[Research Note]

Fischer-Tropsch Reaction over Bimodal Porous Ru/SiO₂ Catalysts Prepared by Alkoxide Method

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Bimodal porous Ru/SiO₂ catalysts for the Fischer-Tropsch reaction were prepared by modifying the surface of macro-porous silica with Ru-SiO₂ prepared by the alkoxide method. The Ru particle size estimated by H₂ adsorption increased with the pore size of the macro-porous silica, whereas the Ru crystallite size evaluated by XRD line broadening did not show much variation. The bimodal catalysts showed high and stable activity in the slurry phase under the reaction conditions of $T = 493\text{--}503\text{ K}$, $P = 1\text{ MPa}$, $\text{H}_2/\text{CO} = 2/1$, and $W/F = 5\text{ g-catal.h/mol}$, with reduction in the used amounts of the expensive alkoxide. Selectivity for higher hydrocarbons increased with increasing pore diameter of the catalysts, which can be explained in terms of diffusivity of the slurry solvent and/or the products in the pores, and the effect of the Ru particle size depending on the macro-pore size of the catalysts.

Keywords

Alkoxide method, Bimodal pore structure, Fischer-Tropsch reaction, Particle size, Ruthenium catalyst

1. Introduction

Uniformly dispersed Ru-SiO₂ catalysts prepared by the alkoxide method show stable Fischer-Tropsch (F-T) reaction activity in the slurry phase¹⁾, and is thought to result from the ultra uniform structure. However, small pore size of the catalyst will generally limit the mobility of higher molecular weight products and the slurry solvent because of the low diffusivity^{2,3)}, which may give rise to unfavorable secondary reactions, such as cracking and further hydrogenation of products, resulting in low selectivity for higher hydrocarbons.

High F-T activity can be obtained over Co catalysts supported on bimodal pore-structured materials prepared by simply modifying wide pore silica with silica sol, zirconia sol, alumina sol, and so on^{4)~10)}. The high dispersion of Co and the improved diffusion of the products in the wide pores of the bimodal catalysts are probably responsible for the high activity. If the internal surface of the wide pores of an inert support is modified with alkoxide-derived catalyst, instead of silica sol, the efficiency of the alkoxide-derived catalyst will increase, resulting in greater selectivity for higher hydrocarbons as well as high and stable activity.

In the present study, the surface of macro-porous silica was modified with alkoxide-derived Ru-SiO₂ precursor, to prepare bimodal pore-structured Ru/SiO₂ catalysts.

2. Experimental**2.1. Preparation of Catalysts**

The detailed procedure of the alkoxide method has been described elsewhere¹⁾. The required amount of ruthenium nitrosyl nitrate (Soekawa Chemicals) was dissolved in 0.35 mol of ethylene glycol (Nakarai Tesque), then mixed with 0.15 mol of tetraethyl ortho-silicate (Nakarai Tesque) to form a homogeneous solution by heating below 343 K. The required amount of finely ground macro-porous silica (Fuji Silysia, Q-10, Q-15, Q-30, and Q-50; average pore diameter (D) = 10, 15, 30, and 50 nm, respectively) was impregnated with the homogeneous solution at room temperature. Distilled water (11 cm³) was added to the impregnated mixture at room temperature, resulting in slow hydrolysis at 363 K for 40 h to form gel. The gel was dried and calcined in air flow at 823 K for 15 h to remove organic compounds, resulting in Ru-SiO₂(alk)/Q- n , where $n = 10, 15, 30$ and 50 .

2.2. Fischer-Tropsch Reaction

After reduction in H₂ flow at 473 K, 0.5 g of Ru-SiO₂(alk)/Q- n catalyst was suspended in 50 cm³ of hexadecane under an inert atmosphere, and utilized as the catalyst for the F-T reaction in a continuous stirring tank reactor (CSTR; $V = ca. 100\text{ cm}^3$) with a specially designed stirring rod¹¹⁾ to achieve complete mixing in the reactor. The reaction conditions were as follows: $\text{H}_2/\text{CO} = 2/1$, $T = 493\text{--}503\text{ K}$, $P = 1\text{ MPa}$, and $W/F = 5\text{ g-catal.h/mol}$. The effluent gas was periodically analyzed with Shimadzu on-line gas chromatographs,

