[Regular Paper]

CO₂ Reforming of Heptane Using Ruthenium-loaded Lanthanum Oxide Catalyst

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Reforming of heptane with CO₂, using Ni and Ru catalysts was carried out. Ruthenium, supported on La₂O₃ exhibited high catalytic activity at 600°C in the CO₂ reforming of heptane, but the activity decreased rapidly. Deactivation of the catalyst during reaction was reduced by adding LiOH (Li/Ru=3) to the catalyst, which eliminated carbon deposition. Ratio of CO/H₂ was greater than that expected from the stoichiometric reaction of CO₂ and C₇H₁₆. This is considered to be caused by the reverse water gas shift reaction, giving CO by reducing CO₂ with H₂ produced. To maintain higher catalytic activity, the formation of La₂O₂CO₃ seems to be essential.

1. Introduction

Steam reforming of hydrocarbons to give synthesis gas or hydrogen is practiced on established technologies^{1)~4)}. Recently, use of carbon dioxide, replacing of steam has attracted much attention from the view point of chemical utilization of carbon dioxide^{5)~7)}. Carbon dioxide is believed to be one of the major causes of global warming, and making recovery and recycle use of which important tasks for the chemist. Carbon dioxide reforming of methane provides equal amounts of carbon monoxide and hydrogen, as described below. The reaction in Eq. (1), being slightly more endothermic (261 kJ/mol) than the steam reforming reaction (210 kJ/mol), lead us to propose possibility of an efficient heat transfer system^{8),9)}. Although with fuel cell operated at lower temperatures, the CO poisoning problem becomes much more severe, hydrogen and carbon monoxide can be used with a solid electrode fuel cell operated at a high temperature^{10),11)}.

Combined with carbon dioxide reforming, it is believed to be one of the most efficient approach to utilization of energy.

Use of Ni catalyst, which is active in steam reforming, was reported in the CO₂ reforming of

methane^{12)~16)}. In general, a large amount of carbon was deposited on the catalyst and activity of the catalyst rapidly deteriorated. Supported platinum group metals are proposed^{6),7),17)~19)}. Especially, Ru and Rh are suitable for this reaction. Rostrup *et al.*⁶⁾ reported on relationship between the activity and carbon deposition, in which the activity was correlated to the heat of adsorption of carbon monoxide on the metals. Perera *et al.*¹⁷⁾ reported that Eu₂O₃ was effective in the support of Ru, and Eu₂O₃ was considered to be reduced to the metal. Richardson *et al.*¹⁸⁾ reported that Rh/Al₂O₃ catalyst was effective at a low ratio of CO₂/CH₄ (1.11-1.40). Attention was directed to rare earth oxides as supports. Zhaolong *et al.*²⁰⁾ reported that Ni/La₂O₃ exhibits high performance for this reaction in prolonged runs. X-Ray diffraction study revealed that large amounts of CO₂ was stored in the support as La₂O₂CO₃.

Heptane was studied frequently as object of steam reforming²¹⁾. Few studies, however, was carried out on CO₂ reforming of heptane²²⁾. This paper deals with CO₂ reforming of heptane over supported ruthenium catalyst. The effects of supports and additives on the activity and stability of the catalyst are discussed. The authors found that Ru/La₂O₃ catalyst afforded high activity in CO₂ reforming of heptane, in which lanthanum carbonate or CO₃²⁻ was formed during the initial stages of the reaction.

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2. Experimental

2.1. Materials

Catalysts were prepared by impregnating aqueous solutions of nickel nitrate (Wako Pure Chemical Industries Ltd.) to yield a 23 wt% nickel or using ruthenium chloride (Mitsuwa Pure Chemicals) to yield 0.2 wt% or 1.0 wt% ruthenium on various supports. The Ni catalyst is supported on γ - Al_2O_3 (surface area 174 m^2/g ; Kanto Kagaku Co.) and Ru is impregnated onto γ - Al_2O_3 and La_2O_3 (surface area 3.6 m^2/g ; Wako Pure Chemical Industries Ltd.). The catalysts were dried in reduced pressure and calcined in air at 550°C for 300 min.

