

[Research Note]

Effects of Pore Size of Ru–Al₂O₃ Catalysts Prepared by Alkoxide Method on Fischer-Tropsch Reaction

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10 wt% Ru–Al₂O₃ catalysts with uniform pore sizes in the range of 3–7 nm were prepared by the alkoxide method by changing the added amount of H₂O highly diluted with butanol at the gelation stage of sol-gel preparation. The prepared catalysts were used to catalyze the Fischer-Tropsch (F-T) reaction in the slurry phase under reaction conditions of $T = 503$ K, $P = 1$ MPa, $H_2/CO = 2/1$, and $W/F = 5$ – 10 g-catal.h/mol. The Ru crystallite size evaluated by XRD line broadening increased with pore diameter. Stable activity in the F-T reaction was obtained for more than 40 h, probably because of the uniform structure of the catalysts. CO conversion and selectivity for higher hydrocarbons increased, and selectivity for CH₄ decreased with pore size of the catalysts. The effect can be explained in terms of diffusivity of the slurry solvent and/or the products in the uniform meso-pores, suggesting that the F-T reaction results depend more on the effect of the pore size of the catalysts than the Ru particle size.

Keywords

Alkoxide method, Fischer-Tropsch reaction, Particle size, Pore size, Ruthenium catalyst

1. Introduction

Investigations of conventional catalysts with non-uniform structure^{1)–5)} have not revealed any clear relationship between pore size and the catalytic performance in the Fischer-Tropsch (F-T) reaction, since the wide distribution of pore sizes allows no unambiguous findings. Correct evaluation of the effect of pore size requires the preparation of the catalysts with ultra-uniform structure.

Ru–SiO₂ catalysts prepared by the alkoxide method are reported to have uniform structures with stable activity in the F-T reaction⁶⁾. The sol-gel formation of SiO₂ proceeds relatively slowly by the alkoxide method, so the preparation conditions can be varied over a wide range to accurately control the pore size⁷⁾. In contrast, Al-alkoxides are more rapidly hydrolyzed to form Al₂O₃, so the potential for accurate control of the pore size is more limited.

Evaluation of conventional Ru-based catalysts prepared by impregnation suggests that catalysts supported on Al₂O₃ generally show higher catalytic activity than those on SiO₂, because higher dispersion of Ru can be easily obtained over Al₂O₃. TPR results indicate that Ru/SiO₂ is reduced at lower temperature than Ru/Al₂O₃⁸⁾, suggesting stronger interaction between Ru and Al₂O₃ preventing the sintering of Ru, resulting in higher

dispersion of Ru on Al₂O₃.

In the present study, Ru–Al₂O₃ catalysts with various uniform pore structure were prepared by carefully controlling the preparation conditions in the alkoxide method to investigate the effect of pore size on the catalytic performance in the F-T reaction.

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

The detailed procedure of the alkoxide method has been described elsewhere⁹⁾. The required amount of ruthenium chloride (Wako Pure Chemical Ind.) was dissolved in a mixture of 0.3 mol of hexylene glycol (Kanto Chemical Co.) and 1 mol of 2-butanol (Nakarai Tesque). The solution was mixed with 0.09 mol of aluminum tri-*s*-butoxide (Kanto Chemical Co.) at 337 K in a moisture-free system to form a highly diluted homogeneous solution. After stirring at 337 K for 4 h, distilled water diluted with butanol (2.4–16 cm³/150 cm³) was added to the solution at room temperature, resulting in hydrolysis to form gel. After 15 h, the obtained gel was dried and calcined in an air flow at 823 K for 15 h to remove organic compounds, resulting in 10 wt% Ru–Al₂O₃.

2.2. Fischer-Tropsch Reaction

After reduction at 573 K, 0.5 g of Ru–Al₂O₃ was suspended in 50 cm³ of hexadecane, and utilized as the catalyst for the F-T reaction in a continuous stirring tank

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Table 1 Effect of Added H₂O on Physical Properties of 10 wt% Ru-Al₂O₃ Catalysts Prepared by the Alkoxide Method

[H ₂ O]/[Al] ^{a)}	<i>S</i> [m ² ·g ⁻¹]	<i>V_p</i> [cm ³ ·g ⁻¹]	<i>D_p</i> [nm]
1.5	210	0.3	3.3
3	190	0.4	4.6
10	200	0.6	6.5

a) Molar ratio of H₂O and Al at the stage of gelation.

reactor (CSTR; $V = ca. 100 \text{ cm}^3$) with a specially designed stirring rod¹⁰⁾ to achieve complete mixing in the reactor. The reaction conditions were as follows: H₂/CO = 2/1, $T = 503 \text{ K}$, $P = 1 \text{ MPa}$, and $W/F = 5\text{-}10 \text{ g-catal.h/mol}$. The effluent gas was periodically analyzed with Shimadzu on-line gas chromatographs, model 17A with FID (hydrogen-flame ionization detector) and model 14B with a TCD (thermal conductivity detector), 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 previously¹¹⁾.

