Sodium-promoted iron catalysts prepared on different supports for high temperature Fischer–Tropsch synthesis

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ABSTRACT

The paper addresses the effect of sodium promotion on the structure and catalytic performance of iron catalysts supported on alumina, silica, CMK-3 and carbon nanotubes in high temperature Fischer-Tropsch synthesis giving general rules for the selection of supports for selective synthesis of olefins in the presence of promoter.

Our results show that the effect of sodium promotion strongly depends on the support. In silica and CMK-3 carbon support, iron species interact with sodium with formation of inactive sodium-iron mixed oxides or carbides which results in higher olefin selectivity and chain growth probability but lower Fischer-Tropsch reaction rate. In alumina supported catalysts, sodium promotion preferentially leads to formation of sodium aluminate with a relatively small effect in Fischer–Tropsch synthesis. The effect of promotion with sodium is more pronounced on carbon nanotubes which contain iron carbide species stabilized by encapsulation in the carbon matrix. The sodium promoted catalysts supported on carbon nanotubes exhibit higher selectivity to both light and long-chain olefins.

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1. Introduction

Light olefins (C_2–C_4) are among the most important building blocks for the petrochemical industry. The traditional way to produce them is thermal or catalytic cracking of petroleum fractions. High temperature Fischer-Tropsch (FT) synthesis is one of the most interesting alternatives for selective olefin synthesis. This process converts syngas produced from natural gas, coal or biomass into a mixture of hydrocarbons on a metal catalyst at 300–350 °C [1,2]. Iron is the most efficient catalyst for high temperature FT synthesis due to its low methanation activity, higher selectivity to olefins and higher stability in the presence of contaminants in comparison to Co-based catalysts [3]. Because of its significant water gas shift, iron catalysts can convert syngas with different H_2/CO ratios. The light olefin selectivity over unpromoted iron catalyst is, however, insufficient for industrial implementation.

The catalytic performance of iron catalysts can be improved by promotion. Most of iron FT catalysts contains potassium [4–9].

Other promoters such as copper [7,10–16], sodium [4,17–22], zinc [10], vanadium [23] and sulfur [20,24] have also been used. It is well-known that sodium addition leads to lower methane selectivity and a significant increase in the olefin-to-paraffin ratio and water-gas shift (WGS) activity [4,17,18]. The effect of sodium is usually explained by a decrease in the strength of C—O bonds, which leads to a higher coverage of dissociated CO on the surface [4,18,20]. The presence of sodium could also result in a higher extent of iron carbidization, the maximum extent of carbidization being attained for the optimal sodium content [18]. Higher concentrations of sodium inhibit iron carbide formation and result in lower activity and higher rate of light hydrocarbons formation. Sodium suppresses the secondary olefin hydrogenation and increases the chain growth probability. Recently, de Jong and co workers [25,26] showed that the performance of iron catalyst supported on α-alumina or carbon nanofibers can be considerably improved by simultaneous promotion with sodium and sulfur. However, in comparison with potassium promotion, fewer papers about sodium promotion have been reported so far.

Because of low iron cost, most R&D activities have focused on bulk iron catalysts. Supported iron catalysts have however, several advantages for high temperature FT synthesis compared to their bulk counterparts such as a higher density of active sites, bet-

Table 1
Catalysts characterization.

Sample	Fe	N$_2$ adsorption over supports					Iron oxide[a] diameter (XRD)		
	(wt.%)	S$_{BET}$	S$_{mic}$	V$_{tot}$	V$_{mic}$	Pore size	(nm)		
		(m^2/g)	(m^2/g)	(cm^3/g)	(cm^3/g)	(nm)	Na/Fe		
							0	0.1	0.5
Fe/SiO$_2$	9.6	307	25	1.31	0.01	17.5	13.7	13.9	13.9
Fe/CMK-3	10.2	1326	557	1.32	0.12	3.8	8.5	4.4	3.9
Fe/Al$_2$O$_3$	9.7	186	5	0.51	0.0	11.0	–	–	–
Fe/CNT	9.9	163	17	0.56	0.01	5	13.3	20.3	18.0

[a] Based on the diffraction peaks of hematite (H) or magnetite (M).

ter mechanical stability and higher intrinsic activity. The effect of support chemical composition on the structure and catalytic performance of unpromoted iron catalysts in high temperature FT synthesis has been addressed in recent publications [27]. It was shown that the catalyst structure and iron species were strongly affected by the nature of the support. Iron phase composition seems to be a major parameter which may affect catalytic performance sometimes even more importantly than iron dispersion. Higher catalytic performance was attributed [27] to the presence of iron carbides and iron–magnetite composites. In supported catalysts, the promoter can interact differently with both support and active phase. The effect of promotion can be strongly affected by these interactions. This could be a reason why the promotion with sodium and other metals could be more beneficial in some supported catalysts compared to others.

