

Progresses of Selective F-T Synthesis in ICC-CAS

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Introduction

Two categories of Co-based FTS catalysts are being developed for the production of heavy hydrocarbons and middle distillates, respectively. Several methods including sol-gel method, mesopore confinement or localization by polymer were adopted to prepare different Co catalysts. By tuning both pore structure and support surface, the Co-catalysts with tunable array of products were developed, accompanying with CH₄ selectivity being lower than 5%. Besides, the correlation of the catalyst structure with the FT performance is being well established.

Research Development of Co-based F-T Catalysts

Co Catalyst Preparation. Co catalysts are usually prepared by the impregnation methods while the co-precipitation and melting methods are preferred for Fe catalyst. Although these techniques have great practical feasibility, their drawbacks are clear: the low metal loadings, the undesired distribution of paraffin and low dispersion of the active phase in the ultimate catalysts. The homogeneous deposition-precipitation (HDP) has been developed for the preparation of highly loaded and highly dispersed oxide-supported metal catalyst. In this case, a solvated metal precursor is deposited exclusively onto the surface of a suspended support by the slow and homogeneous introduction of a precipitating agent, which then avoided nucleation of solid precursor compound in the bulk solution.

- **Organic groups modified Co-catalysts.** CH₃-modified SiO₂ ((CH₃-SiO₂), (CH₃)₂-modified SiO₂ ((CH₃)₂-SiO₂), (CH₃)₃-modified SiO₂ ((CH₃)₃-SiO₂), NH₂-modified SiO₂ (NH₂-SiO₂) and NH₂(CH₂)₂NH-modified SiO₂ (en-SiO₂) were prepared through the surface reaction between organotrialkoxysilane and Si-OH groups on SiO₂ aerogel.
- **Polymer localized Co-catalysts.** The Co/SiO₂ catalysts were synthesized by a sol-gel route from 3-aminopropyltriethoxysilane (APTS) as aminopropyl introducer for choice addition on certain condition, polymethylhydrosiloxane (PMHS) as methyl introducer and TEOS as main silica source. The catalysts were named as Si_pA-R_{NH}B, in which A meant the molar ratio of Si from PMHS to Si from other silica source; B meant the molar ratio of aminopropyl groups in APTS to Co²⁺ ions.
- **Mesopore confined Co-catalysts.** Hollow mesoporous silica sphere (HMSS) was prepared according to literature¹. The supported cobalt catalyst containing 30 wt% Co was prepared by the “two-solvent” technique which reported by this literature². The catalyst was eroded to confirm the particle size of Co₃O₄.

Catalytic performance

1. Performance of surface organic modified Co-catalysts

(CH₃-SiO₂), (CH₃)₂-SiO₂ and (CH₃)₃-SiO₂ reduced the surface silanol (Si-OH) concentration of SiO₂ support, suppressed the interaction between cobalt and silica, enhanced the reducibility of the supported cobalt species, and thus increased the catalytic activity of Co catalysts for FT synthesis (see **Table 1**). However, coordination

compounds were formed between $\text{NH}_2\text{-SiO}_2$ and Co^{2+} cations, and thus the interaction between cobalt and silica was enhanced, the reducibility of Co catalysts for FT synthesis was decreased. Such a catalyst showed the poorest performance in FT synthesis, probably because chelated compounds were formed between en-SiO_2 and Co^{2+} cation (see **Table 1**).

Table 1. FTS performance of Surface organic modified catalysts

Sample	CO Conversion (%)	Hydrocarbon distribution (wt%)					
		C ₁	C ₂ -C ₄	C ₅ +	C ₅ -C ₁₁	C ₁₂ -C ₁₈	C ₁₉ +
Co/SiO ₂	21.4	36.5	13.5	50.0	34.8	11.3	3.9
Co/en-SiO ₂	0	–	–	–	–	–	–
Co/NH ₂ -SiO ₂	4.43	7.0		88.3	33.6	48.1	6.6
Co/(CH ₃) ₃ -SiO ₂	34.3	19.8	12.0	68.2	29.5	30.2	8.5
Co/(CH ₃) ₂ -SiO ₂	45.7	13.7	11.3	75.0	31.1	25.2	18.7
Co/CH ₃ -SiO ₂	51.8	10.5	10.0	79.5	24.6	30.0	24.9

2. Performance of Polymer localized Co-catalysts

Catalyst Si_p1.8-R_{NH}0 performed obviously higher catalytic activity in FT synthesis than Si_p1.8-R_{NH}0.6 (see **Table 2**). And hydrocarbons obtained by Si_p1.8-R_{NH}0 catalyst were mainly low valuable C₁-C₄ paraffin, while high valuable heavy wax was main product from the FT reaction catalyzed by Si_p1.8-R_{NH}0.6. Structural characterization show little difference between them. The dramatic effect on selectivity might result from the variety of organic groups.

