

[Research Note]

Effects of Ru Precursors on Activity of Ru-SiO₂ Catalysts Prepared by Alkoxide Method in Fischer-Tropsch Synthesis

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(Received June 14, 2006)

Ru-SiO₂ catalysts with uniform structure were prepared by the alkoxide method using various Ru precursors, and used to catalyze the Fischer-Tropsch (F-T) synthesis in the slurry phase under the reaction conditions of $T = 503$ K, $P = 1$ MPa, $H_2/CO = 2/1$, and $W/F = 5$ g-catal.h/mol. All catalysts showed stable activity during the F-T reaction for 40 h. The CO conversion was relatively low over the catalyst prepared from ruthenium chloride, because of the trace amounts of residual Cl on the surface. The catalysts prepared from ruthenium nitrosyl nitrate and ruthenium acetylacetonate showed high activity, with suppression of CH₄ and CO₂ formation. The CO conversion linearly increased with the loading amounts of Ru, indicating identical dispersion of Ru regardless of the amount. The olefin/paraffin ratio of the products could be explained in terms of the electronic state of Ru on the catalysts.

Keywords

Alkoxide method, Fisher-Tropsch reaction, Ruthenium precursor, Ruthenium catalyst

1. Introduction

Ruthenium is a well known active component of catalysts for the Fischer-Tropsch reaction, although Ru-based catalysts are not so commonly used as Fe- and Co-based catalysts, because of the high cost¹. As a result, investigations of the Fischer-Tropsch reaction over Ru-based catalysts have been limited. The supports of Ru-based catalysts affect the CO/H₂ reaction². Although the main products are light hydrocarbons including CH₄, Ru/TiO₂ catalysts have higher turnover frequencies and better olefin selectivity. A strong metal-support interaction (SMSI) is presumably responsible for "the epitaxial stabilization of preferred crystal faces, and/or transfer of electrons between the metal particles and the support"². The electronic effect of K and P addition to Ru/Al₂O₃ catalyst increases or decreases the olefin/paraffin ratios in the products of CO hydrogenation, and decreases CO conversion³. The basic properties of rare earth promoters added to Ru/Al₂O₃ catalysts increases the selectivity for higher hydrocarbons⁴. However, in both cases, the main products were light hydrocarbons. High selectivity for olefins was obtained over Ru/MnO₂ catalysts, but the chain growth probability (α) was less than 0.8⁵. Supercritical phase Fischer-Tropsch synthesis over Ru/Al₂O₃

catalysts with various pore size distributions showed that the α -value increased with the pore diameter⁶. Excellent selectivity was obtained, but the supercritical process is not practical for industrial use.

We previously reported that uniformly dispersed Co-Ir-SiO₂ catalysts prepared by the alkoxide method had stable activity for the Fischer-Tropsch reaction in the slurry phase^{7,8}. The ultra uniform structure is thought to be responsible for the stability. However, the catalytic activity of Co-based catalysts is generally not high enough without the inclusion of noble metal promoters such as Ir or Ru, because most Co in the catalysts prepared by the alkoxide method is strongly bound to the silica matrix. In contrast with Co- and Fe-based catalysts, Ru is easily activated under mild conditions, and high activity can be expected. Therefore, if high selectivity is obtained, Ru-based catalysts with uniform structure have the potential to provide better performance in the Fischer-Tropsch reaction than Co- and Fe-based catalysts, in spite of the high cost.

In the present study, Ru-SiO₂ catalysts with uniform structure were prepared by the alkoxide method, and the effects of the Ru precursors on the catalytic activity for the Fischer-Tropsch reaction in the slurry phase were investigated.