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Table 1 BET Surface Area (S), Pore Volume (V_p) and Pore Diameter (D_p) of Macro-porous Silica^{a)} and Bimodal Porous Catalysts^{b)}

	S [$\text{m}^2 \cdot \text{g}^{-1}$]	V_p [$\text{cm}^3 \cdot \text{g}^{-1}$]	D_p [nm]
Q-10 ^{a)}	260	1.0	12
Q-15 ^{a)}	170	1.0	18
Q-30 ^{a)}	110	1.0	31
Q-50 ^{a)}	70	1.0	48
Ru-SiO ₂ (alk)/Q-10 ^{b)}	380	0.5	4, 8
Ru-SiO ₂ (alk)/Q-15 ^{b)}	280	0.5	4, 13
Ru-SiO ₂ (alk)/Q-30 ^{b)}	390	0.5	4, 23
Ru-SiO ₂ (alk)/Q-50 ^{b)}	310	0.5	4, 45
Ru-SiO ₂ (alk) ^{c)}	710	0.5	4

a) Commercial SiO₂ (Fuji Silysia).

b) [20 wt% Ru-SiO₂(alk)]/[Q- n] = 1 : 1 by weight (n = 10, 15, 30 and 50).

c) 10 wt% Ru-SiO₂ catalyst prepared by the alkoxide method.

model 17A with hydrogen-flame ionization detector (FID) and model 14B with a thermal conductive detector (TCD), to determine the C₁-C₁₀ hydrocarbons and inorganic gases, respectively. The C₁₁+ hydrocarbons in the slurry were determined separately by gas chromatography after the reaction. The procedure was described in detail previously¹²⁾.

2. 3. Characterization of Catalysts

X-Ray powder diffraction (XRD) patterns were recorded using a Mac Science MPX-18 diffractometer with Cu-K α irradiation (40 kV, 150 mA). Multipoint BET surface area, pore volume, and BJH pore size distribution of the catalysts were calculated from the adsorption-desorption isotherm of N₂ at 77 K, using an automatic gas adsorption apparatus, ASAP-2000.

3. Results and Discussion

Table 1 shows the BET surface areas and pore volumes of the macro-porous silica and the bimodal porous catalysts. The increase in surface area and decrease in pore volume of the catalysts, compared to the corresponding macro-porous silica, suggest that the surface of the silica was effectively covered with alkoxide-derived Ru-SiO₂⁷⁾.

Figure 1 is an image of a bimodal porous catalyst. The surface of the macro-porous silica is covered with Ru-SiO₂(alk) prepared by the alkoxide method. The macro-pore size of the catalyst is somewhat smaller than that of the macro-porous silica due to thickness of the covering Ru-SiO₂(alk), whereas the meso-pore size of the catalyst is the same as that of Ru-SiO₂(alk) with uniform pore size.

The pore size distributions of the catalysts are depicted in **Fig. 2**. The meso-pore size of the bimodal porous Ru-SiO₂(alk)/Q-30 catalysts ((b), (c)) was identical to that of the Ru-SiO₂(alk) catalyst (a) prepared by the alkoxide method, whereas the bimodal porous catalysts had smaller macro-pore size compared to the original macro-porous Q-30 silica (d). As the [Ru-SiO₂(alk)]/

Fig. 1 Image of Bimodal Pore Structure

Fig. 2 Pore Size Distribution of (a) Ru-SiO₂(alk) Catalysts Prepared by the Alkoxide Method, (b) Bimodal Porous Ru-SiO₂(alk)/Q-30 Catalyst with [Ru-SiO₂(alk)]/[Q-30] = 4 : 1 by Weight, (c) Bimodal Porous Ru-SiO₂(alk)/Q-30 Catalyst with [Ru-SiO₂(alk)]/[Q-30] = 1 : 1 by Weight, and (d) Q-30 Silica

[Q-30] ratio increased, the macro-pore size became smaller, indicating a thicker layer of Ru-SiO₂(alk). These results clearly indicate that the bimodal pore structure was effectively formed.

The time courses of the F-T reaction over the catalysts are shown in **Fig. 3**. Relatively stable F-T activity was obtained over bimodal porous Ru-SiO₂(alk)/Q-15 (b) and Ru-SiO₂(alk)/Q-30 (c) catalysts, as well as Ru-SiO₂(alk) catalyst (a) prepared by the alkoxide method.

