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Fuel Processing Technology 88 (2007) 29 – 33

FUEL PROCESSING TECHNOLOGY

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# Solid state NMR investigation of silica aerogel supported Fischer–Tropsch catalysts

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Received 31 December 2005; accepted 30 June 2006

## Abstract

The Fischer–Tropsch (F–T) catalyst is the critical component for the F–T synthesis of a variety of hydrocarbons from syngas. Fischer–Tropsch cobalt, iron and ruthenium catalysts supported on silica aerogel have been prepared using a combination of sol–gel chemistry and vapor phase deposition methods. Solid state NMR spectroscopy, a very powerful technique for analyzing the structure and dynamics of various materials, was employed in the study of these F–T catalyst systems. The silica aerogel supported F–T catalysts have been investigated using both solid state $^{29}$Si and $^{13}$C NMR methods. The silica aerogel's tetrahedral sub-unit structure and the influence of the loaded metal compounds have been observed. Three types of $Si(O_{1/2})_4$ tetrahedral unit structure ($Q_2$, $Q_3$ and $Q_4$) are clearly resolved in the silica aerogel samples. The calcining process and the loading of metal compounds produce line broadening in the $^{29}$Si spectra sufficient to prevent clear resolution of the three distinct $Q_n$ spectral lines, but the broadened spectra indicate that the three Q sub-unit structures are still present. The ferrocene and ruthenocene molecules used in the vapor phase deposition method exhibit a rapid exchange within the silica aerogel support similar to what one would expect in the gas or liquid state.

*Keywords:* Solid state NMR; Fischer–Tropsch catalysts; Silica aerogel

## 1. Introduction

The Fischer–Tropsch (F–T) synthesis [1–3], i.e. the hydrogenation of CO over heterogeneous metal catalysts to produce higher hydrocarbons, has recently attracted renewed interest because of the increasing demand for high quality and environmentally friendly transportation fuels [4–8]. The F–T catalyst is the critical component for the CO hydrogenation process. Generally, cobalt, iron, or ruthenium based catalysts loaded on different supports such as $SiO_2$, $Al_2O_3$, $TiO_2$, etc. have been widely used in the F–T synthesis [2–9]. Cobalt based catalysts are generally favored for F–T synthesis due to their high activity, selectivity for linear hydrocarbons, and low activity for the water–gas shift reaction [10,11], especially for natural gas derived syngas. Iron based catalysts are preferred in F–T synthesis of hydrocarbons from coal- or biomass-derived syngas because of their lower cost, lower methane selectivity, lower sensitivity to poisoning, flexible product slate and robustness at low $H_2$/CO ratios [2–4,12]. Ruthenium based catalysts are highly active and work at the lower reaction temperatures. However, the high cost of this precious metal limits its commercial application [10].

Among the various supporting materials used for F–T synthesis, silica is one of the most popular and has been widely employed [4,5,7,8,13,14]. Cobalt catalysts supported on mesoporous silica based SBA-15 have been studied by Ohtsuka et al. [7] and Martínez et al. [8]. The influence of metal loading, cobalt precursor, and promoters on the physico-chemical and catalytic properties of mesoporous Co/SBA-15 catalysts for the F–T reaction were investigated [8]. Sol–gel derived silica aerogel has ultra-low density (~0.07 g/cm$^3$), high surface area (~800 m$^2$/g), and a high degree of porosity (~96%) [15]. The pores lie in the mesoporous (2–50 nm) regime and exist as an interconnected, three-dimensional network. This pore structure allows mass transport within the silica aerogel to approach the

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doi:10.1016/j.fuproc.2006.06.008

gas-phase diffusion limits [16]. Because of these unique properties, silica aerogel supported catalysts have become attractive candidates for F–T synthesis [5,17].

Many techniques have been applied to characterize the structure of the F–T catalysts [4–9], such as X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), temperature-programmed reduction (TPR), Mössbauer spectroscopy, NMR spectroscopy [18], etc. Among these techniques that have been used for the characterization of catalysts, NMR spectroscopy is unique in its ability to provide both structural and dynamic information [19]. Modern solid state NMR makes it possible to detect signals from distinguishable sites in molecules and materials, and to monitor the connectivities, correlations, and dynamics of these sites. Okabe et al. [18] confirmed the Al incorporation into the silica framework of cobalt catalysts from solid state $^{27}$Al-MAS NMR spectra. Komaya et al. [20] investigated the activity of Ru/$TiO_2$ and $TiO_2$-promoted Ru/$SiO_2$ catalysts for F–T synthesis. The fraction of the Ru surface available for $H_2$ adsorption was determined by a $^{1}$H NMR experiment.

In the present work, three types of silica aerogel supported F–T catalysts (cobalt, iron and ruthenium based catalysts) were studied using solid state $^{29}$Si NMR and $^{13}$C NMR methods. The silica aerogel's tetrahedral sub-unit structure and the effect of the loaded metal compounds were obtained from these experiments. This paper focuses on the structure and interaction of metal compounds with the silica aerogel support material as the catalyst activity and other characteristic results have been reported elsewhere [5].

