Fischer Tropsch synthesis from H₂-deficient biosyngas over Mn added Co/SiO₂ catalysts

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Abstract: Co/SiO₂ catalysts with 0.4-7.0wt.% of Mn addition were prepared and evaluated for Fischer-Tropsch synthesis (FTS), using H₂-deficient biosyngas (H₂/CO/CO₂/N₂=45/45/7/3, vol%) as feed gas. 0.8wt.% of Mn addition to Co/SiO₂ increased Co dispersion and weakened Co-Si interaction on Co-(0.8%)Mn/SiO₂ catalyst. Co reducibility was improved to 32.1% and 79.3% at 150-400°C and 150-750°C respectively by H₂-temperature programmed reduction (TPR), which resulted in CO conversion of 52.6% and C₅₊ yield of 43.6% at 24h time on stream when H₂-deficient biosyngas was used as feed gas for FTS. Co was further dispersed with low reducibility at higher Mn addition amount, which decreased CO conversion and favored gaseous hydrocarbon synthesis over Co-(2.0%)Mn/SiO₂ and Co-(7.0%)Mn/SiO₂. The higher H₂/CO usage ratio was obtained over Co/SiO₂ using H₂-deficient biosyngas, compared with that using feed gas with H₂/CO ratio of 2.0 over the same catalyst. The existence of small amount of CO₂ (like 7.0vol%) in biosyngas might be the main reason to inhibit water gas shift reaction and impel CO₂ conversion.

Key words: Fischer Tropsch synthesis; H₂-deficient biosyngas; Co/SiO₂; Mn addition

1. Introduction

Catalytic conversion of biomass-derived syngas to long-chain hydrocarbons by Fischer-Tropsch synthesis (FTS) is a promising process for the sustainable liquid fuel supply^[1]. However the costly composition adjustment procedures of biosyngas such as H₂ adding, reforming and CO₂ removal, are usually needed because the raw gas after biomass gasification is H₂-deficient and CO₂-rich, which does not fit the stoichiometric requirement of FTS^[2]. Enormous efforts have been made to improve the gas utilization efficiency of these H₂-deficient biosyngas^[3, 4]. It was reported that H₂ content was increased by water-gas shift

(WGS) reaction over Fe-based FTS catalysts^[5-7], for the following FTS^[8]. However the increased CO₂ content after WGS reaction and the low CO₂ hydrogenation rate decreased the carbon utilization efficiency of biosyngas^[9, 10].

Co-based catalyst, promoted by noble metal (Ru, Rh, Pt, et al) and metal oxide (ZrO₂, La₂O₃, MnO, et al)^[11, 12], seem to be an attractive option for H₂-deficient biosyngas conversion to hydrocarbons due to their high hydrogenation ability and C₅⁺ selectivity^[13, 14]. As a promoter, Mn is promising because of its high H₂ bonding energy^[15]. Although it is proved that FTS performance depends on catalyst composition, feed gas composition and reaction condition, due to the adsorption and hydrogenation difference of CO₂ and CO on the active catalyst surface^{[16] [17]}, few concrete studies have been focused on the conversion characteristics of biosyngas^[18, 19]. In this work FTS was carried out over Mn-added Co/SiO₂ catalysts, using model biosyngas(H₂/CO/CO₂/N₂=45/45/7/3, vol%; H₂/CO=1.0) as feed gas. Particular attention was paid towards the influence of Mn addition amount, feed gas composition and catalyst stability on FTS performance to improve the utilization efficiency of H₂-deficient biosyngas.

2. Experimental

2.1 Catalyst preparation

20wt.% of SiO₂ supported Co catalysts were prepared by incipient-wetness impregnating method(IWI). 1.0mol/L cobalt nitrate aqueous solution was added to SiO₂(BET surface area of 101m²/g, pore volume of 0.58ml/g, pore diameter of 40nm, NH₃ uptake of 0.02mmol/g) at room temperature to completely wet the SiO₂ samples. The impregnated solid was dried at 120⁰C for 12h and calcined in air at the ramp rate of 2⁰C/min to 400⁰C with holding at 400⁰C for 4h. The impregnation of Co on SiO₂ was repeated until the total of 20wt.%Co/SiO₂ was obtained. The sample was then used as the support material for IWI of 0.5mol/L manganese nitrate aqueous solution, following the same drying and calcination procedures as mentioned above. The calcined sample was pressed under 15MPa and sieved to the desired pellet size (20-40 mesh). The catalysts prepared were denoted as Co-(x%)Mn/SiO₂, where x referred to Mn amount (wt.%, 0.4, 0.8, 2.0,7.0 respectively).