As promoter, ten times as much amount of alkali metal (Li, Na, K, Cs) in mole against Ru(0.2 wt%) was co-loaded from hydroxide of respective metal. These were calcined at 550°C for 300 min in a flow of CO_2 .

2.2. Apparatus and Procedure

All reactions were performed using a fixed bed quartz reactor having an internal diameter of 10 mm and height of 300 mm, which was set vertically in an electric furnace. In the center part of the reactor, quartz wool plug was packed and a 100 to 200 mg of catalyst was charged. CO_2 was fed at a flow rate of 20 ml/min. Heptane was supplied, together with flow of CO_2 into the reactor through a vapor saturator maintained at $40 \pm 0.5^\circ\text{C}$ (CO_2 to heptane ratio of ca. 7.3). The temperature of reaction was controlled by monitoring the catalyst bed temperature, using a programmable controller. Before the catalyst bed reached to the desired temperature, flow of Ar was passed. At the exit of the reactor, a cold trap containing 1-butanol immersed in ice-water bath was attached to collect excess heptane, water and other liquid products.

CO , H_2 produced and CO_2 were analyzed with a Simadzu model GC-8A gas chromatograph, equipped with a TCD detector, using an activated carbon column. The light hydrocarbon gases were analyzed with a Hitachi model 163 gas chromatograph, equipped with a FID detector, using a porapak Q column. A long-run activity test was monitored by a M200 chromat analyzer (Nippon Tyan Co.), which can separate H_2 , CO , CH_4 and CO_2 , within a few hundred seconds. Excess heptane and any other liquid products were analyzed by a Shimadzu model GC-14A, with an OV1 capillary column. Carbon deposition was calculated on the basis of carbon balance in reaction products. Produced H_2O was determined by Karl Fischer automatic volumetric

titration (Hiranuma Co., AQV-55).

The specific surface area of catalysts were measured by one point method of BET. Catalyst and supports were subjected to X-ray diffraction analyses with a Jeol model JDX-3530S X-ray diffractometer system.

3. Results and Discussion

Figure 1 shows the rate of formation of CO against time on stream, over various catalysts. Possible reactions involved in CO_2 reforming of heptane are shown in Eqs. (2)-(6). As side reactions, formation of H_2O (3), (4) and carbon (4), (6) are considered. Thus, observed CO/H_2 ratio was larger than the stoichiometric ratio of 14/8.

Catalyst=100 mg, $W/F=28 \text{ g-cat}\cdot\text{h}\cdot\text{mol}^{-1}$, 600°C.
○ Ru/ La_2O_3 , □ Ru/ Al_2O_3 , ◆ Ni/ Al_2O_3 .

Fig. 1 Effect of Reaction Time on the Rate of Formation of CO

Ni/Al₂O₃ catalyst showed high activity in the reaction of heptane with CO₂. This reaction afforded a large amount of carbon deposition on the catalyst, and such carbon deposition on Ni catalysts was reported previously in the reaction of CH₄ with CO₂^{15),23),24)}. The catalytic activity did not decrease after 120 min. This seems to be attributed to the high level of loading of Ni to alumina (23 wt%). Even though a part of Ni was covered with carbon, or formation of whisker carbon did occur, catalytic activity did not deteriorate drastically. Attributed to a large amount of carbon deposition, it became difficult to continue further, the reaction using Ni(23 wt%)/Al₂O₃ by the pressure build up in the inlet of the reactor. Because of low catalytic activity, no further long-run was carried out for Ru/Al₂O₃ catalyst.

Rostrup *et al.* reported that carbon deposition was less on Ru and Rh supported on Al₂O₃ than on Ni⁶⁾. Ru and Ir supported on Eu₂O₃ were used, and Ru loadings as low as 1 wt% was reported to be highly effective as compared to highly loaded catalysts¹⁷⁾.

