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The effect of sulfur on supported cobalt Fischer–Tropsch catalysts

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Abstract

TiO_2- and SiO_2-supported, 10% by mass cobalt Fischer–Tropsch (F–T) catalysts, loaded with low concentrations of sulfur (100–2000 ppm) from different sources ($(NH_4)_2S$, $(NH_4)_2SO_4$, and $(NH_4)_2SO_3$), have been synthesized and characterized using DRIFTS and TPR. CO adsorption and F–T reaction, monitored by DRIFTS, revealed that small amounts of sulfur (100 ppm) increased the strength of most types of metal–CO interactions and enhanced F–T catalyst activity, as reflected by more intense metal–CH_x infrared intensities relative to the unsulfided catalyst. Sulfur concentrations between 200 and 2000 ppm gave infrared spectra with decreased intensity of the absorbance peaks due to adsorbed hydrocarbons. It was found that the presence of sulfur resulted in a slight increase in the reduction temperature of the titania-supported catalysts. Sulfur on the surface of the silica supported catalysts decreased the intensity of the TPR peak related to a reducible silicate. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Co; TiO_2; SiO_2; Supported catalysts; IR spectra of adsorbed CO; TPR; Fischer–Tropsch

1. Introduction

Supported cobalt catalysts are important for the Fischer–Tropsch (F–T) synthesis of long chain hydrocarbons from natural gas, a reaction that occurs at relatively low temperatures and pressures [1,2]. As with many supported transition metal catalysts, the activity and selectivity is influenced by the structure of the catalyst, the dispersion and degree of reduction of the metal, and the strength of adsorption of reactant molecules on the metal surface [3–5].

Sulfur is considered to be one of the worst poisons for an F–T catalyst, its action resulting predominantly from the blockage of active sites [6]. However, a few instances have been recorded where low concentrations of sulfur have promoted F–T catalysts by increasing activity and olefin selectivity [7], improving the heavier hydrocarbon selectivity [8], and increasing the activity per metal surface area exposed [9,10]. The data imply an electronic promoting action of sulfur that remains to be explored and understood. For this reason, a study of the effect of low concentrations of sulfur on the surface of transition metal catalysts can provide an understanding of these observations.

In this paper, we report on the use of diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) for the in situ monitoring of CO adsorption and hydrocarbon formation during F–T reactions on 10% Co supported on titania and silica catalysts. These catalysts have been further loaded with low concentrations of sulfur from various sources, with the

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novelty lying in the method of addition and choice of the sulfur sources. The cobalt catalysts have also been investigated by TPR studies.

2. Experimental

2.1. Catalyst preparation

TiO_2 (Degussa P25) supported catalysts were prepared by incipient wetness impregnation using an aqueous solution of $Co(NO_3)_2 \cdot 6H_2O$ (SAARCHEM 99%) to produce a 10% Co loading. After drying at 393 K for 16 h the catalysts were further loaded with sulfur using an aqueous solution of $(NH_4)_2S$ (SAARCHEM 10% solution by mass) and incipient wetness impregnation to produce catalysts containing 50, 100, 200, 500, 1000, and 2000 ppm sulfur. $(NH_4)_2SO_4$ (BDH 99.5%) and $(NH_4)_2SO_3$ were also used as sources of sulfur. Catalysts were also produced by impregnating the support with the $Co(NO_3)_2 \cdot 6H_2O$ and $(NH_4)_2S$ together from the same solution. A third type of catalyst was produced by loading the sulfur onto the titania before the cobalt. All samples were then calcined in air at 673 K for 4 h.

SiO_2 (Degussa Aerosil 200) supported catalysts were synthesized using the first method of preparation (cobalt loaded before the sulfur), with sulfur concentrations of 200, 500, 1000 and 2000 ppm.