2.2 Catalyst characterization

X-ray powder diffraction (XRD) patterns were obtained on a Rigaku D/max-rC using Cu K α radiation source. The line broadenings of Co diffraction peaks localized at 36.8 $^{\circ}$ and 44.6 $^{\circ}$ were used to estimate Co crystallite sizes of the calcined and reduced catalysts respectively, according to Scherrer equation. Before H $_2$ chemisorption, 0.1g samples were reduced at 400 $^{\circ}$ C under 30ml/min of 5%H $_2$ /95%N $_2$ (vol) flow for 8h and then purged with N $_2$ at 400 $^{\circ}$ C for 1h. H $_2$ was then pulsed to the reduced catalysts at 100 $^{\circ}$ C, according to the reports that H $_2$ chemisorption at 100 $^{\circ}$ C is most reliable for silica-supported cobalt catalyst^[20]. Co dispersion was estimated by the uptake amount of H $_2$ chemisorption at 100 $^{\circ}$ C.

In H $_2$ -temperature programmed reduction (H $_2$ -TPR), about 0.10g calcined catalyst was placed in a quart tube reactor, then heated from room temperature to 900 $^{\circ}$ C at the ramp rate of 5 $^{\circ}$ C/min in 5%H $_2$ /95%N $_2$ (vol) flow at 30ml/min. TCD detector was used to monitor H $_2$ consumption amount. The 5 Å molecular sieve trap was set after the reactor to remove the formed water before entering TCD detector. The catalyst reducibility at 150-750 $^{\circ}$ C were evaluated according to the hydrogen consumption amount from 150 $^{\circ}$ C to 750 $^{\circ}$ C, which was determined by comparing with the calibration areas of 5vol% H $_2$ in N $_2$ and correlated to percentage of metal reduced during standard reduction processure(ramp 2 $^{\circ}$ C/min to 400 $^{\circ}$ C, hold for 8h). And the TPR spectrum was integrated and normalized to unity for qualitative analysis of cobalt reducibility at 150-400 $^{\circ}$ C, which was calculated as: (Integrated area_{150-400 $^{\circ}$ C}/Integrated area_{150-750 $^{\circ}$ C}) $\times$ Reducibility_{150-750 $^{\circ}$ C}.

2.3 FTS reaction

FTS reaction was carried out in a fixed-bed reactor under 2.0MPa, 240 $^{\circ}$ C and gas hour space velocity (GHSV) of 1000 h $^{-1}$. The model H $_2$ -deficient biosyngas(H $_2$ /CO/CO $_2$ /N $_2$ =45/45/7/3, vol%; H $_2$ /CO=1.0) was used as feed gas to simulate the biosyngas, produced after O $_2$ gasification of biomass and CO $_2$ removal. In each FTS run, 1.00g catalyst was reduced in situ at 400 $^{\circ}$ C under 5%H $_2$ /95%N $_2$ (vol) flow for 8h. After that, the catalyst was cooled to 180 $^{\circ}$ C and reheated to the reaction temperature under feed gas flow. The pressure was increased to 2.0MPa with a back-pressure regulator. The tail gas was analyzed by two online gas chromatographs at intervals of 2h. CO, N $_2$, CH $_4$ and CO $_2$ were analyzed by carbon-sieve column(3m $\times$ 3mm i.d., 100 $^{\circ}$ C) with TCD detector. Gaseous hydrocarbons (C $_1$ -C $_5$) were analyzed by Porapak Q column(3m $\times$ 3mm i.d., 110 $^{\circ}$ C) with FID detector. The liquid product in the traps was collected at intervals of 24h, which separated into two phases of water and oil. The oil phase was analyzed by a FID GC equipped with SE-30 capillary

column, heated from 40⁰C to 280⁰C at the ramp rate of 5⁰C/min with holding at 280⁰C for 30mins. Formation of few waxy materials was observed in the traps, which was collected with the initial oil product. N₂ in the feed gas was used as internal standard to calculate conversion and hydrocarbon selectivity. The hydrocarbon selectivity distributions were calculated on the basis of carbon number.