Although the stability of the F-T activity of the catalysts (b) and (c) was slightly less than that of catalyst (a), higher CO conversion was obtained over the bimodal porous catalysts. In contrast, rapid deactivation was observed over conventional Ru/SiO₂ catalyst (d) prepared by impregnation. The uniform structure of Ru-SiO₂(alk) is thought to be responsible for the stable F-T activity, as pointed out previously¹⁾. The effects of macro-pore size (D_p) on the F-T reaction results over the bimodal porous 10 wt% Ru-SiO₂(alk)/Q- n catalysts are illustrated in Fig. 4, as the mean values during reaction for 40 h. With increasing D_p , selectivity for CH₄ decreased, and selectivity for higher hydrocarbons (C₅₊) and carbon chain growth probability (α) increased. As pointed out previously¹³⁾, the higher diffusivity of the slurry solvent and/or the reaction products in larger pores may be responsible for the higher selectivity for

Fig. 3 Time Courses of the F-T Reaction over (a) 10 wt% Ru-SiO₂(alk) Catalyst Prepared by the Alkoxide Method, (b) Bimodal Porous Ru-SiO₂(alk)/Q-15 Catalyst ([Ru-SiO₂(alk)]/[Q-15] = 1 : 1 by Weight, and Loading Amount of Ru = 10 wt%), (c) Bimodal Porous Ru-SiO₂(alk)/Q-30 Catalyst ([Ru-SiO₂(alk)]/[Q-30] = 1 : 1 by Weight, and Loading Amount of Ru = 10 wt%), and (d) 10 wt% Ru/SiO₂(imp) Catalyst Prepared by Impregnation, under Reaction Conditions of $T = 503$ K, $P = 1$ MPa, $H_2/CO = 2/1$, and $W/F = 5$ g-catal.h/mol

higher hydrocarbons, because of effective removal of the local heating caused by the extremely exothermic F-T reaction at the active sites.

When the [Ru-SiO₂(alk)]/[Q-30] ratio was changed in the range of 4 : 1-1 : 3 by weight (or [Ru-SiO₂(alk)]/[SiO₂] = 0.8-0.25, where [SiO₂] = [Ru-SiO₂(alk)] + [Q-30]), CH₄ selectivity decreased, and selectivity for higher hydrocarbons (C₅₊) and carbon chain growth probability (α) increased with decreasing [Ru-SiO₂(alk)]/[SiO₂] ratio, as summarized in Table 2. To adjust the total loading amount of Ru to 10 wt% of the catalyst, each Ru-SiO₂(alk) precursor was prepared according to the ratio. For example, 12.5 wt% Ru-SiO₂(alk) was used as the precursor for preparing the catalyst with the ratio of [Ru-SiO₂(alk)]/[Q-30] = 4 : 1, and 40 wt% Ru-SiO₂(alk) precursor was used for preparing the catalyst with the ratio of [Ru-SiO₂(alk)]/[Q-30] = 1 : 3. Higher [Ru-SiO₂(alk)]/[SiO₂] ratio resulted in thicker coating layer of the bimodal porous catalyst as described above, resulting in smaller macro-pore size (D_p). The dependency of the F-T reaction selectivity on the ratio coincided well with the explanation of the relationship between selectivity and D_p , as

Fig. 4 Effect of Macro-pore Diameter (D_p) of Bimodal Porous 10 wt% Ru-SiO₂(alk)/Q- n Catalysts ($n = 10, 15, 30$, and 50) on the F-T Reaction, under Reaction Conditions of $T = 503$ K, $P = 1$ MPa, $H_2/CO = 2/1$, and $W/F = 5$ g-catal.h/mol

Table 2 Effect of [Ru-SiO₂(alk)]/[SiO₂] Ratio on Fischer-Tropsch Reaction^{a)} over Bimodal Porous Ru-SiO₂(alk)/Q-30 Catalysts Prepared by the Alkoxide Method