2.2. Measurements

TPR measurements were preceded by sample drying under a flow of nitrogen at 423 K for 30 min. A gas mixture consisting of 5% H_2 in nitrogen at a flow rate of 4 ml min^{-1} was passed over the calcined 100 mg samples (850–1180 μm particles) at a heating rate of 10.5 K min^{-1}.

The IR spectroscopic study (CO adsorption) was carried out using a Nicolet Impact 420 IR Fourier Transform spectrometer. The diffuse reflectance IR spectra were recorded using a standard reflection accessory (Harrick Scientific), equipped with a flow cell into which the ground catalyst (~100 mg) was loaded. The catalysts were treated with pure carbon monoxide at 2 bar and 503 K after being reduced for 3 h at 623 K under hydrogen. In order to record a spectrum without gaseous carbon monoxide, an earlier spectrum consisting of 1024 scans (0–30 min) was subtracted from a subsequent spectrum. The F–T reactions were performed at 8 bar using a 10% CO, 20% H_2 mixture in Ar, at 503 K.

3. Results and discussion

3.1. DRIFTS studies

The F–T reactions were performed on the TiO_2-supported catalysts (after reduction at 623 K for 3 h), and monitored by in situ FTIR spectroscopy. Spectra were recorded every 30 min during the catalytic reactions. Fig. 1 shows the spectra produced after 120 min of reaction on three different titania-supported catalysts. Peaks are evident at 3014 (CH_4), 2960 (CH_3), 2930 and 2875 cm^{-1} (CH_2 symmetric and asymmetric stretches) [11–13]. It can be observed that the addition of a low concentration of ammonium sulfide (100 ppm S; Fig. 1(B)) onto the surface of the catalyst *increases* the intensity of the IR peaks due to adsorbed hydrocarbon products on the surface of the cobalt. However, at a concentration of 2000 ppm of sulfur (from ammonium sulfide), the peak intensity is considerably *decreased* relative to the unsulfided and sulfided (100 ppm S) catalysts (Fig. 1(C)).

The catalysts that were prepared by loading cobalt and sulfur together or by loading sulfur first display a similar trend (see Figs. 2 and 3). Here, however, increasing the concentration of sulfur in these catalysts, from 200 to 2000 ppm, results in a smaller decrease in hydrocarbon peak intensity. It can also be observed that the intensities do not drop below the values seen for the unsulfided cobalt catalyst.

Therefore, our results show that sulfur at levels above 200 ppm and loaded after the cobalt brings about a poisoning effect, while sulfur loaded before the cobalt does not. However, sulfur concentrations below 200 ppm appear to enhance catalyst activity.

Similar experiments were also performed on catalysts loaded with sulfur (200–2000 ppm) in the form of SO_3^{2-} and SO_4^{2-}. Hydrocarbon peak intensities for these catalysts are considerably lower than for the sulfided catalysts discussed above. This implies that the sulfur on the surface of the sulfided catalysts is not expected to be in the form of a sulfite or a sulfate prior to reduction.