## 2. Experimental section

### 2.1. Catalysts preparation

Four silica aerogel samples were prepared using sol–gel chemistry followed by drying under supercritical $CO_2$/ethanol conditions with or without calcination as previously described [5]. Cobalt catalysts supported on silica aerogel have been prepared under supercritical ethanol conditions. Three different loadings of cobalt (2, 6, and 10% by weight) were synthesized. The details of cobalt catalyst preparation were described in Ref. [5].

Iron and ruthenium loaded catalysts were prepared by the gas-phase incorporation of volatile, organometallic compounds of iron and ruthenium [21]. Dehydrated (heated to 200 °C under dynamic vacuum for 1 h) and sieved (45–80 mesh) silica aerogel and either ferrocene or ruthenocene are mixed in a Schlenk flask under vacuum ($10^{-3}$ mm Hg). Within minutes for ferrocene and within hours for ruthenocene the metal-containing compound incorporates into the aerogel via sublimation and, concomitantly, the silica aerogel takes the color of the metal-containing compound (orange for ferrocene and white for ruthenocene). The metallocene-doped silica aerogels exhibit chemical reactivity unlike the native compounds. While ferrocene and ruthenocene are air-stable, within the silica aerogel they readily react with air in a matter of hours; consequently, the metallocene-doped silica aerogel must be handled under an inert atmosphere.

### 2.2. Solid state NMR experiments

Solid state $^{29}$Si and $^{13}$C NMR experiments on F–T catalysts were performed on a Chemagnetics CMX200 spectrometer using a 7.5 mm PENCIL rotor probe. The $^{29}$Si Larmor frequency was 39.74 MHz and the $^{13}$C operating frequency was 50.31 MHz. All the samples were ground into powder before packing into the rotor. Iron and ruthenium catalyst samples were ground and packed in a $N_2$ filled glove box. The $^{29}$Si MAS spectra were obtained using a single pulse sequence at a spinning rate of 4 kHz. No line broadening was used in the processing of $^{29}$Si spectra. The $^{29}$Si 90° pulse was 8.0 μs. The pulse delay for $^{29}$Si MAS experiments was either 50 s or 200 s depending on the samples. The $^{29}$Si $T_1$ values of cobalt loaded catalysts were obtained by the saturation recovery method, in which an array of eight waiting times in the range of 30 s and 500 s or 50 s to 1500 s was used in the $\pi/2$–$\pi/2$ sequence. All $^{29}$Si chemical shifts were externally referenced to TMS.

$^{13}$C NMR spectra were obtained using both static CP and CP/MAS methods. Fifty hertz line broadening was applied in processing the $^{13}$C spectra. The proton 90° pulse was 4.3 μs. The contact time was 5 ms and the pulse delay was 3 s. The $^{13}$C spectra were referenced externally to a CP/MAS spectrum of hexamethylbenzene (HMB) with the methyl peak at 17.35 ppm relative to TMS.

## 3. Results and discussion

Silicon-29 is the only magnetic isotope of the three naturally occurring isotopes ($^{28}$Si, $^{29}$Si and $^{30}$Si) with a natural abundance of 4.7%. $^{29}$Si has a spin of 1/2 and a magnetic moment of −0.9609, therefore it has a receptivity of $3.69 \times 10^{-4}$ compared with $^{1}$H. The chemical shifts of most silicon compounds fall between +50 and −200 ppm. Solid state $^{29}$Si NMR has been successfully applied to a wide range of crystalline and amorphous silicates or other related materials [22]. There are five types of $Si(O_{1/2})_4$ tetrahedral units (designated $Q_0$, $Q_1$, $Q_2$, $Q_3$ and $Q_4$) that can be present in the $^{29}$Si NMR spectrum. Typical chemical shift values with characteristic values in the Q region are $Q_0 = -72$ to $-82$ ppm; $Q_1 = -82$ to $-89$ ppm; $Q_2 = -92$ to $-96$ ppm; $Q_3 = -100$ to $-104$ ppm; and $Q_4 \sim -110$ ppm [22–24]. $Q_0$ is designated a single tetrahedron, $Q_1$ an end group, $Q_2$ a middle group, $Q_3$ a branching site, and $Q_4$ a cross-linking group. Fig. 1 shows the stereo-chemical structure of each $Q_n$ unit.

Fig. 2 contains the $^{29}$Si MAS NMR spectra of four silica aerogel support materials prepared under different conditions. Three $^{29}$Si NMR resonances appear distinctly in Fig. 2a and c. A relaxation delay of 50 s was used to obtain the optimal intensity of each silicon site in the $^{29}$Si spectra. The $^{29}$Si chemical shift values are −96 ppm, −104 ppm, −110 ppm in Fig. 2a and −92 ppm, −101 ppm and −110 ppm in Fig. 2c. It can be seen clearly that $Q_2$, $Q_3$ and $Q_4$ $Si(O_{1/2})_4$ tetrahedral sub-units exist in the silica aerogel processed under supercritical ethanol/$CO_2$ conditions without calcination (Fig. 2a and c). After calcination (Fig. 2b and d) three $^{29}$Si resonance peaks from $Q_2$, $Q_3$ and $Q_4$ units become considerably broadened. However, the chemical shift regimes of the three Q sub-units are