Benzene–Oxygen Reaction over Alkaline Earth Metal Oxide Catalysts

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The benzene–oxygen reaction catalyzed by alkaline earth metal oxides was investigated in the temperature range 773–1,073 K to understand the catalytic function of these oxides for hydrocarbon gasification. In the initial stage of reaction, CO, CO₂, H₂O, and biphenyl were concurrently produced. The consumption of CO and H₂O by the water–gas shift reaction subsequently occurred to give CO₂ and H₂. CO oxidation with O₂ hardly occurred in the course of the benzene–oxygen reaction because benzene was preferentially adsorbed on the MgO catalyst. These reaction sequences were compared with those in the benzene–oxygen reaction catalyzed by metallic nickel.

1. Introduction

The catalytic gasification of carbonaceous feedstocks such as heavy distillates of petroleum, tar sand bitumen, and shale oil is a potential route to produce useful gaseous products such as hydrogen, syngas, and fuel gas. In the previous studies^{1,2}, we have shown that alkaline earth metal oxides are effective for steam gasification of carbonaceous feedstocks and resistible to sulfur poisoning. We have recently studied the catalytic functions of alkaline earth metal oxides and reaction networks in the benzene– and hexane–carbon dioxide reactions^{3–5}. These oxides were found to facilitate both decomposition of hydrocarbons to carbon on their surface and its gasification above 973 K.

Oxygen gasification is another possible route to produce gaseous products. Uncatalyzed gasification processes such as Shell and Texaco processes are operated in the high temperature range 1,600–1,800 K, and utilization of a catalyst makes it possible to operate the processes at lower reaction temperatures. Nickel has exclusively been used as a catalyst component for oxygen gasification of natural gas and naphtha. However, sulfur strongly poisons nickel catalysts so that it is difficult to utilize nickel catalysts to oxygen gasification of heavy carbonaceous feedstocks. Moreover, in nickel-catalyzed oxygen gasification it has been considered that combustion occurs solely in the first stage of reaction, making it difficult to con-

trol the reaction temperature.

This paper presents characteristic function of alkaline earth metal oxides in oxygen gasification of hydrocarbon feedstocks. For this purpose, the catalytic function of these oxides will be compared with that of metallic nickel. Benzene was selected as a model hydrocarbon feedstock for making a comparison with the reaction sequences in the benzene–CO₂ reaction⁵.

2. Experimental

Both MgO(BG) and (BE) were prepared from basic carbonate salts (Kanto) by calcination in air at 1,273 K for 5 h: the salt used for preparation of MgO(BE) was a less pure reagent-grade. MgO(O) was obtained by calcination of magnesium oxide (Kanto) in air at 1,273 K for 5 h. Other catalysts were prepared from the carbonate or hydrate of alkaline earth metal oxides using a similar procedure. Alkali and alkaline earth elements were loaded on MgO(O) by impregnation. MgO(O) was soaked in deionated water at room temperature. An appropriate amount of alkali or alkaline earth nitrate was dissolved in the water–MgO(O) mixture. The resulting mixture was dried at 373 K and treated at 1,123 K for 5 h in a stream of N₂. Employing the same procedure, nickel was supported on MgO(O) and γ -Al₂O₃ (Kanto) using nickel nitrate.

The benzene–O₂ reaction was carried out in the temperature range 773–1,073 K in a continuous flow reactor with a fixed bed at atmospheric pressure. The partial pressures of benzene and O₂ were 1 and 3 kPa, respectively, unless otherwise mentioned. Analytical procedures were the same

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as those previously reported^{3),5)}.

The temperature-programmed desorption (TPD) of benzene adsorbed on MgO (BE) was measured as follows. An amount of MgO (BE) weighing 0.5 g was heated to 1,173 K at a rate of 10 K min⁻¹ and maintained at that temperature for 2 h in flowing He. After pretreatment, MgO(BE) was exposed to 76 kPa of benzene or to a mixture of 76 kPa of O₂ and 76 kPa of benzene at 673 K for 0.5 h and then evacuated at that temperature for 0.5 h. TPD measurements were carried out at a heating rate of 10 K min⁻¹ up to 1,173 K in flowing He. The flow rate of He was 3.7×10⁻³ mol min⁻¹ and the pressure of He was 76 kPa. Part of the outlet gas was introduced into a mass spectrometer (NEVA TE-600). The sensitivity of the spectrometer was normalized by using 1,020 ppm of Ar involved in the He carrier.