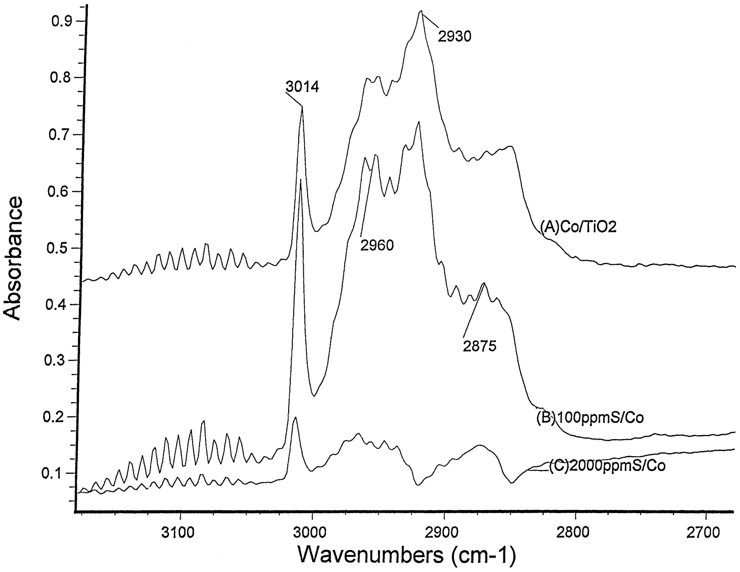

Fig. 1. IR spectra of hydrocarbons adsorbed on Co after 120 min of in situ F–T reaction at 230°C and 8 bar: (A) Co/TiO_2; (B) 100 ppm S/Co/ TiO_2 (sulfur loaded after cobalt); (C) 2000 ppm $S/Co/TiO_2$.

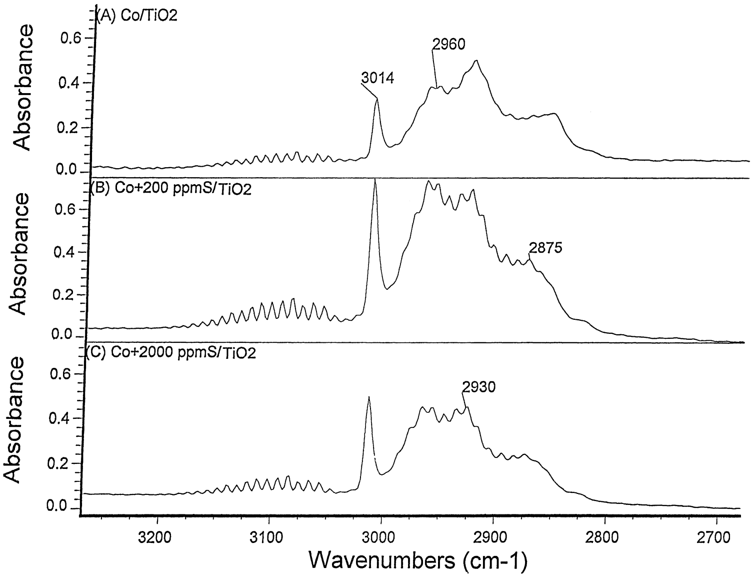

Fig. 2. IR spectra during in situ F–T reactions after 120 min: (A) Co/TiO_2; (B) Co+200 ppm S/TiO_2 (sulfur loaded with cobalt); (C) Co+2000 ppm S/TiO_2.

In all cases the ratio of the CH_4 peak intensity to the CH_3 or CH_2 peak intensities is higher for the catalysts containing sulfur (up to 2000 ppm) than for the unsulfided cobalt catalyst. The CH_3/CH_2 ratio remains unchanged with sulfur loading. The results thus indicate that concentrations of sulfur below 200 ppm not only promote Co/TiO_2 catalyst activity but also increase methane selectivity. Catalytic fixed-bed reac-

