

[Research Note]

Fischer-Tropsch Synthesis over Metal-promoted Co–Ir–SiO₂ Catalysts Prepared by the Alkoxide Method

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A series of metal-promoted 20 wt%Co–0.5 wt%Ir–SiO₂ catalysts was prepared by the alkoxide method, and the effects of additives (MO_x; M = K, Cr, Al, Ce, La, and Mn) on the catalysis of Fischer-Tropsch reaction were investigated. K-Promoter reduced CO conversion. Al- or Cr-promoter resulted in almost the same CO conversion as over the catalyst without additives, but CH₄ selectivity increased. La- or Ce-promoter decreased C₅₊ selectivity. In contrast, CO conversion and the α -value (the chain growth probability of CH_x intermediates) increased up to 57% and 0.85, respectively, over catalysts with 10 wt% Mn promoter. However, further addition of Mn caused deactivation of the catalyst. Selectivity for CH₄ showed a linear relationship with the standard enthalpy of formation ($-\Delta H_f^\theta$) of the promoter oxides (MO_x).

Keywords

Additive, Alkoxide method, Cobalt catalyst, Fischer-Tropsch reaction, Sol-gel method

1. Introduction

Uniformly dispersed Co–Ir–SiO₂ catalysts prepared by the alkoxide method have high and stable activity for the Fischer-Tropsch reaction in slurry phase¹. However, the selectivity for higher hydrocarbons is not greatly improved by changing the pore properties². The activity and selectivity can be adjusted by adding metal oxide promoters (MO_x; M = Zr, La, Cr, etc.) to the Co-based catalysts commonly used in the Fischer-Tropsch synthesis. The promotion effect of the additives may be due to the presence of partially reduced promoter oxides which provide binding sites for the oxygen atoms of CO, thus facilitating its dissociation³, or the coverage of the active surface by the promoter, leading to decreased or increased chemisorption capacity⁴. The present study investigated the effect of the promoters (MO_x; M = K, Cr, Al, Ce, La, and Mn) on the Fischer-Tropsch synthesis over 20 wt%Co–0.5 wt%Ir–SiO₂ catalysts prepared by the alkoxide method, by adding the precursors of MO_x at the preparation stage of the catalysts.

2. Experimental**2.1. Preparation of Co–SiO₂ Catalysts by the Alkoxide Method**

The catalyst preparation by the alkoxide method was described previously¹. The precursors of MO_x additives (KNO₃, Al(NO₃)₃·9H₂O, Cr(NO₃)₃·9H₂O, La(NO₃)₃·6H₂O, Ce(NO₃)₄·6H₂O, and Mn(NO₃)₂·6H₂O) were GR grade chemicals, used without further purification. The required amounts of the metal precursor (M/Co = 0.1, atomic ratio), Co(NO₃)₂·6H₂O, and IrCl₄·H₂O were dissolved in 0.35 mol of ethylene glycol, and mixed with 0.15 mol of tetraethyl orthosilicate (TEOS) 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 with vigorous stirring, resulting in a homogeneous clear sol. The sol was slowly hydrolyzed to form a glassy gel at 353 K for 40 h. The gel was dried and calcined in an air flow at 823 K for 15 h to remove organic compounds in the gel, and then reduced in a H₂ flow at 673 K to form the MO_x–20 wt%Co–0.5 wt%Ir–SiO₂ catalysts (M: additive).

2.2. Characterization of Catalysts

X-Ray powder diffraction (XRD) analysis was performed, using a diffractometer (Mac Science, MPX-18) with Cu–K α radiation (40 kV, 150 mA). X-Ray photoelectron spectroscopy (XPS) measurements were conducted with Shimadzu ESCA-850 with Mg–K α radi-

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Table 1 Effect of Promoters on Catalytic Properties^{a)} and Crystallite Size of Co

M	CO conv. [%]	Selectivity [C-%]				<i>L</i> ^{b)} [nm]
		CH ₄	CO ₂	C ₂₋₄	C ₅₊	
—	48.9	11.5	2.5	23.5	62.5	11.1
K	36.0	13.5	3.6	14.7	68.2	6.6
Al	53.6	13.3	1.5	19.9	65.4	9.7
Cr	52.7	13.8	3.0	20.7	62.4	4.7
La	49.2	13.9	3.6	27.1	55.5	8.1
Ce	56.6	12.9	3.9	24.9	58.3	9.6
Mn	55.3	11.4	2.1	19.5	67.0	9.1

a) Catalyst: MO_x-20 wt%Co-0.5 wt%Ir-SiO₂ (M: additive, M/Co = 0.1).

b) Crystallite size of Co determined by XRD line broadening.

tion (8 kV, 30 mA).