3. Results and Discussion

Reaction products in the benzene-O₂ reaction catalyzed by MgO(BE) comprised of CO, CO₂, H₂O, H₂, biphenyl, and trace amounts of C₁-C₄ hydrocarbons. Table 1 lists the catalytic activities of alkaline earth metal oxides and alkali- or alkaline earth-promoted MgO with those of supported nickel catalysts at 873 K. Nickel catalysts were reduced by H₂ at 1,023 K for 2 h prior to the benzene-O₂ reaction, because they were almost inactive unless reduced. Although MgO (BG) and (O) were less effective, the catalytic activity of MgO(O) was increased by doping it with alkaline earth cations. These results coincide

with those reported by Cunningham *et al.*⁶⁾ who have recently shown that MgO doped with large isovalent cations such as Ca²⁺ effectively catalyze oxidative coupling of methane with O₂. Alkali-promoted MgO catalysts were less active than alkaline earth-promoted MgO, but they were selective for formation of biphenyl. The high selectivities of these catalysts to biphenyl indicate that oxidative coupling of benzene is accelerated by alkali loading. Ito *et al.*⁷⁾ have also shown that the catalytic activity of MgO for oxidative coupling of methane is markedly promoted by Li⁺ loading. MgO(BE), which is the most active catalyst among the alkaline earth metal oxides for the benzene- and hexane-CO₂ reactions³⁾⁻⁵⁾, was prominently effective for the benzene-O₂ reaction among the alkaline earth metal oxide catalysts tested. Both catalysts containing 5 wt% of nickel metal showed higher activities for producing CO, CO₂, H₂, and H₂O without the formation of biphenyl.

We compared the stability of catalytic activity between MgO(BE) and Ni(5 wt%)/Al₂O₃. Figure 1 shows the variation in the yield of carbon oxides and in the CO selectivity, *i.e.*, the molar fractions of CO in carbon oxides with time-on-stream at 873 K. MgO(BE) showed a stable catalytic activity and CO selectivity, whereas Ni/Al₂O₃ was deactivated. As no CO and CO₂ were formed when both of these catalysts were treated with oxygen after 3 h of run, carbon deposition was not important in the course of the benzene-O₂ reaction. It was ascertained that the nickel catalyst

Table 1 Activities of Various Catalysts^{a)}

Catalyst	Benzene conversion[mol%]	Product yield[mol%]				
		CO	CO ₂	BP ^{b)}	H ₂	H ₂ O
MgO(O)	1.1	0.2	0.7	0.2	0.3	0.9
MgO(BG)	2.8	0.3	0.8	1.8	0.3	0.8
MgO(BE)	15.3	5.0	9.5	0.6	3.0	11.8
CaO(1 wt%)/MgO(O)	8.7	3.0	4.9	0.8	1.5	7.2
CaO(9 wt%)/MgO(O)	4.8	1.9	2.9	0.0	0.9	3.4
CaO(C) ^{c)}	8.8	3.5	4.6	0.6	1.4	7.3
CaO(H) ^{d)}	1.9	0.5	1.4	0.0	0.3	0.4
SrO(1 wt%)/MgO(O)	5.4	2.2	3.2	0.0	1.0	3.2
SrO(23 wt%)/MgO(O)	2.2	0.2	0.8	1.1	0.3	1.9
SrO(C) ^{e)}	6.0	3.0	3.0	0.0	1.3	4.7
SrO(H) ^{d)}	1.1	0.0	0.0	1.1	0.1	1.1
BaO(1 wt%)/MgO(O)	3.8	0.5	1.7	1.6	0.6	3.3
BaO(32 wt%)/MgO(O)	2.4	0.1	0.4	1.9	0.3	2.1
Li ₂ O(1 wt%)/MgO(O)	1.3	0.0	0.4	1.0	0.1	1.2
Li ₂ O(4 wt%)/MgO(O)	0.9	0.0	0.3	0.6	0.2	0.7
Na ₂ O(1 wt%)/MgO(O)	1.2	0.0	0.3	0.8	0.2	0.9
Na ₂ O(9 wt%)/MgO(O)	2.3	0.0	0.2	0.1	2.2	2.3
K ₂ O(1 wt%)/MgO(O)	0.9	0.0	0.6	0.2	0.2	0.6
K ₂ O(13 wt%)/MgO(O)	1.2	0.0	0.4	0.0	0.1	1.1
Ni(1 wt%)/MgO(O) ^{e)}	2.7	0.2	2.5	0.0	0.5	2.2
Ni(5 wt%)/MgO(O) ^{e)}	29.1	11.1	18.0	0.0	16.3	11.8
Ni(1 wt%)/Al ₂ O ₃ ^{e)}	11.1	1.2	9.9	0.0	0.5	10.6
Ni(5 wt%)/Al ₂ O ₃	39.3	20.3	19.0	0.0	25.7	13.6