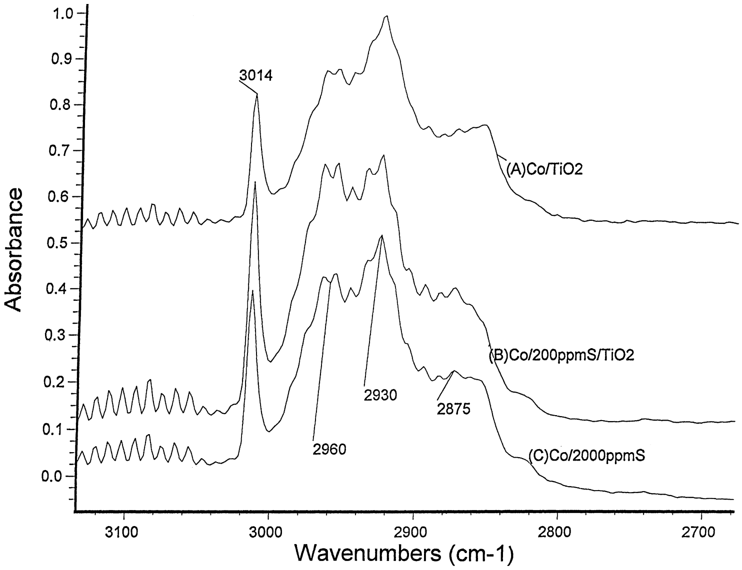

Fig. 3. IR spectra during in situ F–T reaction after 120 min: (A) Co/TiO$_2$; (B) Co/200 ppm S/TiO$_2$ (sulfur loaded before cobalt); (C) Co/2000 ppm S/TiO$_2$.

tor studies are currently underway to correlate these IR activity results with catalyst reactor activity.

Co/SiO$_2$ catalysts produced similar IR spectra during F–T reactions but showed a 50% decrease in hydrocarbon peak intensity even at sulfur concentrations of 200 ppm. It is thus clear that the observed effects of sulfur addition are also related to the choice of support.

Adsorption of CO on the surface of the catalysts was also monitored using DRIFTS in an attempt to understand the effect of sulfur on CO adsorption. Prior to carbon monoxide adsorption the catalysts were reduced at 623 K for 3 h. Carbon monoxide adsorbed onto the reduced Co/TiO$_2$ (no sulfur) catalyst produced an IR spectrum with peaks at 2065, 2001, 1952, 1902, 1838, and 1802 cm^{-1} (see Fig. 4(A)). The first peak can be assigned to Co$^{\delta+}$ linearly bound to CO, the second to Co^0–CO and the rest to bridging CO adsorptions [11–15]. The peaks at 2173 and 2115 cm^{-1} are due to gaseous carbon monoxide [16]. In order to recognize the effect of water during the sulfur loading procedure, water was then added to a dried cobalt on titania catalyst (amount determined by incipient wetness), removed at 393 K for 16 h, and the sample analyzed by DRIFTS (Fig. 4(B)). Changes in the spectrum relative to spectrum 4A were noted. Thus the peak at 2065 cm^{-1} is shifted to slightly lower wave numbers ($\sim$2061 cm^{-1}) while the 2001 and 1952 cm^{-1} peaks are shifted to slightly higher wave numbers ($\sim$2015 and $\sim$1983 cm^{-1}, respectively) after water addition. The reason for these shifts are presently not known, but it appears that redistribution of Co is possible under the incipient wetness conditions used.

Loading 100 ppm S (S^{2-} in H$_2$O) onto the surface of the Co/TiO$_2$ catalyst resulted in a shift (relative to Fig. 4(B)) to lower wave numbers in the linear Co$^{\delta+}$–CO ($\sim$2050 cm^{-1}) and bridging CO ($\sim$1930 cm^{-1}) peaks (Fig. 4(C)). A downward shift in the Co^0–CO ($\sim$1990 cm^{-1}) peak can be detected and an increase in the wave number of a bridging carbon monoxide peak (w.r.t. Fig. 4(A)) is also evident (from 1838 to $\sim$1860 cm^{-1}). These shifts are accompanied by a decrease in the intensity of each of the peaks. The shifts to lower wave numbers may be explained by the decreased CO–CO interaction, i.e. by coverage effects [14]. These υ(CO) shifts are also exhibited when an unsulfided Co/TiO$_2$ catalyst, reduced for only 1 h, is subjected to carbon monoxide adsorption. These results suggest that the carbon monoxide coverage and the shift of the bridging carbon monoxide peak is related to the decreased extent of reduction of the

