Low-temperature steam reforming of *n*-butane over Rh and Ru catalysts supported on ZrO_2

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In the 500 ° C steam reforming reaction of *n*-butane, Rh and Ru catalysts supported on ZrO_2 exhibited high catalytic activities for hydrogen production at a low steam-to-carbon ratio with little activity decline.

Keywords: Steam reforming; low-temperature; rhodium catalyst; ruthenium catalyst; zirconia support

1. Introduction

Steam reforming reactions of hydrocarbons are widely used to produce hydrogen and syngas. Since steam reforming is generally a strongly endothermic reaction [1], current reforming processes for hydrogen production use at high temperature nickel catalysts (800–900°C) which supply heat by fuel combustion. In the near future, it is expected that hydrogen demands will increase due to the development of new fuel cell systems and the processing of heavy and hydro-deficient feedstocks. To obtain higher thermal efficiencies, a hydrogen producing catalyst must have sufficient catalytic activity at the lowest temperature, while also performing steam reforming at a low steam-to-carbon ratio without carbon deposition.

The present paper reports on Rh and Ru catalysts supported on ZrO_2 which were used to obtain outstanding activities during low-temperature steam reforming reactions of *n*-butane.

2. Experimental

The ZrO_2 support was obtained by calcination of hydroxide in a N_2 stream for 1 h at 500°C, with rhodium chloride trihydrate being impregnated onto ZrO_2 when Rh was used as the catalyst's metallic component. The dried material was

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Table 1
Catalytic activities and gas product compositions of Rh/commercial catalysts[a]

Catalyst	Conversion of *n*-butane (%)	Gas product composition (%)			
		CO	CH_4	CO_2	H_2
Rh/ZrO_2	82.6	2.9	14.9	20.3	61.9
Rh/Al_2O_3	31.3	14.0	6.4	10.6	69.0
Rh/SiO_2[b]	4.1	5.9	~0	15.5	78.5
C11-2S-03[c]	90.4	2.3	20.7	19.9	57.1

[a] Temperature: 500°C; *SV*: 40,000 h^{-1}; H_2O/C ratio: 3; and reaction time: 5 h.
[b] SV: 10,000 h^{-1}.
[c] Reaction time: 1 h. Carbon deposition caused a blockage in the reactor at greater than 1.5 h.

again calcined in a N_2 stream for 1 h at 500 ° C, then pelletized and crushed (0.5–1.0 mm in dia.). In addition, other catalysts were similarly prepared by the above impregnation method, i.e., Rh/Al_2O_3 (γ-Al_2O_3, JRC-ALO-4), Rh/SiO_2 (silica gel, Davison "ID"), noble metal catalysts supported on ZrO_2 (Pd, Pt, Ir, and Ru: all obtained from chloride sources), and Ni/ZrO_2 whose Ni source was nitrate. The metallic component of noble metal catalysts was 0.5 wt% and that of Ni/ZrO_2 was 10 wt%. A commercial catalyst for steam reforming of low molecular weight hydrocarbons (CCI: C11-2S-03, 16 wt%, Ni/CaO-Al_2O_3) was used to compare respective activities.

Steam reforming of *n*-butane was performed at atmospheric pressure using a conventional microreactor with a fixed bed catalyst. Reaction conditions were as follows: temperature, 500°C and 450°C; total feed space velocity (*SV*), 40,000 h^{-1}; H_2O/C ratio (mol/atom), 3. All catalysts were reduced in a H_2 stream for 1 h at 500°C.

3. Results and discussion

Table 1 shows the reforming activities (i.e., the %-conversion of *n*-butane per volume of catalyst) and gas product compositions of the Rh and commercial catalysts at 500°C. Only the commercial catalyst's initial activity was determined (1 h) because carbon deposition caused a blockage in the reactor at the reaction time of 1.5 h, thus the catalyst could not be used at the present study's low steam-to carbon reaction conditions, although its initial activity was quite high. It should be noted that the Rh/ZrO_2 catalyst had higher catalytic activity than the Rh/Al_2O_3 catalyst, whereas, in spite of the low space velocity ($SV = 10,000$ h^{-1}), the activity was very low for the Rh/SiO_2 catalyst. Significant variations in the gas product compositions for the Rh/ZrO_2 and Rh/Al_2O_3 should also be noticed. Fig. 1 shows the Rh/ZrO_2 and Rh/Al_2O_3 catalytic activities with respect to reaction time (500°C), where the Rh/ZrO_2 catalyst appears to have a