Reaction conditions: temperature, 873 K; W/F, 1.00×10³ g-cat. min mol⁻¹, the partial pressure of benzene, 1.0 kPa; the partial pressure of oxygen, 3.0 kPa.

a) Data shown in this table was taken after 0.5 h on stream. b) Represents biphenyl. c) Prepared from carbonate salt.

d) Prepared from hydroxide. e) Reduced by H₂ at 1,023 K for 2 h.

Open symbols, MgO(BE) catalyst; closed symbols, Ni/Al₂O₃ catalyst.

Fig. 1 Variation in the Catalytic Activity and in the CO Selectivity with Time on Stream in the Benzene-O₂ Reaction at 873 K

was completely regenerated by reducing the used nickel catalyst in H₂ at 1,023 K for 2 h. As a result, we conclude that oxidation of nickel metal was the reason for deactivation.

Uncatalyzed benzene-O₂ reaction was carried out in the temperature range 873–973 K. As shown in Fig. 2(a), biphenyl and CO started to appear at around 973 K. Production of carbon oxides was manifested with increasing reaction temperature. Figure 2(b) shows temperature dependency of the level of benzene conversion and of the yields of carbon oxides and biphenyl in the benzene-O₂ reaction catalyzed by MgO(BE). The catalytic reaction occurred above 773 K. The temperature at which the reaction started to take place was reduced by about 150 K by use of

MgO(BE) catalyst. We have previously shown in the study of the benzene-CO₂ reaction⁵⁾ that benzene was allowed to decompose on the MgO surface to give deposited carbon above 973 K irrespective of the presence of CO₂. Compared with this reaction, benzene and O₂ could react at considerably lower temperatures. It is, therefore, likely that benzene is activated by the lattice oxygen of MgO above 973 K in the absence of oxygen in the gas phase, whereas oxygen species adsorbed on the catalyst surface is capable of activating benzene, leading to the initiation of the benzene-O₂ reaction at lower temperatures.

Figures 3(a) and (b) show TPD spectra for benzene adsorbed on MgO(BE) at 673 K in the absence and in the presence of O₂, respectively. When benzene was adsorbed on MgO(BE) in the absence of O₂ after heat treatment *in vacuo* at 1,173 K, the desorption peaks of CO (*m/e*=28) and CO₂ (*m/e*=44) were observed at temperatures above 500 and 670 K, respectively, with a broad desorption peak of benzene (*m/e*=77) over the whole temperature range. These results indicated that benzene adsorbed on MgO(BE) appeared to partly react with lattice oxygen to give CO and CO₂. On the other hand, as shown in Fig. 3(b), when benzene was adsorbed on MgO(BE) in the presence of O₂, the desorbed amount of benzene was significantly increased. In addition, CO₂ started to desorb at around 420 K and the amount desorbed markedly increased. These results suggest that the adsorbed oxygen species works as the active site for adsorption of benzene and possesses higher activity for oxidation of benzene than the lattice oxygen.