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2. Experimental

2.1. Preparation of Catalysts

The detailed procedure of the alkoxide preparation method has been described previously^{7),8)}. The required amounts of ruthenium chloride (Kanto Chemicals), ruthenium nitrosyl nitrate (Soekawa Chemicals), or ruthenium acetylacetonate (Wako Pure Chemicals) were dissolved in 0.35 mol of ethylene glycol (Nacalai Tesque). If necessary, a small amount of ethanol was added to promote dissolution, and the solution was mixed with 0.15 mol of tetraethyl orthosilicate (Nacalai Tesque) to form a homogeneous solution by heating below 343 K. Distilled water diluted with ethanol (11 cm³/11 cm³) was added to the solution at room temperature, resulting in slow hydrolysis at 353 K for 40 h to form transparent glassy gel. The obtained gel was dried and calcined in an air flow at 823 K for 15 h to remove organic compounds, resulting in 2-20 wt% Ru-SiO₂. The catalysts are named Ru(Cl)-SiO₂, Ru(N)-SiO₂, and Ru(acac)-SiO₂, according to the Ru precursor.

2.2. Fischer-Tropsch Reaction

After reduction at 773 K, 1 g of Ru-SiO₂ was suspended in 50 cm³ of hexadecane, 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 rod^{9),10)} to achieve complete mixing system in the reactor. The reaction conditions were as follows: H₂/CO = 2/1, $T = 503 \text{ K}$, $P = 1 \text{ MPa}$, and $W/F = 5 \text{ g-catal.h/mol}$. The effluent gas was periodically analyzed with a Shimadzu on-line gas chromatograph (model 17A with FID detectors and model 14B with a TCD 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 previously¹⁰⁾.

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). X-Ray photoelectron spectroscopy (XPS) measurements were conducted with a Shimadzu ESCA-850 with Mg-K α irradiation (8 kV, 30 mA), without exposure to air after pretreatment at 573 K for 1 h in a flow of H₂ within a

pre-chamber of the apparatus. The binding energies of XPS were referred to the evaporated Au on the surface as an internal standard with Au 4f_{7/2} level at 83.8 eV. Bulk concentrations of the catalysts were determined by an X-ray fluorescence spectrometer, Seiko SEA 2010. Multi point 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. The metallic surface area of the catalysts was determined by H₂ adsorption at 308 K, using the ASAP-2000.

3. Results and Discussion

The bulk and surface compositions of the catalysts are listed in **Table 1**. Since the solubility of ruthenium acetylacetonate in ethylene glycol was slightly low, the loading amount of Ru in the corresponding catalyst, Ru(acac)-SiO₂, was slightly less than in the others. The bulk concentrations of impurities were less than the detection limit of X-ray fluorescence analysis (XRF).

The surface concentration of Ru was almost identical in all the catalysts, irrespective of the Ru precursor. The atomic ratio Ru/Si determined by XPS contains a large experimental error, and Ru/Si = 0.1 corresponds to about 15 wt% Ru, which is less than the bulk amount determined by XRF. A small amount of Cl was detected on the surface of Ru(Cl)-SiO₂. The XPS Ru 3p_{3/2} line of Ru(N)-SiO₂ showed lower binding energy than that of the other two catalysts, suggesting that the Ru on Ru(N)-SiO₂ was electronically richer.

The uniform dispersion of particles observed by TEM and the sharp distribution of pore sizes indicated the uniform structure of the catalysts prepared by the alkoxide method⁷⁾.

The products of the Fischer-Tropsch reaction over 20 wt% Ru-SiO₂ catalysts are summarized in **Table 2** as the mean values during 40 h of reaction. All catalysts showed stable activity, and the deviation was within 6%. The CO conversion over Ru(Cl)-SiO₂ catalyst was lower than that over Ru(N)-SiO₂ and Ru(acac)-SiO₂, probably because of the residual Cl. A similar effect of Cl has been reported for Ru/Al₂O₃ catalysts prepared by impregnation¹¹⁾. The residual Cl on the surface inhibits both CO and H₂ chemisorp-

Table 1 Bulk^{a)} and Surface^{b)} Compositions of 20 wt% Ru-SiO₂ Catalysts Prepared by the Alkoxide Method

Catalyst	Ru (bulk) ^{a)} [wt%]	Ru/Si ^{b)}	Cl/Si ^{b)}	$E_b(\text{Ru})^{\text{c)}$ [eV]
Ru(Cl)-SiO ₂	17 ± 2	0.1 ± 0.05	0.01 ± 0.005	461.2 ± 0.1
Ru(N)-SiO ₂	18 ± 2	0.1 ± 0.05	—	461.0 ± 0.1
Ru(acac)-SiO ₂	15 ± 2	0.1 ± 0.05	—	461.3 ± 0.1

a) Determined by XRF.

b) Determined by XPS.

c) Binding energy of XPS Ru 3p_{3/2} line.