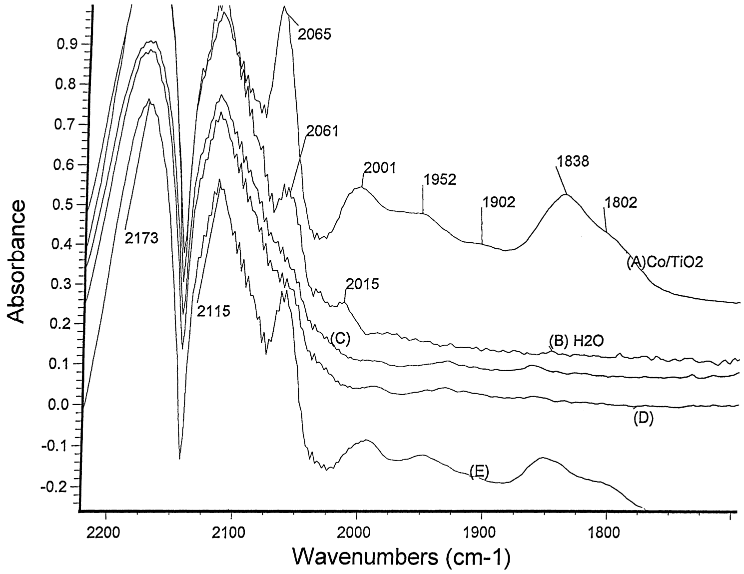

Fig. 4. IR spectra after 30 min of CO adsorption on Co at 230°C and 2 bar: (A) Co/TiO_2; (B) $H_2O/Co/TiO_2$; (C) 100 ppm $S/Co/TiO_2$; (D) 2000 ppm $S/Co/TiO_2$; (E) Co/2000 ppm S/TiO_2 (Peaks at 2173 and 2115 cm^{-1} due to gaseous CO).

catalyst in the presence of sulfide ions. However, increasing the concentration of sulfur from 100 to 2000 ppm (Fig. 4(D)) does not reduce the carbon monoxide coverage further, nor enhance the peak shifts. Increasing the concentration of sulfur on the surface of the catalysts does, however, reduce the number of CO bridging peaks observed (i.e. peaks below 1990 cm^{-1}). This may be due to steric effects, i.e. the blockage of cobalt surface sites by sulfur, since a bridging CO molecule requires larger sites than does linear CO for binding. This observation is supported by the fact that those catalysts prepared by loading (i) cobalt and sulfur together or (ii) sulfur before cobalt, show similar peak shifts (i.e. Fig. 4(E)), but no reduction in the number of bridging CO peaks. Relatively less sulfur would be expected on the surface of the latter catalysts. An electronic effect cannot, however, also be excluded.

SO_4^{2-} loaded onto the surface of the catalyst clearly inhibits cobalt reduction, i.e. an additional peak appeared in the IR spectrum at ~2086 cm^{-1} (Fig. 5(A)) which can be assigned to CO bound linearly to Co^{1+} [15], and bridging CO bonds are absent (bridging CO is not expected to form on unreduced cobalt [13]).

SO_3^{2-} loaded onto the surface of the catalyst also shows Co^{1+}–CO bonding, but bridging peaks are clearly evident in the IR spectrum (Fig. 5(B)) and the intensity of the peaks is higher than for the catalyst loaded with SO_4^{2-}. There is a clear difference in the number and intensity of peaks observed in the spectra of the SO_3^{2-} and SO_4^{2-} loaded catalysts when compared to the S^{2-} (Fig. 5(C)) loaded catalysts. This supports the conclusion reached earlier that sulfide loaded onto the surface of the Co/TiO_2 catalysts is not in the form of SO_3^{2-} or SO_4^{2-} prior to reduction [10].

Co/SiO_2 catalysts produced IR peaks at 2080, 2056, 2030, 2010, 1990, 1970, and 1960 cm^{-1} (Fig. 6). It was observed that the addition of 200 ppm sulfur on the surface of the catalyst results in a 50% decrease in the intensity of the peaks relative to the unsulfided catalyst. No further changes in peak intensity or wave number are observed upon increasing the concentration of sulfur from 200 to 2000 ppm. What is clear is that the sulfur reduces the amount of CO adsorbed on the surface of the catalyst. The CO that does adsorb has a weaker CO bond strength (lower wave numbers) than that bonded to the unsulfided catalyst.

