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TiO₂ Promoted Co/SiO₂ Catalysts for Fischer-Tropsch SynthesisSukamon Hinchiranan^{†1)}, Yi Zhang^{†1)}, Satoshi Nagamori^{†1)}, Tharapong Vitidsant^{†2)}, and Noritatsu Tsubaki^{†1)*}^{†1)} Dept. of Applied Chemistry, School of Engineering, University of Toyama,
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The addition of small amount of TiO₂ to silica supported cobalt catalysts significantly increased the dispersion of cobalt and Co metallic surface area, resulting in the remarkable enhancement of the Fischer-Tropsch synthesis (FTS) activity in the slurry-phase reaction. The addition of TiO₂ adjusted the interaction between cobalt and silica support quite well, to realize the favorite dispersion and reduction degree of supported cobalt at the same time, leading to high catalytic activity in FTS.

Keywords

Fischer-Tropsch synthesis, Cobalt catalyst, Titania, Silica, Syngas

Cobalt-based catalysts attract most of current attention for the direct conversion of syngas in FTS because of their high activity, high selectivity for long chain paraffins, and low water gas shift reaction activity. Besides cobalt, some supports such as SiO₂, Al₂O₃ and TiO₂, are indispensable. Synthesis of highly dispersed Co catalysts requires strong interaction between the support and the Co precursor, but in turn such strong interactions generally lower the reducibility of such precursors¹⁾. Different from silica, TiO₂ and Al₂O₃ tend to have a strong interaction with cobalt precursor, causing highly dispersed Co but very low reducibility²⁾.

The present work investigated the TiO₂ promotional effects on Co/SiO₂ catalyst. This kind of catalyst was tested in a semi-batch slurry-phase FTS reaction and its properties were characterized by *in situ* FT-IR, XRD, TPR and H₂ chemisorption.

The titania-modified silica supports were prepared by incipient wetness impregnation of commercially available silica gel (Q-10, Fuji Silysia

Chemicals Ltd., specific surface area: 283 m²·g⁻¹, pore volume: 1.22 ml·g⁻¹, pore diameter: 10 nm) with aqueous solution of a titanium dihydroxide. After impregnation, the samples were dried at 393 K for 12 h, and then calcined at 673 K for 2 h. The loading amount of TiO₂ was 2, 5 and 10 wt% in total support base, respectively. The aqueous solution of cobalt nitrate was further impregnated onto the obtained supports by incipient wetness method. The loading of cobalt was 10 wt% for all catalysts in total catalyst base. The catalysts were dried at 393 K for 12 h and calcined at 673 K for 2 h. Then, the calcined samples were reduced with H₂ at 673 K for 10 h followed by passivation with 1% O₂ in N₂.

The FTS reaction conditions and catalysts characterization details were reported elsewhere³⁾.

As shown in **Table 1**, TiO₂ promoted catalyst with 2 wt% titania loading showed the highest CO conversion in slurry-phase FTS reaction and the selectivity of CH₄ were higher than that of unpromoted Q-10 catalyst. On the other hand, the

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Table 1 Reaction Performances of Various Co/SiO₂ Catalysts with Different TiO₂ Loading in Slurry-Phase FTS

Catalyst	TiO ₂ loading [wt%]	CO conv. [%]	Sel. [%]		α
			CH ₄	CO ₂	
Q-10	0	50.4	5.6	0.92	0.84
2 TiO ₂	2	68.7	8.4	1.65	0.82
5 TiO ₂	5	64.9	7.3	1.33	0.82
10 TiO ₂	10	64.5	8.3	1.26	0.81

Reaction conditions: 513 K; 1.0 MPa; H₂/CO: 2; W/F: 5g-cat·h·mol⁻¹; catalyst: 1 g; cobalt loading: 10 wt%.

catalysts, promoted by 5 wt% or 10 wt% titania loading, exhibited the similarly high catalytic activity to the 2 wt% titania promoted catalyst, with higher CO conversion, than that of Q-10 catalyst. Q-10 catalyst shows the lowest CO conversion in this study.

The supported cobalt particle size of various catalysts was determined by XRD and H₂ chemisorption. It is considered that due to the stronger chemical effects of titania structure, the titania promoted catalyst formed smaller supported cobalt particle size than silica Q-10 catalyst, resulting in higher supported cobalt dispersion, as shown in **Table 2**. For titania promoted catalyst, due to its small supported cobalt particles, the reduction degree was lower than that of Q-10 catalyst, and the reduction degree of titania promoted catalysts decreased from 40.4% to 26.8%, with the increased titania loading. Concerning the cobalt surface area, as exhibited in **Table 2**, 2 wt% titania promoted catalysts formed larger metallic cobalt surface area than Q-10 catalyst, indicating that this kind of catalysts kept relatively high reduction degree, contributing to formation of high cobalt surface area, resulting in the highest activity in FTS reaction.

Based on *in situ* FT-IR, titania promoted catalysts formed stronger and broader peak of the bridged

Table 2 Properties of Co/SiO₂ Catalysts with Different TiO₂ Loading

Catalysts	TiO ₂ loading [wt%]	Co particle size [nm]		Red. degree [%] ^{b)}	Co surf. area [m ² /g]	TOF [s ⁻¹]
		XRD	H ₂ ^{a)}			
Q-10	0	18.9	14.3	59.7	2.8	0.13
2 TiO ₂	2	12.3	7.1	40.4	3.8	0.15
5 TiO ₂	5	10.7	6.8	29.2	2.9	0.17
10 TiO ₂	10	10.2	6.2	26.8	2.8	0.18

a) Calculated from H₂ chemisorption at 373 K.

b) Calculated by TPR from 323 K to 673 K.

adsorbed CO than Q-10 catalyst. As pointed out, the bridged adsorbed CO was much more active than linearly adsorbed CO³⁾. The high activity of titania promoted catalysts could be attributed to the increase in bridge-type adsorbed CO, which was easily dissociated to carbon and oxygen, contributing to the higher TOFs as shown in **Table 2**.

Compared to silica Q-10 catalyst, titania promoted catalyst had higher activity, due to the hetero-atom structure in the titania promoted catalysts, and fine balance between reduction degree and dispersion of supported cobalt, leading to high metallic cobalt surface area.

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References

- 1) Tsubaki, N., Sun, S., Fujimoto, K., *J. Catal.*, **199**, 236 (2001).
- 2) Voß, M., Borgmann, D., Wedler, G., *J. Catal.*, **212**, 10 (2002).
- 3) Zhang, Y., Koike, M., Yang, R., Tsubaki, N., *Appl. Catal. A: General*, **292**, 252 (2005).