zn-HZSM-5>HZSM-5 and Ga-HZSM-5>Pt-HZSM-5>Zn-HZSM-5>HZSM-5, respectively.

These metal species are said to provide catalytic sites for the dehydrogenation of propane to propene and naphthenes to aromatics. Since the catalytic sites for the dehydrogenation should also accelerate the hydrogenation, the metal species may be expected to act as the catalytic sites for the reduction of carbon dioxide, as well. This was confirmed through the reverse water gas shift (RWGS) conversion. As shown in Fig. 4, the catalytic activity for RWGS conversion increased with the addition of metals. The activity pattern is Pt-HZSM-5>Zn-HZSM-5>Ga-HZSM-5>HZSM-5. The above-mentioned results that Zn-HZSM-5 is more active for the reduction of carbon dioxide by propane than is Ga-HZSM-5 may be interpreted by this activity pattern, *i.e.*, Zn-HZSM-5 is more active in RWGS conversion than Ga-HZSM-5.

The activity patterns for propane aromatization and RWGS conversion mentioned above suggest that Pt-HZSM-5 would be the best catalyst for the reduction of carbon dioxide with simultaneous propane aromatization, because Pt-HZSM-5 is most active for the RWGS conversion and for conversion of propane, and is second most active for the formation of aromatics. As mentioned above, however, Pt-HZSM-5 exhibited rather low

activity for the reduction of carbon dioxide by propane (**Table 1** and **Fig. 3**). This may be understood by considering the high yield of ethane over Pt-HZSM-5 shown in **Table 1**. Thus, the yield of ethane was much higher over Pt-HZSM-5 than those over the other catalysts. High yield of ethane over Pt-loaded HZSM-5 has been attributed to high activity for hydrogenation of ethene and for hydrogenolysis of alkanes^{14),15)}. Thus, lower activity of Pt-HZSM-5 for the reduction of carbon dioxide may be due to higher activity for the hydrogenation and hydrogenolysis of hydrocarbons rather than that for the hydrogenation of carbon dioxide. Or, in other words, higher activity of Zn-HZSM-5 may be attributed to higher selectivity for the activation of carbon dioxide than that for the activation of hydrocarbons.

4. 2. Effect of Carbon Dioxide on Aromatization of Propane

The introduction of carbon dioxide had some effect on the aromatization of propane. Both of the conversion of propane and the selectivities of hydrocarbon products were modified, as shown in **Figs. 1—3** and **Table 1**. **Figure 5** indicated that the deactivation caused by coke deposition is suppressed by carbon dioxide. These effects of carbon dioxide will be discussed in the light of the reaction mechanism by using, as an example, the results over Zn-HZSM-5, which exhibited the highest activity for the reduction of carbon dioxide.

4. 2. 1. Activity and Selectivity

It has been widely accepted that rate of aromatization may be determined by the formation of olefinic species from propane, such as dehydrogenation into propene on metal sites and cracking into ethene and methane on acid sites^{3),4)}. Mole *et al.*⁸⁾ suggest that the zinc cation acts as a hydride acceptor to form $[Zn-H]^+$ species. This proposal for the activation of propane was followed by a more detailed mechanism by Meriaudeau and Naccache⁷⁾. They proposed heterolytically dissociative adsorption of propane forming metal hydride and metal alkoxide species. Thus, two kinds of sites are required for the dehydrogenation of propane: metal cation sites for accepting hydride ions and oxygen anion sites for propyl carbenium ions. On the other hand, carbon dioxide is known to be adsorbed at oxygen vacancies on zinc oxide surface to form formate species at elevated temperature in hydrogen atmosphere¹⁷⁾. This would lead to the supposition that carbon dioxide covers the metal sites and suppresses the dehydrogenation of propane, resulting in lower conversion of propane. Carbon monoxide formed also might suppress the con-

Fig. 6 Selectivities of Ethane (▲△), Ethene (●○), and Propene (■□) in the Reaction of Propane Alone (▲●■) and in the Reaction of Propane and Carbon Dioxide (△□) on 10%Zn-HZSM-5

version of propane by covering metal sites. Typical example may be decreased conversion of propane on Pt-HZSM-5 at higher temperature in the presence of carbon dioxide, shown in **Fig. 3**, because carbon monoxide is well known to adsorb strongly on the surface of Pt metal.

The introduction of carbon dioxide little affected the selectivities of methane and aromatics. On the other hand, as shown in **Fig. 6**, the selectivity of ethane was considerably decreased, and those of ethene and propene were increased. The decrease in the selectivity of ethane and the increase in that of ethene may be interpreted in terms of the retardation of hydrogenation of ethene, which is considered to proceed on extraframework zinc cations¹⁸⁾. As mentioned above, carbon dioxide is considered to cover the metal cation sites through the formation of formate species. And, further, hydrogen produced through the dehydrogenation and dehydrocyclization is consumed through the hydrogenation of carbon dioxide. Both of these should lead to the suppression of hydrogenation of ethene.