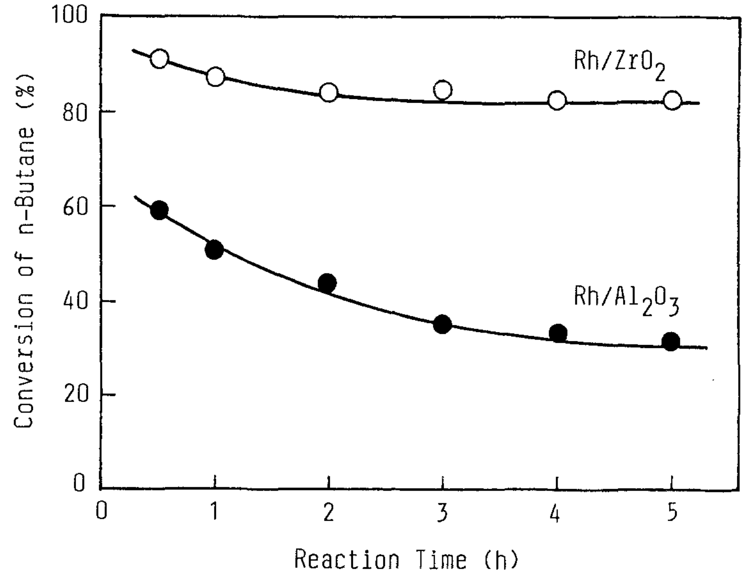

Fig. 1. Catalytic activities of the Rh/ZrO_2 and Rh/Al_2O_3 catalysts. Temperature: 500°C; *SV*: 40,000 h^{-1}; and H_2O/C ratio: 3.

lower deactivation rate as compared to the Rh/Al_2O_3 catalyst. The effect of the H_2O/C ratio on the Rh/ZrO_2 catalytic activity is shown in fig. 2, and it is clear that Rh/ZrO_2 has high activity even at a low H_2O/C ratio. The theoretical gas

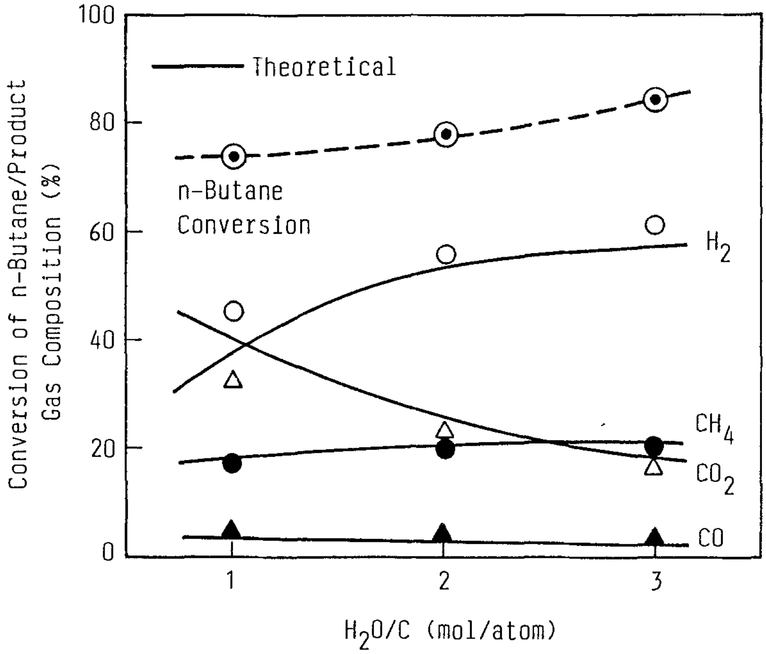

Fig. 2. Effects of the H_2O/C ratio on the catalytic activity and gas product compositions (○: H_2; ●: CO_2; △: CH_4; ▲: CO) of the Rh/ZrO_2 catalyst. Temperature: 500°C; and *SV*: 40,000 h^{-1}.

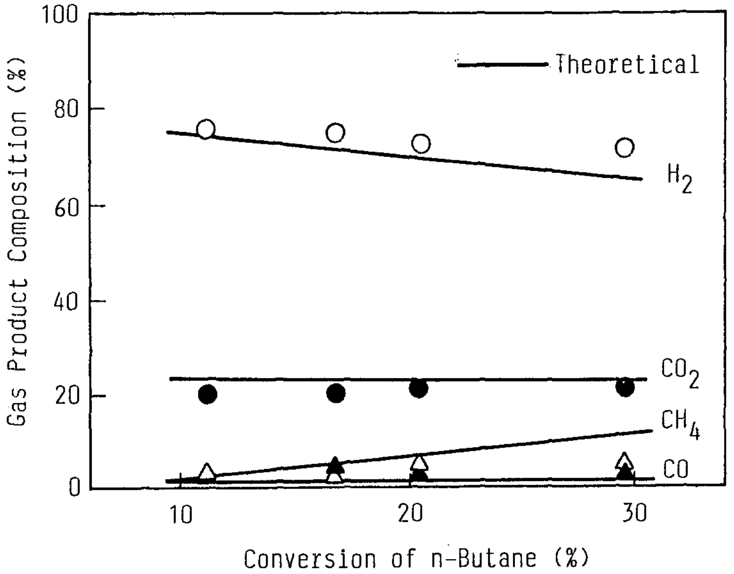

Fig. 3. Comparison of experimental and theoretical gas product compositions over a Rh/ZrO_2 catalyst. The symbols are the same as for fig. 2. Temperature: 450°C; *SV*: 40,000 h^{-1}, and H_2O/C ratio: 3.