Table 2 Fischer-Tropsch Reaction Products^{a)} over 20 wt% Ru-SiO₂ Catalysts Prepared by the Alkoxide Method

Catalyst	CO conv. [%]	CH ₄ selec. [C-%] ^{b)}	CO ₂ selec. [C-%] ^{b)}	C ₅₊ selec. [C-%] ^{b)}	α^c	O/P ^{d)}
Ru(Cl)-SiO ₂	22.7 ± 2.7	5.6	0.2	86.3	0.83	1.5
Ru(N)-SiO ₂	61.8 ± 6.0	3.9	0.6	89.7	0.82	0.9
Ru(acac)-SiO ₂	67.6 ± 2.6	3.0	0.8	91.1	0.84	1.3
Co-Ir-SiO ₂ ^{e)}	48.9 ± 2.5	11.5	2.5	62.5	0.79	0.4

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) 20 wt% Co-0.5 wt% Ir-SiO₂ catalyst prepared by the alkoxide method as a reference¹⁶⁾ ($W/F = 10$ g-catal.h/mol, apparent dispersion = 0.4%).

Table 3 Results of Hydrogen Adsorption on 20 wt% Ru-SiO₂ Catalysts^{a)} Prepared by the Alkoxide Method, and Crystallite Size of Ru Estimated by XRD

Catalyst	H ₂ volume adsorbed [cm ³ /g STP]	Dispersion of Ru ^{b)} [%]	Ru crystallite size [nm]
Ru(Cl)-SiO ₂	0.8 ± 0.1	3.6 ± 0.2	16
Ru(N)-SiO ₂	1.0 ± 0.1	4.6 ± 0.2	15
Ru(acac)-SiO ₂	1.1 ± 0.1	5.1 ± 0.2	16

a) After F-T reaction.

b) Calculated from H₂ adsorption.

tion¹²⁾, resulting in the low activity of the catalysts. In fact, the H₂ volume adsorbed on Ru(Cl)-SiO₂ was smaller than that on Ru(N)-SiO₂ and Ru(acac)-SiO₂, as shown in **Table 3**. The identical crystallite sizes of Ru for these three catalysts suggested that the smaller amount of H₂ adsorption inhibited by the trace amount of the residual Cl on the surface resulted in the apparent low dispersion of Ru on Ru(Cl)-SiO₂.

Relatively higher CH₄ selectivity and lower C₅₊ selectivity were obtained over the Ru(Cl)-SiO₂ catalyst. The C₅₊ selectivity generally increases with increasing CO conversion over a series of Co-based catalysts^{13),14)}. At high conversion, the H₂/H₂O ratio of the gas phase in the reactor is low under the same reaction conditions, resulting in low CH₄ selectivity and high C₅₊ selectivity¹⁵⁾. A similar explanation may be applicable to the present reaction results.

The olefin selectivity in the C₂₋₄ hydrocarbon products was lower over Ru(N)-SiO₂ catalyst. As mentioned above, the electron density of surface Ru on Ru(N)-SiO₂ catalyst was relatively higher (or Ru on the catalyst was more metallic) than the other two catalysts, suggesting that the hydrogenation activity of the former was higher, resulting in enhancement of the secondary hydrogenation of olefins.