The benzene-O₂ reaction was carried out at 873 K on MgO(BE), alkaline earth-promoted MgO,

$W/F = 1.00 \times 10^3$ g-cat. min mol⁻¹.

Fig. 2 Temperature Dependency of Benzene Conversion and Product Yield in (a) Uncatalyzed and (b) MgO(BE)-catalyzed Benzene-O₂ Reactions

CO ($m/e=28$, - - - - -), CO_2 ($m/e=44$,), and benzene ($m/e=77$, —) were monitored.

Fig. 3 TPD Spectra for Benzene Adsorbed on $\text{MgO}(\text{BE})$ at 673 K (a) in the Absence of O_2 , and (b) in the Presence of O_2 in the Gas Phase

Catalyst: $\circ$, $\text{MgO}(\text{BE})$; $\bullet$, $\text{CaO}(1 \text{ wt}\%)/\text{MgO}(\text{O})$; Δ , $\text{CaO}(9 \text{ wt}\%)/\text{MgO}(\text{O})$; ∇ , $\text{SrO}(1 \text{ wt}\%)/\text{MgO}(\text{O})$; $\square$, $\text{Ni}(5 \text{ wt}\%)/\text{MgO}(\text{O})$; $\blacksquare$, $\text{Ni}(5 \text{ wt}\%)/\text{Al}_2\text{O}_3$.

Fig. 4 Variation in the CO Selectivity as a Function of the Yield of Carbon Oxides in the Benzene- O_2 Reaction at 873 K

and nickel catalysts. **Figure 4** shows the variation in the CO selectivity with the yield of carbon oxides. The CO selectivities of Ni/MgO and $\text{Ni}/\text{Al}_2\text{O}_3$ were overlapped and they approached to zero with decreasing yield of carbon oxides. Therefore, one can conclude that in the first stage of the benzene- O_2 reaction on nickel catalysts, combustion of benzene to give CO_2 occurs solely. On the other hand, the CO selectivity of $\text{MgO}(\text{BE})$ was extrapolated to about 0.4 at 0% yield of carbon oxides. This result indicated that both CO and CO_2 were concurrently formed via the reaction of benzene with O_2 in the initial stage of reaction.

This is the feature of MgO catalysts to be most emphasized. As shown in **Fig. 4**, the CO selectivity of calcium- and strontium-promoted MgO satisfied a similar relationship between the CO selectivity and the yield of carbon oxides. The CO selectivity of these catalysts slightly decreased with increasing yield of carbon oxides.

Possible reactions for the formation of carbon oxides are listed as follows:

Formation of CO_2

(1) . . . Combustion

(2) . . . CO oxidation with O_2

(3) . . . Water-gas shift reaction

(4) . . . Steam gasification

(5) . . . Boudouard reaction

Formation of CO

(6) . . . Partial oxidation

(7) . . . Steam gasification

(8) . . . CO_2 gasification

(9) . . . Reverse Boudouard reaction

(10) . . . Reverse water-gas shift reaction

Figure 5 shows the variation in H_2 selectivity, *i.e.*, the molar fraction of H_2 in $(\text{H}_2 + \text{H}_2\text{O})$, with the yield of carbon oxides. In the case of catalysts based on MgO , the initial H_2 selectivity was found to be zero, suggesting that no H_2 was formed via partial oxidation of benzene in the first stage. Similarly, the H_2 selectivity of Ni catalysts reached zero at around 10% yield of carbon oxides, being in agreement with the conclusion that only combustion is the initial reaction on these catalysts.