product composition was obtained using a kinetic equilibrium calculation [2] of the following reactions:

$$n\text{-}C_4H_{10} + 4\ H_2O \rightarrow 4\ CO + 9\ H_2 \tag{1}$$

$$CO + 3\ H_2 \rightleftarrows CH_4 + H_2O \tag{2}$$

$$CO + H_2O \rightleftarrows CO_2 + H_2. \tag{3}$$

The good agreement shown between the calculated and experimental values indicates that the reactions over the Rh/ZrO_2 catalyst are close to those obtained at a 500°C thermodynamic equilibrium state. Figs. 3 and 4 compare the experimental and theoretical gas product compositions over the Rh/ZrO_2 and Rh/Al_2O_3 catalysts at 450°C, respectively. The relationship between the %-conversion of *n*-butane and the gas product compositions was obtained by changing the space velocity. As shown in fig. 3, the experimental and theoretical values were initially approximately equal, thereby indicating that kinetic equilibrium is established and that oxidation of CO, i.e., the water-gas shift reaction (2), occurs markedly fast over the Rh/ZrO_2 catalyst. By contrast, fig. 4 shows that the experimental CO_2 content for Rh/Al_2O_3 was much less than the theoretical one, being in good agreement with Kikuchi et al. [3] for the steam reforming of *n*-butane over Rh/Al_2O_3. These results indicate slow CO oxidation over the Rh/Al_2O_3 catalyst. The catalytic activities and gas product compositions of Rh, Ru, and Ni catalysts supported on ZrO_2 (450°C) are also shown in table 2. Pd, Ir, and Pt catalysts supported on ZrO_2 had little catalytic activity. It should be

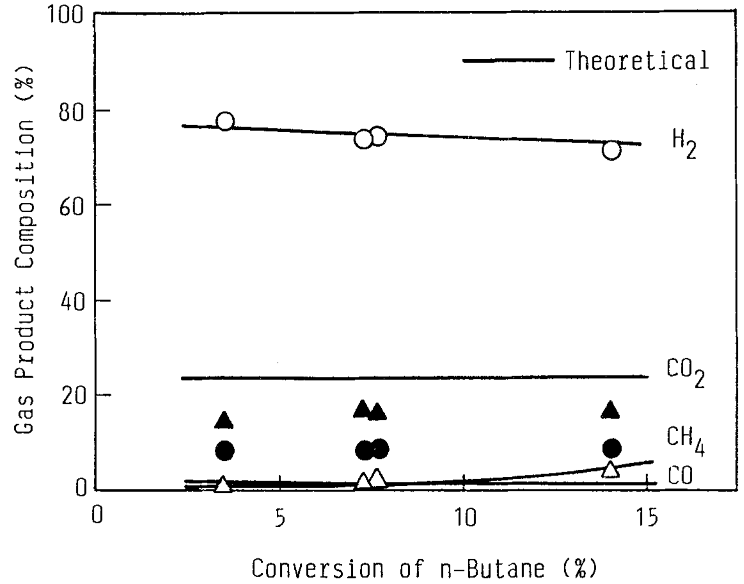

Fig. 4. Comparison of experimental and theoretical gas product compositions over a Rh/Al_2O_3 catalyst. Symbols are the same as fig. 2. Temperature: 450°C; SV: 40,000 h^{-1}, and H_2O/C ratio: 3.

noted that the Ru/ZrO_2 and Rh/ZrO_2 catalysts have nearly equal high activities, an important result for industrial catalyst applications since Rh is more expensive than Ru. Although the Ni/ZrO_2 catalyst showed very high activity, carbon deposition caused a blockage in the reactor at reaction times greater than 4 h. These high Rh and Ru catalytic activities correlate with both Dowden's prediction [4] and the experimental results of steam reforming of methane and ethane when respectively using SiO_2 [5] and Al_2O_3 [6] as supports. It is also interesting to note that the Ru/ZrO_2 catalyst's CH_4 content is at the equilibrium value as compared with the Rh/ZrO_2 catalyst's CH_4 content, thus indicating that the reaction proceeds very smoothly over the Ru/ZrO_2 catalyst.

Based on these results, it is believed that ZrO_2 supports have superior properties for low-temperature steam reforming over Rh and Ru catalysts.

Table 2
Catalytic activities and gas product compositions of Rh, Ru, and Ni catalysts [a]

Catalyst	Conversion of *n*-butane (%)	Gas product composition (%)			
		CO	CH_4	CO_2	H_2
Rh/ZrO_2	50.6	2.1	12.3	19.2	66.4
Ru/ZrO_2	53.8	0.9	23.8	20.0	55.3
Ni/ZrO_2 [b]	78.7	2.1	25.1	19.0	53.8

[a] Temperature: 450°C; SV: 40,000 h^{-1}; H_2O/C ratio: 3; and reaction time: 5 h.

[b] Carbon deposition caused a blockage in the reactor at greater than 4 h.

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