The effect of the loading amount of Ru on CO conversion over Ru(N)-SiO₂ is illustrated in **Fig. 1**. The CO conversion increased linearly with the loading amount, suggesting that the intrinsic activity of the Ru particles was the same, irrespective of the loading amount. The effects of the loading amounts on the dispersion of Ru particles determined by H₂ adsorption

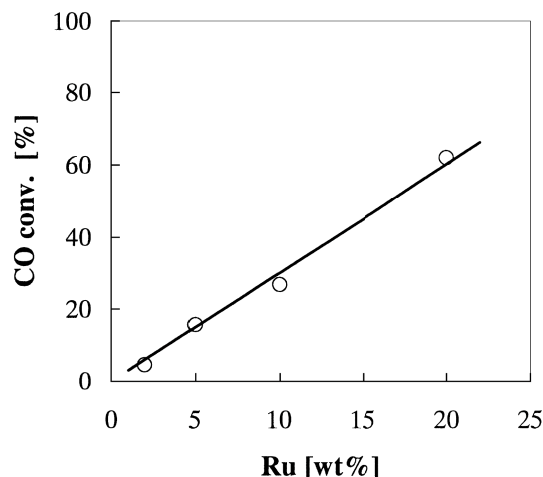


Fig. 1 Effect of Loading Amount of Ru on CO Conversion over Ru(N)-SiO₂ Catalysts Prepared by the Alkoxide Method

and on the Ru crystallite sizes are depicted in **Fig. 2**. The dispersion and the crystallite sizes slightly varied with the loading amount, indicating that the particle sizes were almost the same irrespective of the loading amount, and that the numbers of the particles only increased, resulting in an increase in the number of active sites. Therefore, catalysts with identical particle size of Ru were obtained by the alkoxide method.

In conclusion, high selectivity for C₅₊ hydrocarbons of about 90% was obtained over uniform Ru-SiO₂ catalysts prepared by the alkoxide method from ruthenium nitrosyl nitrate and ruthenium acetylacetonate precursors, with suppression of CH₄ formation to less than

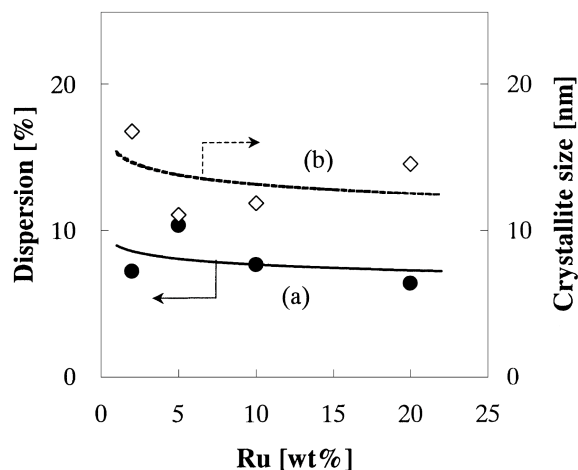


Fig. 2 Effect of Loading Amount of Ru on (a) Dispersion and (b) Crystallite Size of Ru on Ru(N)-SiO₂ Catalysts Prepared by the Alkoxide Method

4%, under mild reaction conditions. The formation of undesirable CH₄ was much lower over Ru-SiO₂ catalysts than over Co-based catalysts prepared by the alkoxide method¹⁶⁾.

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要 旨

アルコキシド法により調製した Ru-SiO₂ 触媒上での Fischer-Tropsch 合成における Ru 前駆体の影響

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各種の Ru 前駆体を用い, 均質な構造を有する Ru-SiO₂ 触媒をアルコキシド法で調製し, $T=503\text{ K}$, $P=1\text{ MPa}$, $\text{H}_2/\text{CO}=2/1$, $W/F=5\text{ g-catal.h/mol}$ の反応条件下で, スラリー相での Fischer-Tropsch 合成を行った。塩化物から調製した触媒では, 表面に残留する微量の Cl のために活性が低かった。ニトロシル硝酸塩やアセチルアセトン錯塩から調製した触媒は高く安定

した活性を示し, CH₄ や CO₂ の生成が抑制された。Ru 担持率と CO 転化率の間にはよい直線関係が得られたことから, Ru 分散度は担持量によらず一定であることが示唆される。生成物中に含まれるオレフィン/パラフィン比の違いは, 触媒の Ru の電子状態の違いによって説明された。