[Ru-SiO ₂]/[SiO ₂] ^{b)}	CO conv. [%]	CH ₄ selec. [C-%] ^{c)}	CO ₂ selec. [C-%] ^{c)}	C ₅₊ selec. [C-%] ^{c)}	α ^{d)}	O/P ^{e)}
0.80	13.8 ± 1.3	6.3	0.0	80.8	0.82	1.8
0.67	13.0 ± 1.2	5.7	0.0	79.0	0.84	1.8
0.33	12.7 ± 1.1	5.4	0.0	83.9	0.84	1.8
0.25	10.9 ± 1.5	5.1	0.0	83.8	0.86	1.7

a) Reaction conditions: $T = 493$ K, $P = 1$ MPa, $H_2/CO = 2/1$, $W/F = 5$ g-catal.h/mol.

b) [SiO₂] = [Q-30] + [Ru-SiO₂(alk)]; total loading amount of Ru = 10 wt%.

c) Carbon-based selectivity.

d) Carbon chain growth probability.

e) Olefin/paraffin ratio in C₂-C₄ hydrocarbon products.

Fig. 5 Effect of Macro-pore Diameter (D_p) of Bimodal Porous 10 wt% Ru-SiO₂(alk)/Q- n Catalysts ($n = 10, 15, 30$, and 50) on Ru Crystallite Size Evaluated by XRD Line Broadening (L^X), and Ru Particle Size Estimated by H₂ Adsorption (L^H)

Fig. 6 TEM Photographs of (a) 10 wt% Ru-SiO₂(alk) Catalyst Prepared by the Alkoxide Method, and (b) Bimodal Porous 10 wt% Ru-SiO₂(alk)/Q-50 Catalyst

mentioned above. However, the changes in CO conversion in **Table 2** cannot be explained, since the total loading amounts of Ru in these catalysts were nominally identical. The Ru particle size depending on the ratio (or D_p) may be responsible for the CO conversion.

Figure 5 shows the effects of macro-pore diameter (D_p) of the bimodal porous Ru-SiO₂(alk)/Q- n catalysts (Ru loading amount = 10 wt%) on Ru crystallite size (L^X) evaluated by XRD line broadening, and Ru particle size (L^H) estimated by H₂ adsorption. The crystallite size slightly varied, whereas the particle size increased with the pore diameter.

Transmission electron microscope (TEM) photographs of the fresh catalysts are shown in **Fig. 6**. Uniform dispersion of Ru particles was observed on Ru-SiO₂(alk) catalysts. However, some agglomerations of Ru particles were observed on Ru-SiO₂(alk)/Q-30 and Ru-SiO₂(alk)/Q-50 catalysts, indicating that uniform small Ru particles of Ru-SiO₂(alk) were aggregated into larger particles, and the sizes were dependent on the pore sizes of the catalysts. Since macro-pore sizes of

Fig. 7 Effect of Ru Particle Size (L^H) on C₅₊ Selectivity and Carbon Chain Growth Probability (α) in the F-T Reaction over Bimodal Porous 10 wt% Ru-SiO₂(alk)/Q- n Catalysts ($n = 10, 15, 30$, and 50) under Reaction Conditions of $T = 493$ - 503 K, $P = 1$ MPa, H₂/CO = 2/1, and W/F = 5 g-catal.h/mol

Q- n silica were not so uniform as Ru-SiO₂(alk), a distribution was observed in the sizes of the agglomerated Ru particles. The slight deactivation over bimodal porous catalysts may be related to this distribution.

The dependencies of C₅₊ selectivity and carbon chain growth probability (α) on Ru particle size (L^H) in the present investigation are shown in **Fig. 7**. With increasing L^H , both C₅₊ selectivity and α tended to increase, but large variations were observed. Based on the Ru particle size dependency on the macro-pore size of the bimodal porous catalysts, another explanation may be also applicable to the relationship between macro-pore size and F-T selectivity; *i.e.* larger Ru particles are favorable to higher selectivity for higher hydrocarbons. Lower C₅₊ hydrocarbon selectivity has been already reported over Ru catalysts with smaller particle size or higher dispersion¹⁴⁾. Modeling of catalysts containing metal clusters has suggested that large ensembles of Ru atoms are required for steady formation of long chain products¹⁵⁾.