Table 2. FTS performance of polymer localized Co-catalysts

Sample	T (°C)	CO Conversion (%)	Hydrocarbon distribution (wt%)				
			C ₁	C ₂ -C ₄	C ₅ -C ₁₁	C ₁₂ -C ₁₈	C ₁₉ +
Si _p 1.8-R _{NH} 0	200.1	70.42	68.21	25.98	5.70	0.09	0.03
	210.3	89.79	73.22	22.15	4.30	0.24	0.08
Si _p 1.8-R _{NH} 0.6	200.6	39.21	14.57	5.07	1.88	0.28	78.19
	210.0	61.78	7.46	2.01	6.70	0.33	83.49

3. Performance of mesopore confined Co-catalysts

The Co₃O₄ particle size were shown to be 100 ~ 200 nm by TEM, but X-ray broadening illuminated that the particle size of Co₃O₄ was 10 ~ 20 nm. Therefore the Co₃O₄ particles cluster was composed of small primary Co₃O₄ particles, that were of nano dimension. Actually, these mono-dispersed Co₃O₄ nano-particles were loaded equably in the pore channels of the HMMS and were divided by the pore walls each other. From **Table 3** it can be seen that at reaction temperature of 210 °C the catalyst had good performance and hydrocarbon distribution which concentrated on C₅ ~ C₁₈ in FT synthesis, methane selectivity was only 4.8 wt%, C₅+ selectivity reached up to 93.6 wt%.

Table 3. FTS performance of mesopore confined Co-catalysts

CO Conversion (%)	Hydrocarbon distribution (wt%)					
	C ₁	C ₂ -C ₄	C ₅ -C ₁₈	C ₁₉ -C ₂₅	C ₂₆₊	C ₅₊
83.1	4.8	1.6	70.8	15.7	9.9	93.6

Kinetics

The active sites of Co/SiO₂ catalysts for FT synthesis are discriminated kinetically. Several Co/SiO₂ catalysts with well-defined structure were prepared. By sol-gel route, silicas of various porosity, but of similar chemical property were realized. In TPR profiles, there were four peaks after deconvolution. The relative intensity of those peaks changed as the silica pore size increased, with the low-temperature peaks (547, 588K) enlarging at expense of high temperature peaks. Quantitative analysis suggests that the extent of reduction increased gradually.

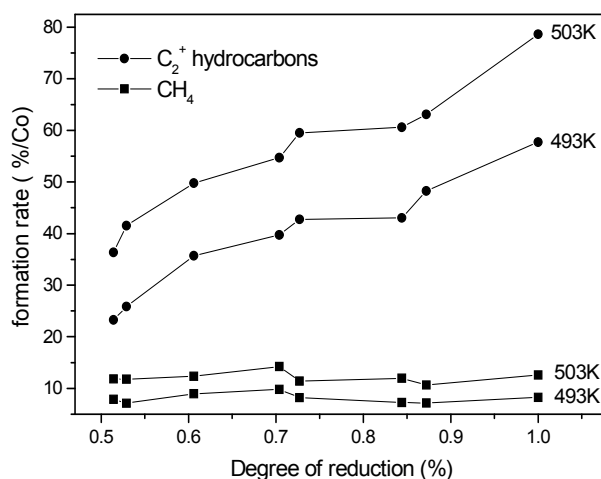


Fig.1 The absolute yield of CH₄ or C₂⁺ relating to extent of reduction

Those catalysts were evaluated in FT synthesis under conditions of 2.0MPa, 1500GHSV and H₂/CO =2. The CH₄ production was insensitive to the reducibility whereas the C₂⁺ yield responded to reducibility regularly. This meant that the CH₄ formation depended on the total cobalt, no matter how much it was reduced. In contrast, the C₂⁺ products (featured with carbon chain growth) only formed on reduced Co. On light of the above results, the F-T synthesis over cobalt was simplified as two reactions with the same feedstock. The product of reaction 1 was CH₄ and that of 2 was C₂⁺. These two reactions were independent and was first order to H₂ partial pressure. The pre-exponential factors and active energies were derived according to the parallel reactions mechanism. The difference of kinetic constants between two reactions was remarkable. The coincidence of C₂⁺ reaction parameter might confirm the presence of two active sites.

Outlook

In summary, the selective synthesis of hydrocarbon could be more controllably carried out via suitable surface modification or active sites confinement over Co-catalysts. The proposal of two active sites was supported by characterization and kinetic results. This may provide a potential solution for adjusting the products distribution

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