The reactant conversion and hydrocarbon selectivity (mol%) were calculated by the following formulas:

$$X_{\text{reactant}}(\%) = [(\text{moles of reactant}_{\text{in}} - \text{moles of reactant}_{\text{out}}) / \text{moles of reactant}_{\text{in}}] \times 100\%, \text{ reactant} - \text{CO, CO}_2, \text{H}_2;$$

$$S_{\text{Cn}}(\%) = [n \times \text{moles of Cn}_{\text{produced}} / (\text{moles of (CO+CO}_2)_{\text{in}} - \text{moles of (CO+CO}_2)_{\text{out}})] \times 100\%, \text{ Cn} - \text{the hydrocarbon product with carbon number of n};$$

$$\text{H}_2/\text{CO usage ratio} = X_{\text{H}_2}/X_{\text{CO}};$$

$$S_{\text{CO}_2} = [(\text{moles of CO}_2_{\text{out}} - \text{moles of CO}_2_{\text{in}}) / (\text{moles of CO}_{\text{in}} - \text{moles of CO}_{\text{out}})] \times 100\% (\text{in the cases that CO}_2 \text{ was produced});$$

$$\text{Yield}_{\text{C}_{5+}}(\%) = X_{\text{CO}} \times (1 - S_{\text{CH}_4} - S_{\text{C}_2-\text{C}_4} - S_{\text{CO}_2}) \times 100\%;$$

The total carbon balance for the majority of the experiments was within 100±10%. Because in most cases, the selectivity to heavier wax(>C₂₈), alcohols and acetones was less than 3%, their values were ignored in the selectivity calculation.

3. Results and discussion

3.1. Catalyst characterization

Fig.1 (A) and Fig.1(B) illustrate the XRD patterns of the calcined and reduced Co-Mn/SiO₂, which exhibit the phase of Co₃O₄ and cubic metallic Co, respectively. Yet the existence of weak CoO diffraction line for the reduced catalyst in Fig.1(B) was the result of the reoxidation of metal Co under atmosphere condition during XRD analysis. No peaks corresponding to MnO or Mn-support species were displayed, even for Co-(7.0%)Mn/SiO₂ with 7.0wt.%Mn addition, probably because of the high dispersion of Mn species. But the existence of Co-Mn mixed species could be deduced by the slightly smaller 2θ values of Co₃O₄ reflections in Mn-promoted catalysts in Fig.1 (A), resulted from the decrease in the cell parameters of Mn³⁺ incorporation into the Co₃O₄ lattice^[21].

XRD patterns of the calcined and reduced Co-Mn/SiO₂ catalysts shows the wider diffraction peaks at 36.8° of Co₃O₄ and 44.6° of Co⁰ respectively, with the increase of Mn addition amount. The particle size calculated by Scherrer's equation is not completely accurate, because of the neglected contribution of crystallite strain to the diffraction line broadening. However, the differences in Co particle sizes indicate that Mn addition affects the size and crystallinity of Co₃O₄ particles, as a result of a physicochemical interaction between these compounds during calcination treatment.

The most intensive peaks of Co₃O₄ and Co⁰ in XRD pattern of Co/SiO₂ resulted in the largest Co⁰ particle size of 11.3nm and 16.5nm for the calcined and reduced catalysts respectively in Table 1. For Co-Mn/SiO₂ catalysts, the decrease of Co⁰ size with Mn addition amount increase indicated the increasing effect of Mn species on Co dispersion. It is also confirmed by the calculated Co⁰ size from H₂ chemisorption results, which decreased from 15.7nm to 8.7nm when Mn amount was increased to 7wt.%. And the larger Co⁰ size calculated from H₂ chemisorption method, compared with those obtained from XRD, should attribute to the incomplete reduction of Co-support and Co-Mn species, which had suppressed H₂ chemisorption amount and enlarged the calculation results. Furthermore, Co⁰ size of the calcined catalyst, calculated by $d(\text{Co}^0)=0.75d(\text{Co}_3\text{O}_4)$, was smaller than the corresponding result of the reduced catalyst in Table 1. In the same time, the difference of Co⁰ particle size between the reduced and calcined catalysts decreased with the increase of Mn addition amount, which suggested that the increased MnO addition had weakened the aggregation of Co⁰ particles during reduction treatment^[21].