2. 3. Fischer-Tropsch Reaction

After reduction, the catalyst (2 g) was suspended in 50 cm³ of hexadecane under an inert atmosphere. The F-T reaction was carried out with the catalyst slurry in an autoclave-type semi-batch reactor (flow type for gas phase), with a volume of approximately 100 cm³. The feed gas (H₂ : CO : Ar = 60 : 30 : 10) was bubbled into the slurry, and dissolution of the gas into the slurry was promoted by a specially designed stirring rod⁵⁾. The reaction conditions were as follows: *T* = 503 K, *P* = 1 MPa, and *W/F* = 10 g-cat.·h/mol. The effluent gas was periodically analyzed with a Shimadzu on-line gas chromatograph model 14B or 17A with thermal conductivity detector (TCD) and hydrogen-flame ionization detector (FID) detectors, and inorganic gases and C₁₋₁₄ hydrocarbons were determined, using Ar in the sample gas as the internal standard. The C₁₀₊ hydrocarbons in the slurry were determined separately by gas chromatography after the reaction. The procedure was described previously in detail¹⁾.

3. Results and Discussion

Table 1 shows the effects of additives (MO_x) on the Fischer-Tropsch reaction. The additives were divided into 4 groups, based on the activity and selectivity of the catalysts: (a) K, which decreased the CO conversion; (b) Al and Cr, which did not affect the conversion significantly, but increased CH₄ selectivity; (c) La and Ce, which decreased C₅₊ selectivity; and (d) Mn, which increased CO conversion and C₅₊ selectivity.

XPS measurement of the group (a) catalyst found that K had accumulated on the surface of the catalyst, which might block the active sites. Similar "site blocking" was also found on K-promoted Ru/SiO₂ catalysts⁶⁾. The effect may operate either by reducing the availability of H₂ on the surface, or an ensemble effect due to the presence of K.

Among the numerous promoters of the Fischer-

Tropsch synthesis catalysts, Al is the most frequently investigated as a textural promoter. As shown in **Table 1**, the Co⁰ crystallite size decreased from 11.1 nm for Co-Ir-SiO₂ catalyst to 9.7 nm and 4.7 nm for Al- or Cr-Co-Ir-SiO₂ catalysts, respectively, suggesting that the Al and Cr in the catalysts prevented the growth of the Co⁰ particles. C₅₊ selectivity increases with the dispersion of Co⁰, but we did not observe any significant improvement in the selectivity for group (b) catalysts, because of the small dispersion range. Investigation of Cr promoted Co/MnO catalysts found obvious changes in hydrocarbon selectivity with an increase in chain growth probability (α)⁸⁾. However, we did not observe any remarkable effect on the catalysts prepared by the alkoxide method, though CH₄ selectivity increased slightly.

Adequate conversion was obtained over the group (c) catalysts, as shown in **Table 1**. However, the selectivity for heavy hydrocarbons clearly decreased, whereas CH₄ selectivity slightly increased. Rare earth oxides are generally used as promoters^{9),10)}. La and Ce promoters improved the activity and the selectivity for olefins and higher hydrocarbons over carbon-supported Co catalysts¹¹⁾. The effect was explained as new active sites formed by the migration of patches of partially reduced rare earth oxides to the Co surface during activation. However, the opposite effect was also reported¹²⁾. The reduction of Ce might lead to the active surface being covered with the promoter, resulting in decreased chemisorption capacity to "the detriment of the C₂₂₊ fraction." Our results were close to the latter finding, with no positive effect was observed on C₅₊ selectivity over the La- or Ce-promoted catalysts prepared by the alkoxide method.

Compared with the Co-Ir-SiO₂ catalyst (without MO_x promoter), the group (d) catalyst showed higher selectivity for C₅₊ hydrocarbons. The addition of light transition metal oxides, LTMO (Mn¹³⁾, V¹⁴⁾, Mo¹⁵⁾), has been extensively explored and reviewed¹⁶⁾. These compounds facilitate CO dissociation at the sites of the metal-promoter interface, and lower the surface H/C ratio, due to electronic interaction with the metal surface.

Figure 1 shows the good correlation between the selectivity for CH₄ and the standard enthalpy of formation of the promoter, $-\Delta H_f^\circ$ ¹⁷⁾. The selectivity for CH₄ increased with $-\Delta H_f^\circ$. A similar result was also observed over catalysts supported on mesoporous metallo-silicates¹⁸⁾.

Mn²⁺ can be easily oxidized to Mn³⁺, Mn⁴⁺, Mn⁶⁺, and even Mn⁷⁺, because MnO has low $-\Delta H_f^\circ$. As mentioned above, the role of LTMO is to facilitate CO dissociation at the interface sites of the Co metal and MO_x, due to electronic interaction. Thus, the charge of the electrostatic field caused by the variation of the electrovalence of MnO_x might promote the back-dona-