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, 100 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

The effects of various amounts of H₂O added at the stage of gelation in the alkoxide method on the physical properties of the final catalysts are summarized in **Table 1**. Increasing amounts in the range of [H₂O]/[Al] = 1.5-10 did not cause the specific surface area (*S*) to vary so much, but the pore volume (*V_p*) and the pore diameter (*D_p*) increased. Consequently, the pore diameter of Ru-Al₂O₃ catalysts prepared by the alkoxide method was enlarged from 3.3 nm to 6.5 nm. The pore size distribution curves are shown in **Fig. 1**. A sharp peak indicates uniform pore structure. The peak width increased slightly with the pore diameter, but was still sharper than commercially available Al₂O₃.

The effect of the pore size on the crystallite size (*L*) of Ru evaluated by XRD line broadening is depicted in **Fig. 2**. The crystallite size increased with the pore diameter (*D_p*), and *L* was always larger than *D_p*. This relationship was already discussed previously¹²⁾.

The time courses of the F-T reaction are illustrated in **Fig. 3**. CO conversion was stable for more than 40 h, probably because of the uniform structure of the catalysts. The products of the F-T reaction over 10 wt% Ru-Al₂O₃ prepared by the alkoxide method are listed in

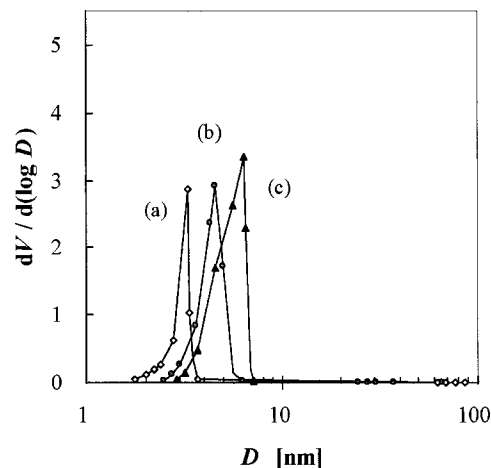


Fig. 1 Pore Size Distribution of 10 wt% Ru-Al₂O₃ Catalysts Prepared by the Alkoxide Method with Added Amounts of H₂O in the Highly Diluted Homogeneous Sol of (a) [H₂O]/[Al] = 1.5, (b) [H₂O]/[Al] = 3, and (c) [H₂O]/[Al] = 10

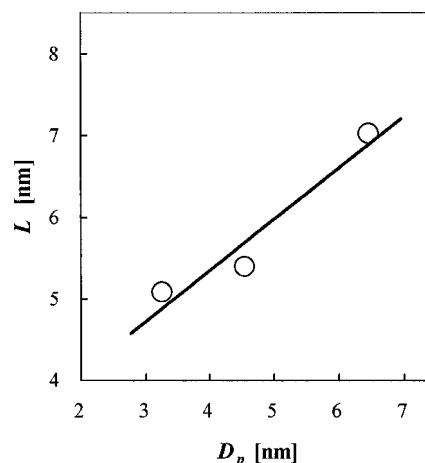


Fig. 2 Effect of Pore Diameter of 10 wt% Ru-Al₂O₃ Catalysts Prepared by the Alkoxide Method on Crystallite Size of Ru Evaluated by XRD Line Broadening

Table 2 as the mean values observed during 40 h of reaction. Increasing pore size resulted in increased CO conversion and selectivity for higher hydrocarbons, but decreased CH₄ selectivity (Runs 1-3). To verify the influence of conversion level on selectivity, the F-T reaction was conducted at $W/F = 10 \text{ g-catal.h/mol}$ (Run 4) over the same catalyst as Run 1. Run 4 showed higher CO conversion than Run 1 because of the increased W/F , but the selectivity did not change so much under the present investigation conditions. Therefore, the changes in the selectivity among Runs 1-3 cannot be ascribed to different conversion levels.

The changes in selectivity may be explained in terms of diffusivity of the slurry solvent and/or the products in the meso-pores of the catalysts. The diffusivity increases with pore size. If the diffusion rate is high enough, the heat of the extremely exothermic F-T reaction on the

active sites in the small pores may be effectively removed by the slurry solvent and/or the reaction products, resulting in prevention of local over-heating in the pores of the catalysts. At lower temperatures, the selectivity for higher hydrocarbons may be higher, so suppressing CH₄ formation¹³). If the diffusion rate is low in small pores, the chances of secondary reactions such as cracking of hydrocarbon products may also increase, resulting in lower selectivity for higher hydrocarbons^{1)~5}). Therefore, the higher diffusivity in larger pores may be responsible for higher conversion, by minimizing the effects of the diffusion limits of reactants and products.

Another explanation proposed for gas-phase or supercritical phase F-T reaction simulation¹⁴) suggests that the different diffusion rates between CO and H₂ in small pores of a catalyst may lead to a low CO/H₂ ratio at active sites in the pores, resulting in higher CH₄ selectivity.