There is H₂ consumption above 750°C in all catalysts during H₂-TPR in Fig.2, especially for Co/SiO₂. It was due to the inefficient reduction of the metal-support species such as cobalt silicate and Co-Mn species during TPR procedure. Those species were easily formed between the hydroxides of SiO₂ and water ligands of metal salts during catalyst preparation, which were hardly reduced at low temperature and undetectable by XRD^[22].

H₂-TPR profile of Co/SiO₂ shows two main peaks at 305°C and 390°C, which were identified as the reduction of bulk Co₃O₄ to Co²⁺ and Co²⁺ to Co⁰ respectively. And Co reduction degree from TPR profile at 150-750°C was calculated as 77.2%, relatively lower than the results from some literature^[23]. It may be due to the formation of some Co-Si species that are not necessarily reduced at the temperatures applied during TPR procedures, although the reduction can be induced by holding Co/SiO₂ at 400°C for a prolonged time span^[24].

The two reduction peaks shifted to higher temperature of 330⁰C and 450⁰C when Mn addition amount was enhanced from 0.4wt.% to 2.0wt.%. At higher Mn loading of 7.0wt.%, the reduction peaks of Co-(7.0%)Mn/SiO₂ shifted back to 312⁰C and 407⁰C. H₂-TPR behavior suggests that Mn interacts strongly with Co and support at lower Mn content, which caused the formation of Co-Mn species and small-sized Co particle in Co-(0.4%)Mn/SiO₂ that is not completely reduced during TPR procedure. For Co-(0.8%)Mn/SiO₂, slightly higher reduction degree at 150-750⁰C and dispersion, compared with those of Co/SiO₂ (77.2%), were obtained. It seems that the addition of optimal amount of Mn could act as support to decrease Co-Si interaction and accelerate the Co-Si species' reduction at the temperature applied during TPR procedure. Further increasing Mn addition to 2.0wt.% and 7.0wt.% decreased Co reduction at 150-750⁰C, likely due to the coverage of Co particles by the excessive amount of Mn and the decrease of the available amount of Co species.

The reducibility at 150-400⁰C is especially important because it correlated with the catalyst reducibility during practical FTS. The highest normalized Co reducibility (46.8%) in Co/SiO₂ was due to the large Co₃ particles, which was easy to be reduced. Yet Mn hampers the reduction of CoO to Co⁰ in Mn-added catalysts, as indicated by the decrease of Co reducibility at 150-400⁰C and the higher relative intensity of the reduction peak centered at 450⁰C.

And for each Co-Mn/SiO₂ catalyst, the reducibility difference between 150-750⁰C and 150-400⁰C increased with the increase of Mn addition amount to 0.8wt.%, and then decreased with higher Mn content. These results indicate that adding proper amount of Mn to Co/SiO₂ could increase the small-sized Co reduction, which provided more active sites and contributed to FTS activity. The highest reduction degree was obtained over Co-(0.8%)Mn/SiO₂, which resulted in the highest CO conversion of 52.6% when H₂-deficient biosyngas was used as feed gas in Table 2.

3.2 FTS performance

For comparison, FTS was also carried out over Co/SiO₂ using the syngas(H₂/CO/CO₂=64/32/4, vol%) with H₂/CO ratio of 2.0, which showed CO conversion of 99.3% at 24h time on stream(TOS). While CO conversion decreased greatly to less than 60% over Co/SiO₂ and Mn-added Co/SiO₂ as H₂-deficient biosyngas(H₂/CO/CO₂/N₂=45/45/7/3, vol%; H₂/CO=1.0) was used as the feed gas. It might be due to the inefficient H₂ adsorption on the active sites as H₂-deficient biosyngas was applied. For Mn-added catalysts,

CO conversion of the biosyngas increased from 38.7% to 52.6% when Mn addition amount increased to 0.8wt.%, and then decreased to 27.7% when Mn addition was further increased to 7.0wt.%. Therefore, optimizing Mn addition amount is necessary to increase the biosyngas usage efficiency during FTS^[25]. And the phenomenon that an optimized Mn/Co ratio could promote CO conversion is also observed over Mn-Zr-Co/SiO₂ in other literatures^[24, 26].