Here, we employed basic La₂O₃ as a support, and Ru(0.2 wt%)/La₂O₃ showed much higher activity than Ru(1.0 wt%)/Al₂O₃. Ru/La₂O₃, which showed a high initial activity, deactivated rapidly and after 300 min its activity decreased to *ca.* 1/4 of its initial activity. In the run with Ru/La₂O₃, a small amount of carbon deposition was observed after 120 min of the reaction. After oxidizing the catalyst with air to remove carbon, the catalytic activity recovered, which was lower than the initial activity of the fresh catalyst.

Uchijima *et al.*¹⁹⁾ reported on the effects of supports on the catalytic activity in the CO₂ reforming of CH₄ and stated that the catalytic activity of Rh/SiO₂ was improved by physical mixing of basic metal oxides, such as MgO. In order to improve catalyst stability, ten times as much amount of alkali metal (Li, Na, K, Cs), in mole, against Ru(0.2 wt%), was added to Ru/La₂O₃ catalyst, which was calcined at 550°C for 300 min in flow of CO₂. Results of 120 min runs (cumulative amounts of products) are shown in Fig. 2. Ru/La₂O₃ catalyst showed the highest activity, judging from conversion of heptane, whereas the highest yield of CO plus H₂, in 120 min run was obtained with Ru-Li/La₂O₃ catalyst. In the case of Ru/La₂O₃ catalyst, a small amount of carbon deposition was observed, and in addition a large amount of H₂O was produced. On the other hand, addition of other alkali metal hydroxide completely poisoned the catalytic activity. Kikuchi *et al.*³⁾ reported on steam reforming of methane with Ru catalysts supported on γ -Al₂O₃

Catalyst=200 mg, Alkali metal/Ru=10 (mol/mmol), W/F=43 g-cat·h·mol⁻¹, 600°C, 2 h.

Fig. 2 Effect of Various Alkali Metals to Ru/La₂O₃ Catalyst on the Conversion and Yields of CO and H₂ in the CO₂ Reforming of Heptane

Catalyst=200 mg, W/F=43 g-cat·h·mol⁻¹, 600°C. □ Li/Ru=0, ○ Li/Ru=3, △ Li/Ru=10.

Fig. 3 Effect of the Amount of Li Loading to the Ru/La₂O₃ Catalyst on the CO₂ Conversion, the Rate of CO Formation and CO/H₂ Ratio

Catalyst=200 mg, $W/F=43$ g-cat·h·mol⁻¹, 600°C.
 □ Ru-Li/La₂O₃ (air treated), △ Ru-Li/La₂O₃ (CO₂ treated), ○ Ru-Li/La₂(CO₃)₃.

Fig. 4 Effect of CO₂ Treatment and Supports on the CO₂ Conversion, the Rate of CO Formation and CO/H₂ Ratio

and TiO₂, promoted with Li₂CO₃ and K₂CO₃. They found that the activity was drastically reduced by the addition of K₂CO₃. Promotion of activity with alkali metals, therefore seems to depend on the electronegativity of alkali metal cation.

Figure 3 shows the effect of the amount of Li on the Ru/La₂O₃ catalyst. Increasing Li to Ru molar ratio from 3 to 10, the favorable effect of Li decreased slightly. Deactivation of the catalyst decreased, as compared to the catalyst without Li, and improvement in the CO/H₂ ratio after reaction of 100 min was remarkable.

Figure 4 shows effects of pretreatment conditions of catalyst and the use of La₂(CO₃)₃ as support on the activity and its decay. When Ru-Li/La₂O₃ catalyst was treated with CO₂ before introducing heptane, deactivation of the catalyst was greatly reduced. Use of La₂(CO₃)₃ as a

Cu-K α radiation.

○ La₂O₃, □ La₂O₂CO₃.

- a) Ru-Li/La₂O₃ calcined before reaction 550°C for 5 h in air flow.
- b) Ru-Li/La₂O₃ after CO₂ reforming at 600°C for 5 h.
- c) Ru-Li/La₂O₃ calcined before reaction 550°C for 5 h in CO₂ flow.

Fig. 5 XRD Patterns of Ru-Li/La₂O₃ Catalyst before and after the Reaction

support of Ru caused a moderate initial setback in the catalytic activity. These results suggest that interaction between the catalyst or the support and CO₂ are closely related to the deactivation process of the catalyst.