In conclusion, bimodal porous Ru-SiO₂(alk)/Q- n catalysts were prepared by modifying the surface of macro-porous silica (Q- n) with Ru-SiO₂(alk) prepared by the alkoxide method. The selectivity for higher hydrocarbons (C₅₊) and the carbon chain growth probability (α) increased with the macro-pore size of the bimodal porous catalysts. These characteristics of the F-T reaction can be explained in terms of the diffusivity of the slurry and/or the products in the pores of the catalysts, and the effect of Ru particle size depending on the macro-pore size of the catalysts.

References

- 1) Okabe, K., Takahara, I., Inaba, M., Murata, K., Yoshimura, Y., *J. Jpn. Petrol. Inst.*, **50**, (1), 65 (2007).
- 2) Fan, L., Yokota, K., Fujimoto, K., *AIChE J.*, **38**, (10), 1639 (1992).
- 3) Yan, S., Fan, L., Zhang, Z., Zhou, J., Fujimoto, K., *Appl. Catal. A: General*, **171**, (2), 247 (1998).
- 4) Xu, B., Fan, Y., Zhang, Y., Tsubaki, N., *AIChE J.*, **51**, (7), 2068 (2005).
- 5) Zhang, Y., Shinoda, M., Tsubaki, N., *Catal. Today*, **93-95**, 55 (2004).
- 6) Shinoda, M., Zhang, Y., Yoneyama, Y., Hasegawa, K., Tsubaki, N., *Fuel Proc. Tech.*, **86**, (1), 73 (2004).
- 7) Zhang, Y., Yoneyama, Y., Fujimoto, K., Tsubaki, N., *Topics Catal.*, **26**, (1-4), 129 (2003).
- 8) Sun, S., Fujimoto, K., Zhang, Y., Tsubaki, N., *Catal. Commun.*, **4**, (8), 361 (2003).
- 9) Zhang, Y., Yoneyama, Y., Tsubaki, N., *Chem. Commun.*, (11), 1216 (2002).
- 10) Tsubaki, N., Zhang, Y., Sun, S., Mori, H., Yoneyama, Y., Li, X., Fujimoto, K., *Catal. Commun.*, **2**, (10), 311 (2001).
- 11) Okabe, K., Wei, M., Arakawa, H., *Energy & Fuels*, **17**, (4), 822 (2003).
- 12) Okabe, K., Li, X., Matsuzaki, T., Toba, M., Arakawa, H., Fujimoto, K., *Sekiyu Gakkaishi (J. Jpn. Petrol. Inst.)*, **42**, (6), 377 (1999).
- 13) Okabe, K., Murata, K., Nurunnabi, M., Liu, Y., *J. Jpn. Petrol. Inst.*, **52**, (3), 139 (2009).
- 14) Nijs, H. H., Jacobs, P. A., Verdonck, J. J., Uytterhoeven, J. B., *Stud. Surf. Sci. Catal.*, **4**, 479 (1980).
- 15) Welker, C., Moss, J. R., van Steen, E., Claeys, M., *Erdoel Erdgas Kohle*, 223 (2006).

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要 旨

アルコキシド法により調製した二元細孔構造 Ru/SiO₂触媒による Fischer-Tropsch 合成

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アルコキシド法により調製した Ru-SiO₂で大細孔径シリカ表面を修飾することにより二元細孔構造を持つ Ru/SiO₂触媒を調製し, Fischer-Tropsch (F-T) 合成反応を行った。X 線回折の線幅から見積もられる Ru 結晶子径はシリカの細孔径にあまり依存しなかったが, 水素吸着量から推定される Ru 粒子径は大細孔シリカの細孔径の増加に伴って増大した。このようにして調製した二元細孔構造触媒は, $T=493\sim 503\text{ K}$, $P=1\text{ MPa}$, $\text{H}_2/$

$\text{CO}=2/1$, $W/F=5\text{ g-catal.h/mol}$ の反応条件下でのスラリー相 F-T 反応において, 高価なアルコキシドの使用量を軽減した上で, 高く安定した触媒活性を示した。触媒の細孔径の増大に伴って, メタン選択率が減少し, 高級炭化水素への選択率が増加することが認められた。これら選択率の細孔径依存性は, 細孔内におけるスラリー溶媒および反応生成物の拡散速度, ならびに触媒細孔径に依存する Ru 粒子径の違いによって説明された。

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