The high CO conversion of 52.6% using H₂-deficient biosyngas over Co-(0.8%)Mn/SiO₂ should result from its relatively high Co reduction degree for the small-sized Co species and the inhabitation of Co aggregation during reduction treatment, shown by the relatively low difference of Co⁰ size between the calcined and reduced catalyst from XRD results in Table 1. However the drop of CO conversion for 2.0-7.0wt% Mn-added catalysts is probably due to the decrease of the available Co sites by the coverage of excess MnO.

CO₂ was produced as by-product over Co/SiO₂ when the syngas with H₂/CO ratio of 2.0 was used as feed gas. And the main reason of the high CO₂ selectivity as 12.8% is probably ascribed to its high CO conversion of 99.3% and low GHSV of 1000h⁻¹ during FTS process, which means more water was produced and induced partial oxidation of Co metal^[27]. And that had accelerated WGS reaction and resulted in high CO₂ selectivity when the syngas with H₂/CO ratio of 2.0 was used.

Yet in most cases that CO₂-containing biosyngas(H₂/CO/CO₂/N₂=45/45/7/3, vol%) was used, CO₂ acted as a reactant in the feed gas and was converted over Co/SiO₂ and Co-Mn/SiO₂, shown in Table 2. Until now, CO₂ conversion mechanism in FTS is still uncertain. One deduction is that CO₂ is converted to CO by reverse WGS, and then consequently consumed through CO hydrogenation in FTS^[28]. One is that CO₂ is an inert gas to remove reaction heat. The other one is that CO₂ can be directly hydrogenated by competitive adsorption with CO on the active metal surface^[17]. These contradictory conclusions are probably due to the dependence of FTS on reaction conditions, such as feed gas compositions and catalysts. And it is generally accepted that CO₂ is an inert diluent component or has negative effect on FTS below 220°C^[9]. While WGS reaction and/or direct CO₂ hydrogenation with high CH₄ selectivity will occur when Co-based catalysts are used above 220°C^[29]. In the same time, the equilibrium of WGS reaction affects FTS performance when the feed gas contains CO, CO₂, H₂ and H₂O, as it determines either CO can be converted to CO₂ or CO₂ to CO.

In this context, the positive CO₂ conversion and less than 20% CH₄ selectivity using H₂-deficient biosyngas over Co/SiO₂ and Co-Mn/SiO₂ (Mn<7wt%) could state from the inhabitation effect of CO₂ formation during FTS by 7.0vol% CO₂ in the feed gas and the combined effect of the reverse WGS reaction and direct CO₂ hydrogenation on active metals at 240⁰C, along with CO hydrogenation. Similar deduction was also supposed using CO₂-containing syngas over Co/SiO₂ by Weatherbee and Bartholomew^[30]. CO₂ conversion decreased from 14.1% to 8.1%, along with the increased CO conversion from 38.7% to 52.6%, when Mn addition amount increased to 0.8wt.% for H₂-deficient biosyngas conversion. It may attribute to the increased Co metal sites and the competitive hydrogenation of CO and CO₂. Yet the relatively slow CO₂ hydrogenation rate decreased its conversion. The enhanced H₂/CO usage ratio of H₂-deficient syngas over Co-Mn/SiO₂ in Table 2, compared with that of the syngas with H₂/CO ratio of 2.0, is another evidence that reverse WGS or CO₂ hydrogenation of biosyngas might have occurred simultaneously during FTS, which resulted in relatively higher H₂ conversion^[9].

Heavy hydrocarbon selectivity distributions followed Anderson-Schulz-Flory(ASF) model, but the products with low carbon numbers(C₁-C₇) did not match that over all catalysts in Fig. 3. Similar derivations have been observed by many other studies^[31].

The CH₄ selectivity of 31.4% over Co/SiO₂ using the syngas with H₂/CO ratio of 2.0 was higher than those over Co/SiO₂ and Co-Mn/SiO₂ using H₂-deficient biosyngas as feed gas. It may be due to the high surface H/C ratio over Co, which had favored CO hydrogenation activity(CO conversion of 99.3%) and CH₄ formation when the feed gas contained more H₂^[32]. The trend that CH₄ selectivity increased with the syngas conversion was also found by Elbashir et al^[22]. And the low GHSV of 1000h⁻¹ used in this context may be another reason for the high CH₄ selectivity that the primary formed products of 1-olefins may undergo further secondary reactions, such as readsorption and hydrocracking to gaseous products at 240⁰C. While low CH₄ selectivity(less than 17%) was observed over Co/SiO₂ and Co-Mn/SiO₂ when biosyngas was the feed gas, due to the low CO conversion and less H₂ source for secondary reactions. The relatively high CH₄ selectivity of 16.5% over Co-(7.0%)Mn/SiO₂ may be deduced from its small Co particle size, which favored light hydrocarbon synthesis with 28.9% selectivity to C₁ -C₄ from biosyngas.