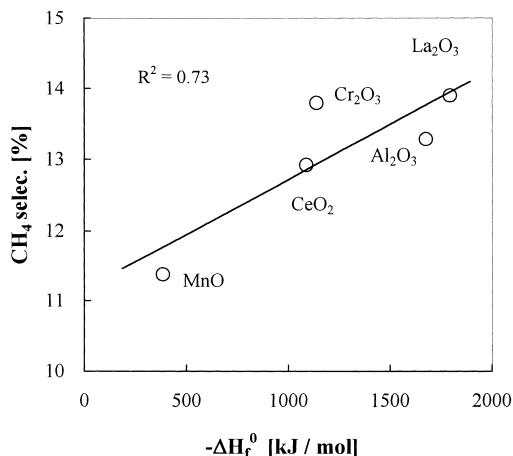


Fig. 1 Relationship between Standard Enthalpy of Formation ($-\Delta H_f^0$) of Promoter Oxide (MO_x) and Selectivity for CH_4 over MO_x -20 wt%Co-0.5 wt%Ir- SiO_2 Catalysts Prepared by the Alkoxide Method ($\text{M}/\text{Co} = 0.1$)

tion of electrons from the Co metal orbital to the 2π orbital of CO, resulting in an increase in the concentration of CH_x precursors and the rate of F-T product formation, as well as the chain growth probability of CH_x (α), while suppressing the formation of CH_4 .

In contrast, the high $-\Delta H_f^0$ value of Al_2O_3 indicates invariable valence of Al. As suggested above, the main role of Al_2O_3 is to prevent the growth of Co particle size. Thus, Al_2O_3 cannot be described as an electronic effect promoter, but as a textual promoter allowing the ensemble effect. CO conversion was too low with the K-promoted catalyst to compare with the catalysts containing the other promoters, and the result was excluded from Fig. 1.

Since the Mn-promoted catalyst showed the highest selectivity for C_{5+} hydrocarbons among the catalysts listed in Table 1, the effect of Mn content on the catalytic properties was investigated, as shown in Fig. 2. CO conversion increased to 57% with Mn content up to 10 wt%, and then decreased significantly with further increases in Mn content. Possibly the active sites were covered with the excessive MnO, or the texture of the catalyst precursor became unstable due to the excessive additive in the alkoxide method. The catalyst with 10 wt%-Mn also showed the highest α -value, too. Further addition of Mn resulted in deactivation of the catalyst during the F-T reaction, because the uniform structure of the catalyst was not achieved with higher content of Mn.

4. Conclusions

The effects of additives on the catalytic properties were investigated. The selectivity of products was obviously influenced by the intrinsic properties of the

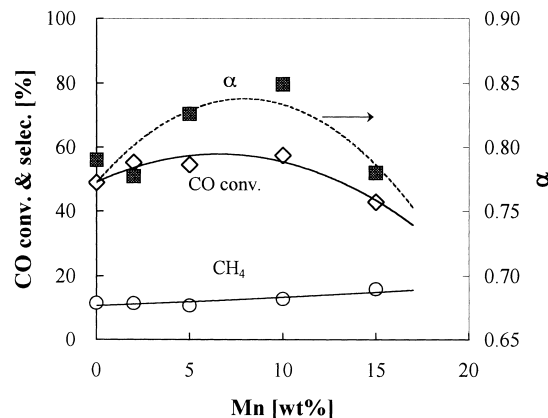


Fig. 2 Effect of Mn Content on Catalytic Properties

promoter oxides. Increasing standard enthalpy of formation of promoter oxides, $-\Delta H_f^0$, was linearly correlated with increased selectivity for CH_4 . The promoters were divided into 4 groups: (a) K decreasing CO conversion; (b) Al and Cr increasing CH_4 selectivity; (c) La and Ce decreasing C_{5+} selectivity; and (d) Mn increasing CO conversion and C_{5+} selectivity.

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要 旨

アルコキシド法で調製した金属酸化物添加 Co-Ir-SiO₂ 触媒上での Fischer-Tropsch 合成

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種々の金属 (M; M = K, Al, Cr, La, Ce, および Mn) 酸化物を含む MO_x-20 wt% Co-0.5 wt% Ir-SiO₂ 触媒をアルコキシド法で調製し, これを用いてスラリー相での Fischer-Tropsch 合成を試み, 金属酸化物添加が CO 転化率や生成物への選択率に及ぼす影響について検討した。K を添加した触媒では活性が低下した。Al または Cr を添加した触媒では, CO 転化率は未添加触媒とほとんど変わらなかったが, CH₄ 選択率がやや増加した。La または Ce を添加した触媒では, C₅₊ 炭化水素選択率が

低下した。これに対し, Mn を添加した触媒では, CO 転化率や C₅₊ 炭化水素選択率が増加することが認められた。10 wt% Mn を含む触媒では 57% の転化率と高い α 値 (反応中間体 CH_x の連鎖成長確率) が得られたが, それ以上添加した触媒では, 活性劣化が著しかった。選択率と添加物特性との関係を調べたところ, 選択率と添加した金属酸化物 (MO_x) の標準生成熱 ($-\Delta H^{\theta}$) との間には直線関係が見い出された。すなわち, 標準生成熱の増大とともに CH₄ への選択率が単調に増加した。