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The modification of SiO_2 by various organic groups and its influence on the properties of cobalt-based catalysts for Fischer–Tropsch synthesis

Lihong Shi [a,b], Debao Li [b], Bo Hou [b], Yuelun Wang [b,c], Yuhan Sun [b,*]

[a] School of Chemistry and Chemical Engineering, Shanxi University, 580 Wucheng Road, Taiyuan 030006, China
[b] State Key Laboratory of Coal Conversion, Institute of Coal Chemistry, Chinese Academy of Sciences, 27 Taoyuan Road, Taiyuan 030001, China
[c] Graduate University of Chinese Academy of Sciences, Beijing 100049, China

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ABSTRACT

SiO_2 was modified by various organic groups before the impregnation of cobalt precursor. These modified supports and the corresponding catalysts were characterized by BET, ^{29}Si CP MAS NMR, XRD, Raman, XPS and H_2-TPR. These characterizations clearly show the changes of morphology as well as reducibility of the catalysts. The organic modification of SiO_2 remarkably influences the reducibility and catalytic properties of Co catalysts. Co catalyst supported on $(CH_3)_3$-modified SiO_2 exhibits high activity and C_5^+ hydrocarbon selectivity. However, COOH-, NH_2-, and $NH_2(CH_2)_2NH$-modified SiO_2 distinctly suppress the catalytic activity of Co catalysts.

1. Introduction

Recently, Fischer–Tropsch (F–T) synthesis has received new interest again due to the severe oil crisis and the tight fuel specifications. Cobalt-based catalysts are the preferred catalysts for hydrocarbon synthesis because of their high F–T synthesis activity and selectivity for long-chain paraffins [1,2]. The catalytic activity and product selectivity of cobalt catalysts are strongly influenced by the surface properties of support, because these properties can change the interaction of cobalt and support, resulting in different dispersion and reducibility of supported cobalt. Zhang et al. [3] have found that the physico-chemical properties of alumina could be influenced by hydrothermal treatment with some solutions, and the dispersion and reducibility of supported cobalt were closely associated with the surface properties of alumina support. Zhao et al. [4] have reported that the calcination had a great influence on the surface acidity of ZrO_2, and consequently changed the dispersion and reducibility of supported cobalt.

There are plenty of silanols on the SiO_2 surface. The change of silanol properties has a strong effect on the dispersion and reducibility of supported cobalt as well as the performance for F–T synthesis. Ming and Baker [5] have studied the influence of the pH of the impregnation solution on the catalytic performance of cobalt–silica F–T catalyst, finding that the pH of the impregnation solution strongly affected the interaction between cobalt precursor and silica support during the preparation of catalyst, changing electric charge distribution on the silica surface, and yielding different dispersion of cobalt metal and reducibility. Steen et al. [6] have reported that the catalytic performance of a cobalt–silica gel F–T catalyst was strongly affected by pH value of solution. Silanol groups act as an amphoteric material and, depending on the pH of the impregnation solution, exist as SiOH, SiO^- or $SiOH_2^+$ species. The relative amount of these species at the silica surface is a function of pH value. At pH higher than the isoelectric point of silica (pH 1–2.2) a surplus of negative charge was present on the silica surface, which favored the adsorption of cobalt complexes on SiO_2 surface and resulted in strong interaction between cobalt and SiO_2. Zhang et al. [7] have studied the catalysts prepared from different cobalt nitrate solutions. The catalyst prepared from dehydrated ethanol exhibited stable activity higher than the catalysts prepared from any other cobalt nitrate solution. The cobalt ion dissolved in dehydrated ethanol favored the distribution of Co over the whole silica surface, resulting in higher dispersion of supported cobalt. Zhang et al. [8] have found that the pretreatment of silica support by organic solvents during catalyst preparation markedly enhanced the catalytic activity in liquid phase F–T synthesis, due to the promotional effects on determining high dispersion and high reduction degree of supported cobalt simultaneously. However, few literatures reported the influence of SiO_2 modified by different organic groups on the dispersion and reducibility of cobalt and the catalytic performance. In the present work, SiO_2 was modified by different organic groups, to change the surface silanol properties of SiO_2 support, and the physico-chemical and catalytic properties of supported cobalt catalysts were investigated.