The relatively high CO conversion level of 52.6% and secondary reactions over Co-(0.8%)Mn/SiO₂ also resulted in a low olefin/paraffin value of 0.92 among Mn-added catalysts when H₂-deficient biosyngas was used. With the proper particle size of Co and selectivity to long-chain hydrocarbons, Co-(0.8%)Mn/SiO₂ showed the highest C₅₊ yield of 43.9% among all Mn-added catalysts under H₂-deficient biosyngas condition. Although this yield is lower than that of 52.1% over Co/SiO₂ when the syngas with H₂/CO ratio of 2.0, the optimized Co-(0.8%)Mn/SiO₂ is still preferred for direct H₂-deficient biosyngas conversion, considering the costs saved by avoiding the composition adjustment procedures of biomass-derived syngas, such as H₂ supplying and CO₂ removal.

3.3 Catalyst stability

To determinate the stability of the enhanced effect with 0.8wt.%Mn addition to Co/SiO₂ for H₂-deficient biosyngas conversion, both Co-(0.8%)Mn/SiO₂ and Co/SiO₂ were applied for a long TOS running under H₂-deficient biosyngas condition. Similar CO conversion of ca. 50% over Co/SiO₂ and Co-(0.8%)Mn/SiO₂ was observed at about 9h TOS in Fig.4.A. After that, Co/SiO₂ shows a rapid decrease of CO conversion, which was 27% at 48h TOS. While CO conversion was stable of about 40% after 120h TOS over Co-(0.8%)Mn/SiO₂. It might result from its proper Co particle size, which was stabilized by the optimized amount of Mn during reduction and FTS. The selectivity of gaseous hydrocarbons was almost the same within 120h TOS and that of C₅₊ exhibited a slight fluctuation after 48h TOS, shown in Fig.4.B. The average selectivity of C₁, C₂₋₄, C₅₋₁₂, C₁₃₋₂₁ and C₂₂₊ was 14.5%, 4.4%, 56.8%, 19.8% and 2.3% respectively. That suggests that the performance of Co-(0.8%)Mn/SiO₂ was stable during long time FTS when H₂-deficient biosyngas was used as feed gas.

4. Conclusion

The effect of different addition amount of Mn on the structure and FTS activity of Co/SiO₂ catalyst was investigated, using H₂-deficient biosyngas as feed gas. The optimal amount of 0.8wt.% Mn addition could improve and stabilize CO conversion from H₂-deficient biosyngas during long time operation, due to the increased reducibility and dispersion of active Co. When Mn amount is higher than 0.8wt.%, the coverage of Co particles by excess MnO and the formation of small-sized Co⁰ decreased CO conversion and C₅₊ selectivity. CO₂ content in the H₂-deficient biosyngas of 7% could be converted over Co-Mn/SiO₂ when Mn addition amount was less than 7wt%. The decreased CO₂ conversion and increased CO conversion with the increase of

Mn addition amount from 0% to 0.8wt.% should attribute to increased Co metal sites by the promotion effect of proper amount of Mn and the competitive hydrogenation of CO and CO₂ as H₂-deficient biosyngas was the feed gas. Although C₅₊ yield of 43.6% from H₂-deficient biosyngas over Co-(0.8%)Mn/SiO₂ was lower than that of 52.3% over Co/SiO₂ using the syngas with H₂/CO ratio of 2.0, direct FTS from H₂-deficient biosyngas as feed gas using modified Co/SiO₂ catalyst may be still efficient, due to avoiding of feed gas composition adjustment procedures. And more work on the catalyst optimization and CO₂ conversion of biosyngas need to be carried out for environmental and sustainable development in future.

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Table 1

The phase properties and reducibility behavior of Co-Mn/SiO₂ catalysts.