We shall consider the reactions involved in the benzene- O_2 reaction system on MgO catalysts. As discussed above, CO_2 and CO were concurrently formed via reactions 1 and 6, respectively. Reac-

Fig. 5 Variation in the H_2 Selectivity with the Yield of Carbon Oxides in the Benzene- O_2 Reaction at 873 K (Symbols are the same as those shown in Fig. 4.)

tions 5 and 9 can be ruled out since no carbon was formed on these catalysts. Reactions 4, 7, and 8 proceeded at temperatures above 973 K as previously reported⁵. Accordingly, we consider that CO is consumed via reactions 2 and/or 3 at 873 K, leading to the decrease in the CO selectivity with increasing yield of carbon oxides. It is apparent from the results shown in Figs. 4 and 5 that reaction 3 is involved in the benzene- O_2 reaction system to produce H_2 and CO_2 . As the amount of CO consumed by reaction 3 should be numerically equal to that of H_2 formed, the amount of CO formed via reaction 6 could be calculated by summing up the amounts of CO and H_2 observed. Then, we can estimate the modified CO selectivity, $(CO+H_2)/(CO+CO_2)$, which represents the molar ratio of CO formed via reaction 6 to CO_2 via reaction 1. Figure 6 shows the modified CO selectivity as a function of the yield of carbon oxides. The modified CO selectivity of MgO catalysts was independent of the yield of carbon

Fig. 6 Variation in the Modified CO Selectivity, $(CO+H_2)/(CO+CO_2)$, with the Yield of Carbon Oxides in the Benzene- O_2 Reaction at 873 K (Symbols are the same as those shown in Fig. 4.)

oxides. Provided that reaction 2 takes place, the modified CO selectivity should decrease with increasing yield of carbon oxides. We, therefore, conclude that reaction 2 hardly contributes to the composition of product gases.

In the case of the benzene- O_2 reaction on nickel catalysts, reaction 1 takes place solely to give CO_2 and H_2O in the first stage as discussed above. Reactions 5 and 9 are not needed to be considered for the lack of carbon formation on these catalysts. Therefore, we conclude that reactions 7 and 8 are responsible for the secondary formation of CO, namely, benzene reacts with H_2O and CO_2 formed by combustion to give CO and H_2 . It seems likely that reactions 3 and 10 proceed simultaneously.

Table 2 compares the composition of product gases experimentally determined with that calculated by assuming the equilibrium of reaction 3. As equilibrium of reaction 3 is independent of pressure, the molar fractions of the gases involved in reaction 3 were normalized for simplicity in such a way that the sum of the partial pressures of CO, CO_2 , H_2 , and H_2O would be unity. The

Table 2 Contribution of the Water-Gas Shift Reaction to the Composition of Product Gases over Different Catalysts in the Course of the Benzene-Oxygen Reaction

Catalyst	$(W/F) \times 10^{-3}$ [g-cat. min mol ⁻¹]	Yield of carbon oxides[mol%]	Oxygen conversion [mol%]	Molar fraction of product gases							
				Experimental value ^{a)}				Calculated value ^{b)}			
				CO	H ₂ O	CO ₂	H ₂	CO	H ₂ O	CO ₂	H ₂
MgO(BE)	3.00	37.9	83.3	0.21	0.33	0.39	0.07	0.12	0.24	0.48	0.16
CaO(1 wt%)/MgO(BG)	4.00	23.6	51.1	0.21	0.26	0.44	0.09	0.14	0.20	0.51	0.15
CaO(9 wt%)/MgO(BG)	3.50	31.0	78.0	0.23	0.23	0.44	0.10	0.17	0.17	0.50	0.16
Ni(5 wt%)/MgO(O)	0.10	9.9	26.0	0.09	0.44	0.46	0.01	0.03	0.39	0.52	0.06
Ni(5 wt%)/MgO(O)	1.00	37.7	55.1	0.25	0.14	0.42	0.19	0.25	0.12	0.43	0.20
Ni(5 wt%)/Al ₂ O ₃	0.15	8.2	17.5	0.08	0.26	0.65	0.01	0.05	0.22	0.69	0.04
Ni(5 wt%)/Al ₂ O ₃	0.50	42.4	65.2	0.31	0.11	0.38	0.20	0.30	0.10	0.39	0.21

a) Calculated from the composition of product gases after 0.5 h on stream.

b) Calculated by assuming the equilibrium of the water-gas shift reaction.

composition of product gases on the nickel catalysts approached and then attained the water-gas shift equilibrium, strongly suggesting that reactions 3 and 10 were involved in the benzene-O₂ reaction system. The product gas composition did not attain the water-gas shift equilibrium on the MgO catalysts, indicating that the rate of oxygen gasification was faster than that of the water-gas shift reaction. This is one of the features of oxygen gasification on the MgO catalysts, in contrast to the fact that the water-gas shift reaction is always in equilibrium in the benzene-CO₂⁹⁾ and -H₂O⁸⁾ reactions catalyzed by alkaline earth metal oxides.