In order to understand the above process, XRD analyses of the catalysts treated under different conditions were conducted. Results of XRD analyses of Ru-Li/La₂O₃ calcined in flow of air (before reaction), Ru-Li/La₂O₃ calcined in CO₂ (before reaction), and Ru-Li/La₂O₃ calcined in flow of air (after reaction) are shown in **Fig. 5**. The chemical species of lanthanum, after the reaction with heptane and calcined in a flow of CO₂ (before reaction), were assigned as La₂O₂CO₃. Formation of La₂O₂CO₃ was more effective for this reaction, and calcination in a flow of CO₂ as pretreatment was beneficial for the formation of La₂O₂CO₃, while Ru/La₂O₃ catalyst had not formed La₂O₂CO₃ after CO₂ reforming.

Catalyst-Ru-Li/La₂O₃(Li/Ru=10)=200 mg, 600°C, 2 h.
 □ n-C₇ conversion, ◇ H₂O, △ H₂, ○ CO, × CH₄.

Fig. 6 Effect of W/F on the Heptane Conversion and the Amounts of Products Formed

Addition of lithium hydroxide greatly enhanced formation of La₂O₂CO₃ species. CO₂ reacted with LiOH to give Li₂CO₃ and formation of Li₂CO₃³⁾, probably promoted formation of La₂O₂CO₃. It seems reasonable that constant activity of the catalyst for long run is responsible for the basic carbonate of lanthanum oxide or CO₃²⁻ species, from which CO₂ may spillover to Ru metal and would react with carbon or C_xH_y species on the Ru surface. Thus higher catalytic activity would be exhibited.

H₂O is considered to be produced by the side reactions shown in Eqs. (3)-(5) as evidenced by the larger CO/H₂ ratio than 14/8. **Figure 6** shows effect of W/F on the amount of H₂O. With increasing W/F above 40 g-cat·h/mol, the amounts of CO and H₂O increased markedly, with a decrease in the amount of H₂. These results seem to suggest that H₂O was produced mainly by Eq. (3).

4. Conclusion

Ru/La₂O₃ catalyst showed higher activity than Ru/Al₂O₃. Ru/La₂O₃ catalyst, however, deactivated rapidly. The high activity of Ru/La₂O₃ catalyst was maintained when lanthanum carbonate or CO₃²⁻ was formed in the initial stages of

the reaction. The best way to prepare the catalysts is to add Li to Ru/La₂O₃ catalyst which is calcined in flow of CO₂ at 550°C before the reaction.

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要 旨

ルテニウム担持酸化ランタン触媒を用いたヘプタンの CO₂ リフォーミング

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Ni および Ru 触媒を用いてヘプタン (C₇H₁₆) の CO₂ リフォーミングを行った。Ni 担持 Al₂O₃ 触媒および Ru 担持 Al₂O₃ 触媒は多量の炭素析出が起こり、2 時間の反応で反応管が閉そくした。一方、Ru 担持 La₂O₃ 触媒はヘプタンの CO₂ リフォーミングに対し、600°C で高い触媒活性を示した。CO₂ リフォーミングでは炭素析出を防ぐ必要があるが、Ru 担持 La₂O₃ 触媒は急速に触媒活性が低下した。しかし、反応中の触媒活性の劣化は触媒に LiOH (Li/Ru=3) を添加することにより防止でき、炭素析出も見られなかった。Ru 担持 La₂O₃

触媒に LiOH を添加することで、CO₂ が触媒担体である La₂O₃ に La₂O₂CO₃ として濃縮されることに対して、促進効果があることが示された。高い触媒活性を維持するためには CO₂ が触媒担体である La₂O₃ に La₂O₂CO₃ として濃縮され、活性種近傍の CO₂ 濃度が増加することが重要であると示唆された。また、CO/H₂ 比はヘプタンと CO₂ の反応の量論比よりも大きくなったが、これは生成した H₂ と未反応の CO₂ との逆水性ガスシフト反応による CO の生成が考えられる。

Keywords

Ruthenium catalyst, Lanthanum carbonate, Carbon dioxide, Heptane, Lanthanum oxide support, Steam reforming