Catalysts	Co ⁰ crystal size (nm) ^a		H ₂ ^c	H ₂ -TPR Peak centers (⁰ C)	Reducibility(%) ^a		Co dispersion (%) ^{a, f}
	XRD				TPR		
	Calcined ^b	Reduced			150-400 ⁰ C ^d	150-750 ⁰ C ^e	
Co/SiO ₂	11.3	16.5	15.7	305, 390	46.8	77.2	6.1
Co-(0.4%)Mn/SiO ₂	11.2	15.8	12.9	319, 424	28.7	68.5	7.4
Co-(0.8%)Mn/SiO ₂	10.4	14.3	11.2	330, 450	32.1	79.3	8.6
Co-(2.0%)Mn/SiO ₂	10.0	13.3	10.4	330, 450	22.3	58.2	9.2
Co-(7.0%)Mn/SiO ₂	8.6	11.6	8.7	312, 407	17.1	34.8	11.0

^a Error of measurements was $\pm 5\%$ ^b Calculated by $d(\text{Co}^0) = 0.75d(\text{Co}_3\text{O}_4)$, according to the Co₃O₄ crystallite size from Scherrer equation at $2\theta = 36.80^\circ$.^c Calculated by $d = 96/D(\%)$.^d Calculated by normalized ratio of TPR spectrum at 150-400°C by Integrated area_{150-400°C}/Integrated area_{150-750°C} × Reducibility_{150-750°C}.^e Calculated by TPR at 150-750°C and correlated to percentage of metal reduced during standard reduction procedure (ramp 2°C/min to 400°C, hold for 8h).^f Calculated by H₂ chemisorption amount at 100°C.

Table 2

FTS performance from H₂-deficient biosyngas over Co-Mn/SiO₂ catalysts

Catalyst ^a	X _{CO} (%)	X _{H₂} (%)	X _{CO₂} (%)	Hydrocarbon selectivity (mol %)					C ₂₋₃ / C ₂₋₃ (mol/mol)	H ₂ /CO usage ratio	Yield _{C₅+} (%)
				CH ₄	C ₂₋₄	C ₅₋₁₂	C ₁₃₋₂₁	C ₂₂₊			
Co/SiO ₂ ^b	99.3	91.4	-12.8 ^c	31.2	9.3	44.9	14.0	0.7	—	0.92	52.1
Co/SiO ₂	38.7	53.6	14.1	12.3	6.2	55.7	22.4	3.3	1.44	1.38	31.6
Co-(0.4%)Mn/SiO ₂	47.8	76.1	11.9	8.1	5.8	51.6	30.1	4.0	1.32	1.59	40.9
Co-(0.8%)Mn/SiO ₂	52.6	74.0	8.1	9.9	6.6	58.2	22.4	2.4	0.92	1.41	43.6
Co-(2.0%)Mn/SiO ₂	36.5	53.9	4.0	13.8	9.4	50.8	24.0	2.0	1.67	1.48	28.0
Co-(7.0%)Mn/SiO ₂	27.7	40.1	-1.9 ^c	16.5	12.4	34.5	32.2	4.3	1.93	1.44	19.7

^a Reaction condition: GHSV=1000h⁻¹, t=240⁰C, P=2.0MPa.^b Using the syngas with H₂/CO ratio of 2.0 (H₂/CO/N₂=64/32/4, vol%).^c The negative values represents CO₂ selectivity in the cases that CO₂ was produced, $S_{CO_2} = [(moles\ of\ CO_{2\ out} - moles\ of\ CO_{2\ in}) / (moles\ of\ CO_{in} - moles\ of\ CO_{out})] \times 100\%$

Fig. 1. XRD patterns of Co-Mn/SiO₂ catalysts: (A) Calcined; (B) Reduced.

Fig.2. H₂-TPR profiles of Co-Mn/SiO₂ catalysts

Fig.3. Hydrocarbon selectivity distribution of FTS using H₂-deficient biosyngas over Co-Mn/SiO₂ catalysts
 (*Using the syngas with H₂/CO ratio of 2.0 as feed gas)

Fig.4. Catalyst stability using H₂-deficient biosyngas: (A)CO conversion with TOS over Co/SiO₂ and Co-(0.8%)Mn/SiO₂; (B) hydrocarbon distributions with TOS over Co-(0.8%Mn)/SiO₂.