According to the discussion described above, we propose plausible reaction sequences for the benzene-O₂ reaction catalyzed by alkaline earth metal oxide catalysts and Ni catalysts as shown in **Fig. 7**. On the alkaline earth metal oxide catalysts, the catalytic combustion to give CO₂, the partial oxidation to give CO, and the oxidative coupling to give biphenyl concurrently proceed in the initial stage. The water-gas shift reaction subsequently occurs. In contrast, the use of nickel catalyst leads to exclusive formation of CO₂ and H₂O via combustion of benzene in the initial stage. The CO₂ and H₂O produced successively gasify the unreacted benzene to give mainly CO and H₂. At high conversion levels, the composi-

tion of product gases attains the water-gas shift equilibrium.

Dependency of the rates of CO and CO₂ formation on the partial pressures of O₂ and benzene was measured with MgO(BE) at 823 K, under the conditions where the conversion levels of O₂ and benzene were kept less than 10%. The partial pressures of benzene and O₂ were varied in the ranges of 0.5–5 and 1–5 kPa, respectively. The time factor was defined by W/F , where W is the weight of catalyst, and F is the flow rate of benzene. As the selectivity to CO was almost unchanged at less than 10% yield of carbon oxides, we considered that the consumption of CO by the water-gas shift reaction was negligible. The following rate equations were obtained by using the nonlinear least squares method:

$$r_{\text{CO}} = 1.24 \times 10^{-4} P_{\text{B}}^{0.04} P_{\text{O}_2}^{0.49} \quad (1)$$

$$r_{\text{CO}_2} = 1.34 \times 10^{-4} P_{\text{B}}^{-0.01} P_{\text{O}_2}^{0.48} \quad (2)$$

where P_{B} represents the partial pressure of benzene and P_{O_2} the partial pressure of O₂.

As shown in Eqs. (1) and (2), the rates of CO and CO₂ production were approximately of the zeroth order with respect to the pressure of benzene, and approximately 0.5th to that of oxygen. These results would be interpreted that benzene was adsorbed on the catalyst surface and the oxygen molecules might have dissociated on the surface.

It should be noted that CO oxidation did not proceed in the benzene-O₂ reaction system as described above. It has generally been shown^{9),10)}, however, that MgO catalyzes CO oxidation with O₂ at considerably lower temperatures, *e. g.* 434 K, than the reaction temperature of this study. Thus, we were prompted to perform CO oxidation on MgO(BE) in the absence of benzene at 873 K. The partial pressures of CO and O₂ were 6.1 and 3.0 kPa, respectively, and W/F was 200 g-cat. min mol-CO⁻¹. It was independently confirmed that CO was not consumed in the noncatalytic reaction at 873 K. As the level of CO conversion after 15 min on stream was 9.38% on MgO(BE), MgO(BE) apparently catalyzes CO oxidation with O₂.

Judging from Eqs. (1) and (2), it could be assumed that CO oxidation with O₂ was inhibited by preferential adsorption of benzene on the surface oxygen species active for oxidation. In order to ascertain this assumption, CO was introduced at a given flow rate into the benzene-O₂ reaction system. The results are shown in **Fig. 8** along with the compositions of the reactant mixtures. Two different partial pressures of CO were introduced as shown in **Figs. 8(a)** and **(b)**. If CO oxidation with O₂ proceeds simultaneously in the course of

Fig. 7 Plausible Reaction Sequences for the Benzene-O₂ Reaction Catalyzed by Alkaline Earth Metal Oxides and Nickel