2. Experimental

2.1. Organic modification of SiO_2

$(CH_3)_3$-modified SiO_2 ($(CH_3)_3$-SiO_2) was prepared as follows: 10.0 g SiO_2 was preheated at 200 °C for 12 h in vacuo to remove all

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[*] Corresponding author. Tel.: +86 351 4121877; fax: +86 351 4041153.
E-mail address: yhsun@sxicc.ac.cn (Y. Sun).

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adsorbed moisture except surface silanols, cooled down to room temperature in vacuo and then transferred into a 250 ml conical flask. After mixing with 40.0 ml toluene and 5.0 ml chlorotrimethylsilane (TMCS), the mixture in conical flask was put into the ultrasonic bath (Sheshin, Japan, operating frequency 50 kHz) for 2 h at ambient temperature. The sample was then obtained by extracting with toluene in a Soxhlet extractor for 24 h and drying at 50 °C in vacuo. The same method was used for the preparation of NH_2-modified SiO_2 (NH_2-SiO_2), $NH_2(CH_2)_2NH$-modified SiO_2 ($NH_2(CH_2)_2NH$-SiO_2) and CN-modified SiO_2 (CN-SiO_2), using (3-aminopropyl)triethoxysilane (APTES), N-[3-(trimethoxysilyl)propyl]ethylenediamine (EDPTMS) and (3-cyanopropyl)triethoxysilane (CPTES).

COOH-modified SiO_2 (COOH-SiO_2) was prepared as follows: 1.0 g CN-SiO_2 was added to 100 ml 48% (v/v) aqueous sulfuric acid with stirring for 4 h at 95 °C. The sample was washed with copious water and then dried at 50 °C in vacuo. The resulting sample was labeled as COOH-SiO_2.

2.2. Preparation of cobalt catalysts

The Co catalysts (5 wt.% cobalt loading) were prepared by impregnating $(CH_3)_3$-SiO_2, NH_2-SiO_2, $NH_2(CH_2)_2NH$-SiO_2, and COOH-SiO_2 with the ethanol solutions of cobalt nitrate. The samples were dried at 120 °C and calcined in air at 600 °C for 6 h, hereafter named Co/$(CH_3)_3$-SiO_2, Co/NH_2-SiO_2, Co/$NH_2(CH_2)_2NH$-SiO_2, and Co/COOH-SiO_2, respectively. Co/SiO_2, which was supported on untreated SiO_2, was used as a reference.

2.3. Catalyst test

The F–T synthesis reaction was carried out at 2.0 MPa, 240 °C, 1000 h^{-1}, and a H_2/CO ratio of 2 in a fixed-bed reactor (i.d. = 10 mm). The catalysts (1.5 ml) were reduced in a flow of hydrogen at 400 °C for 6 h and then cooled to ambient temperature before switching to the syngas. Data were taken at the steady state after 24 h on stream. The gas effluent was analyzed on a GC-8A chromatograph equipped with thermal conductivity and flame ionization detectors. Liquid products and wax were collected in a cold trap and a hot trap respectively and then were off-line analyzed on a GC-920 chromatograph which was equipped with a 35 m OV-101 capillary column.

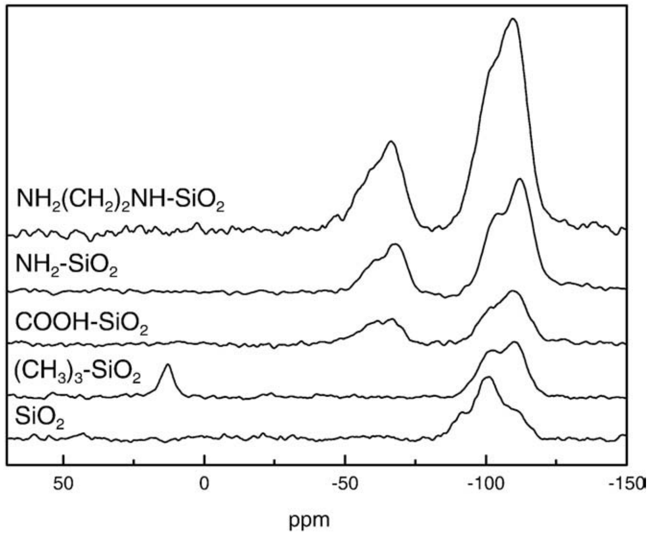

Fig. 1. ^{29}Si CP MAS NMR spectra of different SiO_2 samples.