The increase in propene selectivity can not be interpreted through the kinetic effect of carbon dioxide on the formation of propene. This is because propene is formed through the dehydrogenation of propane which is retarded by carbon dioxide and because propene is converted into naphthenes on acid sites which may be hardly affected by carbon dioxide. Thermodynamic effect may be another possible explanation, because the dehydrogenation of propane is thermodynamically restricted under the present condition, and because hydrogen is consumed

through the reverse water gas shift conversion. The partial pressure of propene, however, was less than the equilibrium pressure: the ratio of partial pressures, *i.e.*, $P(\text{C}_3\text{H}_6) \cdot P(\text{H}_2) / P(\text{C}_3\text{H}_8)$ was 0.016 and 0.061 at 773 and 823 K, respectively, in the presence of carbon dioxide, while the equilibrium constant, K_p , is 0.064 at 800 K. This may suggest that propene undergoes unknown reaction which should be suppressed by carbon dioxide. Further study is in progress to clarify the effect of carbon dioxide on the various reactions of hydrocarbons over HZSM-5 and ZnO.

4.2.2. Deactivation

It is well-known that in the aromatization of propane the deposition of coke occurred to cause catalyst deactivation¹¹⁾. The deactivation caused by coke deposition was clearly observed in the present case, too. As shown in **Fig. 5**, the conversion of propane decreased steeply with time on stream. The color of the used catalyst was highly dark.

Figure 5 also shows that the deactivation can be suppressed by the introduction of carbon dioxide. The effect of carbon dioxide seems greater at high temperature. **Figure 2** shows that, without carbon dioxide, the conversion of propane at 873 K was lower than that at 823 K, indicating more serious deposition of coke occurs at high temperature. On the other hand, the conversion of propane in the presence of carbon dioxide at 873 K was three times as high as that in the absence of carbon dioxide. At high temperature, as shown in **Table 1**, the yield of carbon monoxide was always higher than the conversion of carbon dioxide, suggesting that carbon monoxide is not formed only through the reverse water gas shift conversion. Another probable reaction to form carbon monoxide is the gasification of deposited coke by carbon dioxide. Suzuki *et al.*¹⁹⁾ reported that carbon dioxide can immediately oxidize deposited coke on Sm_2O_3 surface to carbon monoxide at 1,073 K.

The material balance in the catalytic runs confirms the formation of carbon monoxide through the gasification of deposited coke. **Table 1** indicates that the hydrocarbon balance was only 88.9% at 823 K, when carbon dioxide was not fed. The hydrocarbon balance was not improved by admixing carbon dioxide with propane, *i.e.*, the balance was 87.0%. Low hydrocarbon balances can be attributed to the significant deposition of coke. On the other hand, the balance of carbon oxides exceeded 100% and the total carbon balance was very close to 100%. These results confirm that carbon monoxide is formed not only through the reduction of carbon dioxide but also through the

gasification of deposited coke by carbon dioxide, suppressing the accumulation of deposited coke.

5. Conclusion

The catalytic reduction of carbon dioxide with simultaneous aromatization of propane was studied by using Ga-, Pt-, and Zn-loaded HZSM-5 catalysts to examine the possibility of catalytic reduction of carbon dioxide simultaneously producing value-added products from hydrocarbons as reducing reagents. The highest conversion of carbon dioxide was obtained by using Zn-loaded HZSM-5. High activity of Zn-HZSM-5 was attributed to moderate activity for the hydrogenation and higher selectivity for the activation of carbon dioxide than that of hydrocarbons. The introduction of carbon dioxide was found to suppress the formation of ethane and the deposition of coke in the aromatization of propane. The ethane formation was considered to be suppressed through the retardation of side reactions of alkenes such as ethene hydrogenation by carbon dioxide which is adsorbed to cover Zn-cation sites. The suppression of coke deposition was attributed to the gasification of deposited coke by carbon dioxide to form carbon monoxide.

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要 旨

金属添加 HZSM-5 触媒上でのプロパン芳香族化に伴う二酸化炭素の触媒還元

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還元剤である炭化水素から高付加価値物質を製造しつつ二酸化炭素を触媒還元する可能性を検討する目的で, Ga, Zn, Pt 添加 HZSM-5 触媒上でのプロパンと二酸化炭素の常圧流通反応を行った。金属添加 HZSM-5 触媒を用いることにより, プロパンの芳香族化に伴う二酸化炭素の一酸化炭素への還元が可能であることが示された。すなわち, 二酸化炭素は一酸化炭素に還元され, プロパンはベンゼン, トルエン, キシレンを主と

する芳香族化合物と低級オレフィンに変換された。試験した触媒の中では, Zn 添加 HZSM-5 触媒が二酸化炭素の還元にも有効であった。さらに, 二酸化炭素がプロパン芳香族化に好ましい影響を持つことが明らかとなった。すなわち, 二酸化炭素の導入によりコーク析出による触媒劣化が抑制され, また副生成物であるエタンの生成が抑えられ, エチレンやプロピレンのようなオレフィンの選択性が向上した。

Keywords

Catalytic reduction, Carbon dioxide, Carbon monoxide, Aromatization, Propane, Metal loaded HZSM-5