	P_B/kPa	P_{O_2}/kPa	P_{CO}/kPa	P_{Ar}/kPa
A	1.0	3.0	—	97.2
B	1.0	3.0	1.0	96.2

	P_B/kPa	P_{O_2}/kPa	P_{CO}/kPa	P_{Ar}/kPa
A	1.0	3.0	—	97.2
B	1.0	3.0	6.1	91.2

Reaction temperature, 873 K. $W/F_{\text{benzene}} = 1.20 \times 10^3$ g-cat. min mol⁻¹. Compositions of the reactant mixtures for runs (a) and (b) are listed beneath their respective mixtures.

Fig. 8 Effect of Introduced CO in the Benzene-O₂ Reaction System on O₂ Conversion Level

the benzene-O₂ reaction, the introduction of CO should increase the level of O₂ conversion. For example, if CO oxidation occurs simultaneously to consume O₂ under the conditions listed in Fig. 8(a), the CO introduced in the course of the benzene-O₂ reaction should increase the level of O₂ conversion by about 18%, since the partial pressures of CO and O₂ and W/F for CO were the same as those employed in the CO oxidation with O₂ described above. However, it is apparent from the results shown in Figs. 8(a) and (b) that no appreciable increase in the level of O₂ conversion was observed. These results are considered to be evidence for the inhibition of CO oxidation by preferential adsorption of benzene.

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要 旨

アルカリ土類金属酸化物触媒を用いたベンゼン-酸素反応

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炭化水素類の酸素ガス化におけるアルカリ土類金属酸化物の触媒特性および反応経路を検討した。モデル反応としてベンゼン-酸素反応を 773~1,173 K にて行い, その結果を従来より軽質炭化水素のガス化触媒として知られているニッケル系触媒の結果と比較検討した。

Table 1 に各触媒の活性および生成物分布を示す。Ca²⁺ を含む MgO (MgO(BE)) およびニッケル系触媒が高活性であった。**Fig. 1** には MgO(BE) と Ni/Al₂O₃ の CO_x 収率, CO 選択率の経時変化を示す。Ni/Al₂O₃ では活性劣化がみられたが, これは活性点である金属ニッケルが反応中に酸化されたためと考えられた。

MgO(BE)を用いた昇温脱離実験の結果 (**Fig. 3**) から酸素が共存しない場合と比較して酸素共存下でベンゼンを吸着させた場合にはベンゼン吸着量, 生成 CO₂ 量ともに著しく増大することが示された。ベンゼンの CO₂ ガス化の結果⁵⁾とも比較して, MgO の格子酸素よりも吸着酸素がベンゼンの活性化に寄与しているものと結論した。

MgO およびニッケル系触媒上でのベンゼン-酸素反応の反

応経路について検討し (**Figs. 4~6, Table 2**), **Fig 7** に示した反応経路を提案する。ニッケル系触媒では反応の初期においてベンゼンの燃焼反応のみが起き CO₂, H₂O を生成し, 続いて未反応のベンゼンと CO₂, H₂O が反応して CO, H₂ が生成するものと考えられた。一方, MgO 系触媒の場合には CO, CO₂, H₂O, ビフェニルが一次生成物であり, CO_x 収率の増加にともない水性ガスシフト反応によって H₂ が生成することが明らかとなった。また, 本反応中に酸素による CO の酸化は起きなかった。

MgO 系触媒における CO, CO₂ の生成速度のベンゼン, 酸素分圧依存性を検討し, Eqs. (1) と (2) に示す反応速度式を求めた。これより, ベンゼンが触媒上に優先的に吸着し CO の吸着を阻害するために, ベンゼン-酸素反応では CO の酸化が起きなかったものと考えた。**Fig. 8** にはベンゼン-酸素反応の途中で反応ガス中に CO を添加したときの酸素転化率の経時変化を示した。CO の添加によって酸素転化率は変化せず, このことから上記の推測が裏付けられた。

Keywords

Gasification, Oxygen, Oxide catalyst, Alkaline earth oxide, Reaction mechanism