Table 1
The physico-chemical properties of supports and cobalt catalysts.

Sample	S_{BET} (m^2/g)	V_{Pore} (cm^3/g)	Pore size (nm)	Co_3O_4 size[a] (nm)	Reduction degree[b] (%)
SiO_2	332	1.37	16.5	–	–
$(CH_3)_3$-SiO_2	263	1.25	19.1	–	–
COOH-SiO_2	250	1.22	18.6	–	–
NH_2-SiO_2	170	0.85	20.1	–	–
$NH_2(CH_2)_2NH$-SiO_2	160	0.96	23.8	–	–
Co/SiO_2	255	0.61	9.6	12	60
Co/$(CH_3)_3$-SiO_2	251	0.61	9.7	13	80
Co/COOH-SiO_2	264	0.91	13.7	11	39
Co/NH_2-SiO_2	186	0.50	10.8	8	33
Co/$NH_2(CH_2)_2NH$-SiO_2	190	0.55	11.5	–	7

[a] Calculated from the Scherrer equation according to the (311) diffraction peak of Co_3O_4.

[b] Calculated during TPR at 60–400 °C.

2.4. Catalyst characterization

BET surface area, pore volume, and pore diameter were determined on an ASAP-2000 Micromeritics instrument by the N_2 adsorption method. The ^{29}Si CP MAS NMR spectra were recorded on a Varian Infinity Plus spectrometer using 5 mm zirconia rotors and a magic-angle spinning speed of 8.0 kHz. XRD studies were performed using a Rigaku D/max-γA spectrometer at 40 kV and 20 mA using monochromatic Cu Kα radiation. Raman spectra were recorded with a resolution of 1 cm^{-1} in a Renishaw RM 2000 spectrometer using a 514 nm Ar^+ laser. XPS data were obtained with an ESCALab220i-XL electron spectrometer from VG Scientific using 300 W Al Kα radiation. The base pressure was about 3×10^{-9} mbar and the binding energies were referenced to the C1s line at 284.6 eV from adventitious carbon. H_2-TPR experiments were carried out in a quartz microreactor at a ramp rate of 10 °C/min in a 5% H_2/Ar flow of 60 ml/min.

3. Results and discussion

3.1. Organic modification of SiO_2

The ^{29}Si CP MAS NMR spectra in solid state indicated that the covalent bond was formed between silylating agents and silanol groups on the silica surface (see Fig. 1). For SiO_2, three resonances appeared at −109, −101, and −91 ppm, which could be assigned to the silicon sites of Q^4, Q^3, and Q^2 [$Q^n = Si(OSi)_n(OH)_{4-n}$, $n = 2$–4] [9,10], respectively. For $(CH_3)_3$-SiO_2, there was M^1 ($M^1 = (CH_3)_3SiOSi$) signal at 14.6 ppm, showing an effective surface organic modification of TMS [11–13]. For Co/COOH-SiO_2, Co/NH_2-SiO_2 and Co/$NH_2(CH_2)_2NH$-SiO_2, the resonances at −58 and −67 ppm were assigned to $RSi(OSi)_2OH$ and $RSi(OSi)_3$ [14–16], illustrating the successful organofunctionalization of SiO_2 by the organic groups via covalent bonds. After organic modification of SiO_2, the surface area and pore volume decreased (see Table 1), which can be attributed to the existence of organic groups in pores. Meanwhile, some organic groups covered micropores, which resulted in the decrease of the surface area as well as the increase of average pore diameter (see Table 1).

3.2. Phase structure of catalysts

The crystallite phases of cobalt catalysts were characterized by XRD (see Fig. 2). For Co/SiO_2 and Co/$(CH_3)_3$-SiO_2, sharp diffraction peaks of Co_3O_4 phase appeared in XRD patterns. Different from Co/SiO_2 and Co/$(CH_3)_3$-SiO_2, the diffraction peaks of Co_3O_4 phase became wider in XRD patterns of Co/COOH-SiO_2 and Co/NH_2-SiO_2. For Co/$NH_2(CH_2)_2NH$-SiO_2, Co_3O_4 diffraction peaks weren't detected. According to XRD half-width