The effect of sodium promoter on iron FT catalysts has been previously investigated for silica [11] or alumina supports [13,15]. Recent reports suggest that the FT reaction can be significantly improved by using carbon materials (e.g. CNT [21]). No information is available about the effect of sodium promotion on the performance of carbon supported catalysts. Thus, the focus of the present paper is on the investigation of the possible interactions between sodium, iron and different supports in iron-based catalysts and on the effect of these interactions on their catalytic performance in high temperature FT synthesis. Silica, γ-alumina, CMK-3 mesoporous carbon and carbon nanotubes were used as catalyst supports. The catalysts were characterized by a combination of techniques: BET, FTIR, X-ray diffraction (XRD), transmission electron microscopy (TEM), CO$_2$-temperature programmed desorption (CO$_2$-TPD), CO-temperature programmed reaction (CO-TPR) and transient hydrogenation. The catalytic performance was evaluated using a Flowrence high throughput catalytic unit of the REALCAT platform operating under typical conditions of high temperature FT synthesis.

2. Experimental

2.1. Catalyst preparation

Commercial amorphous silica (CARIACT Q-10, Fuji Silysia), γ-alumina (Puralox, Sasol), mesoporous CMK-3 and carbon nanotubes were used as catalytic supports. The synthesis of CMK-3 was carried out according to Ref. [28]. Briefly, 5 g of SBA-15 was added to a solution obtained by dissolving 6.25 g of sucrose and 0.7 g of H$_2$SO$_4$ in 25 g of H$_2$O. The mixture was transferred to a drying oven for 6 h at 100 °C, followed by increasing the oven temperature to 160 °C for 6 h. After dissolving additional 4 g of sucrose, 0.45 g of H$_2$SO$_4$ and 25 g of H$_2$O, the mixture was treated again at 100 and 160 °C using the same drying oven. The carbonization was completed by pyrolysis with heating to typically 900 °C under N$_2$. The obtained carbon -silica composite was washed twice with 1 M NaOH solution (solid-to-liquid ratio 1:100) at 95 °C to remove

the silica template. The template-free carbon material was filtered, washed with deionized water and dried at 120 °C overnight. The synthesized CMK-3 was treated with 1 M nitric acid solution at 50 °C for 2 h to remove sodium.

Multi-wall carbon nanotubes (CNT, purity ≥95%, outer diameter 20–30 nm) prepared by chemical vapor deposition (CVD) were purchased from the Chengdu Limited Company of Organic Chemistry (CCOC) in China. The raw CNTs were refluxed for 16 h in concentrated HNO$_3$ (65 wt.%) at 120 °C in an oil bath. Then, the mixture was filtered and washed with distilled water thoroughly until a neutral pH was reached, followed by drying at 100 °C overnight.

The Fe/SiO$_2$, Fe/Al$_2$O$_3$, Fe/CNT and Fe/CMK-3 catalysts were prepared by incipient wetness impregnation of the relevant supports with an aqueous solutions of hydrous iron nitrate (Fe(NO$_3$)$_3$·9H$_2$O). The concentrations of the impregnating solutions were subsequently calculated to obtain 10 wt.% iron in the final catalysts. After impregnation the catalysts were dried overnight in an oven at 100 °C. Then they were calcined in air (Fe/SiO$_2$, Fe/Al$_2$O$_3$) or N$_2$ flow (Fe/SiO$_2$-N$_2$, Fe/CNT, Fe/CMK-3) at 400 °C for 6 h with 1 °C/min temperature ramping.

The catalysts were promoted with sodium by impregnating calcined samples with aqueous solution of Na$_2$CO$_3$. The catalysts have been subsequently calcined in N$_2$ flow for 6 h. The amount of Na in the samples was calculated to have molar ratios of Na to Fe of 0.1, 0.3 and 0.5. The samples are labeled as **Fe/Support(x)**, where **Support** and **x** indicate respectively the nature of the support (namely SiO$_2$, Al$_2$O$_3$, CNT or CMK-3) and molar ratio Na to Fe in the catalysts. The ICP-OES analysis showed that iron content in all samples (after calcination) is still around 10 wt.% (Table 1).

2.2. Characterization

The Fe content of different samples was tested by inductively coupled plasma optical emission spectrometry (ICP-OES). The BET surface areas, pore volumes and average pore diameters were determined by low temperature N$_2$ adsorption using a Micromeritics ASAP 2000 automated system. The samples were degassed under vacuum at <10 μm Hg in the Micromeritics ASAP 2000 at 300 °C for 4 h prior to N$_2$ physisorption. The ex situ X-ray powder diffraction (XRD) experiments were conducted using a Bruker AXS D8 diffractometer using Cu(Kα) radiation (λ = 0.1538 nm). The XRD patterns were collected in the 20–70° (2θ) range. Peak identification was carried out by comparison with JCPDF standard spectra software. The average crystallite size of Fe$_3$O$_4$ and Fe$_2$O$_3$ was calculated using the diffraction peaks according to the Scherrer equation [29].

The IR spectra of the supports and relevant catalysts were recorded with a Nicolet Protégé 460 FT-IR spectrometer at 4 cm^{-1} optical resolution. Prior to the measurements, the catalysts were pressed with KBr to make discs.

The TEM analyses were carried out on a Jeol 2100F (field emission gun) microscope operating at 200 kV equipped with a probe