The size of Ru crystallites increased with the pore size of the catalysts. The Ru particle size may also affect the selectivity. Lower F-T activity and lower C₅₊ hydrocarbon selectivity have been already reported over Ru catalysts with smaller particle size or higher dispersion¹⁵). Modeling of catalysts containing metal clus-

ters has suggested that large ensembles of Ru atoms are required for steady formation of long chain products¹⁶). A similar explanation for the effect of the metal dispersion on the catalytic performance in the F-T reaction has been suggested by experience with Co catalysts supported on carbon nanofiber with smaller Co particles¹⁷). Cobalt particles larger than 6-8 nm are needed for higher activity and higher C₅₊ hydrocarbons selectivity, since "the F-T reaction comprises of a large number of elementary steps, such as dissociation, hydrogenation, and insertion; *i.e.* a variety of sites may be needed." The particle size must be larger than a certain value to provide a variety of sites on a metallic particle. Similar assumptions may be applicable to the present F-T reaction results over the Ru-Al₂O₃ catalysts prepared by the alkoxide method; *i.e.* the dependency of the Ru particle size on pore size may affect the F-T reaction.

However, it is also reported over some Ru/Al₂O₃ catalysts that no consistent relationship between chain length of hydrocarbon products and metal particle size (dispersion) emerges, although the specific activity decreases with increasing dispersion up to 0.7^{18),19}). If only the Ru particle size, but not the pore size, is responsible for the changes in the F-T reaction results in **Table 2**, the dependency of the selectivity on the catalysts is inexplicable. Therefore, the present F-T reaction results depend more on the effect of the pore size of the catalysts than the Ru particle size.

In conclusion, by varying the amount of H₂O added at the stage of gelation, the uniform pore sizes of Ru-Al₂O₃ catalysts prepared by the alkoxide method were enlarged. Larger pore size resulted in decreased selectivity for CH₄ and increased selectivity for C₅₊ hydrocarbons. These characteristics in the F-T reaction can be explained in terms of the diffusivity of the slurry and/or the products in the meso-pores of the catalysts.

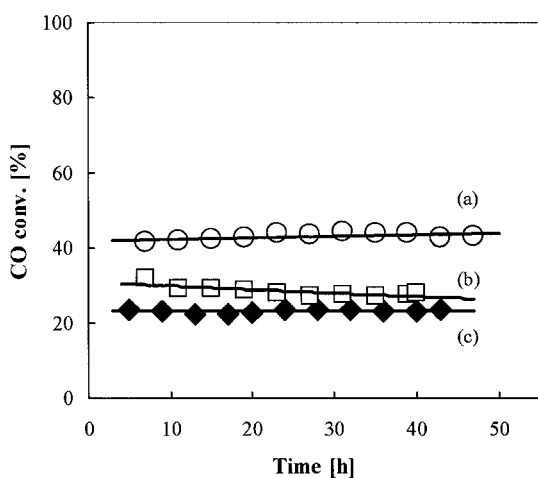


Fig. 3 Time Courses of the F-T Reaction over 10 wt% Ru-Al₂O₃ Catalysts Prepared by the Alkoxide Method with Pore Diameter of (a) 6.5 nm, (b) 4.6 nm, and (c) 3.3 nm

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Table 2 Effects of Pore Diameter on Fischer-Tropsch Reaction^{a)} over 10 wt% Ru-Al₂O₃ Catalysts Prepared by the Alkoxide Method

	D_p [nm]	CO conv. [%]	CH ₄ selec. [C-%] ^{b)}	CO ₂ selec. [C-%] ^{b)}	C ₅₊ selec. [C-%] ^{b)}	$\alpha^c)$	O/P ^{d)}
Run 1	3.3	23.6 ± 0.5	9.8	0.0	73.3	0.83	1.9
Run 2	4.6	28.5 ± 1.4	7.3	0.0	79.7	0.83	1.8
Run 3	6.5	42.9 ± 1.1	5.3	0.0	84.8	0.84	2.0
Run 4 ^{e)}	3.3	42.1 ± 1.8	10.0	0.0	76.1	0.83	

a) Reaction conditions: $T = 503$ K, $P = 1$ MPa, $H_2/CO = 2/1$, $W/F = 5$ g-catal.h/mol.

b) Carbon-based selectivity.

c) Carbon chain growth probability.

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

e) $W/F = 10$ g-catal.h/mol.

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要 旨

アルコキシド法により調製した Ru-Al₂O₃触媒の細孔径の Fischer-Tropsch 合成に及ぼす影響

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アルコキシド法による Ru-Al₂O₃触媒の調製段階において、多量のブタノールで希釈した蒸留水の添加量を変化させることにより、触媒の均質な細孔径を3~7 nmの範囲で変化させた。このようにして調製した10 wt% Ru-Al₂O₃触媒を用い、 $T=503\text{ K}$, $P=1\text{ MPa}$, $\text{H}_2/\text{CO}=2/1$, $W/F=5\sim 10\text{ g-catal.h/mol}$ の反応条件下において、スラリー相での Fischer-Tropsch 合成を行っ

た。触媒の X 線回折のピーク半値幅から求めた Ru 結晶子径は細孔径とともに増大した。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。これらの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によって説明され、Ru 粒子径よりも触媒細孔径の重要性が示唆された。