The CO adsorption data, however, suggest no obvious correlation with the DRIFTS monitored

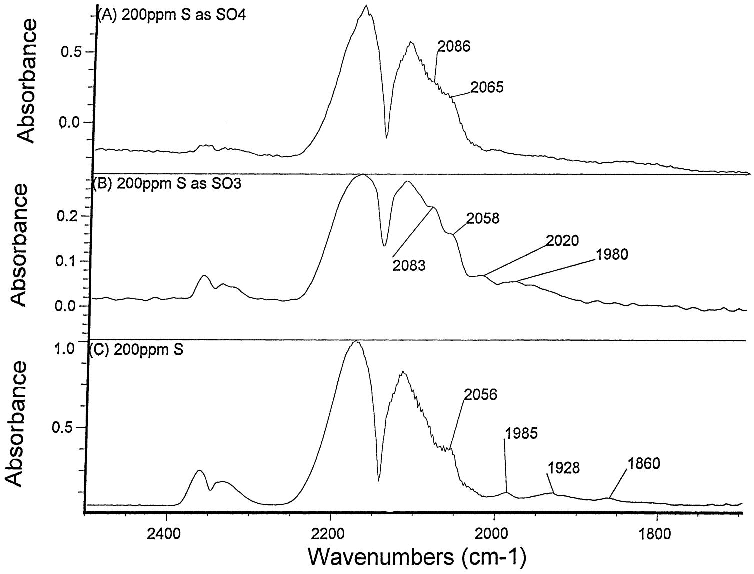

Fig. 5. IR spectra after 30 min of CO adsorption on Co at 230°C and 2 bar: (A) 200 ppm S as SO_4^{2-}/Co/TiO_2; (B) 200 ppm S as SO_3^{2-}/Co/TiO_2; (C) 200 ppm S as S/Co/TiO_2.

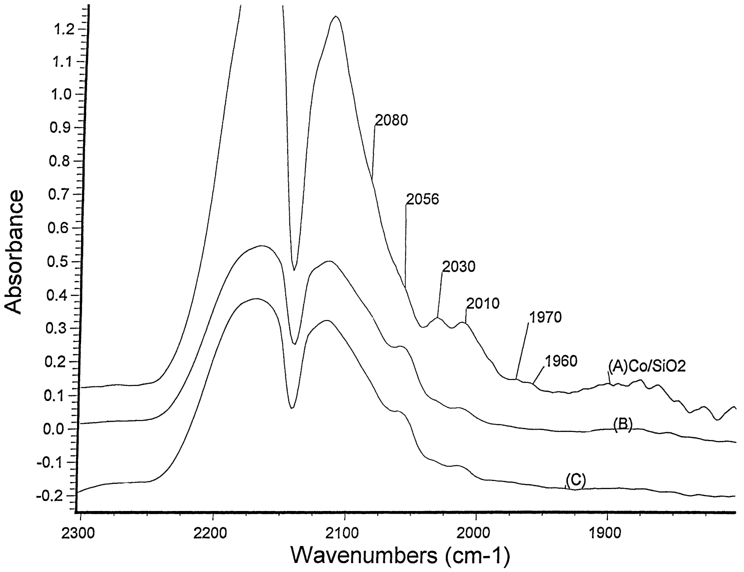

Fig. 6. IR spectra after 30 min of CO adsorption on Co at 100°C and 2 bar: (A) Co/SiO_2; (B) 200 ppm S/Co/SiO_2; (C) 2000 ppm S/Co/SiO_2. (Peaks at 2173 and 2115 cm^{-1} due to gaseous CO.)

F–T reactions (e.g. as sulfur concentration is varied), suggesting that the role of the H_2/CO mixture needs to be considered in assessing surface factors responsible for the F–T activity.

3.2. TPR studies

The results from the TPR experiments with the sulfided, titania-supported catalysts are shown in

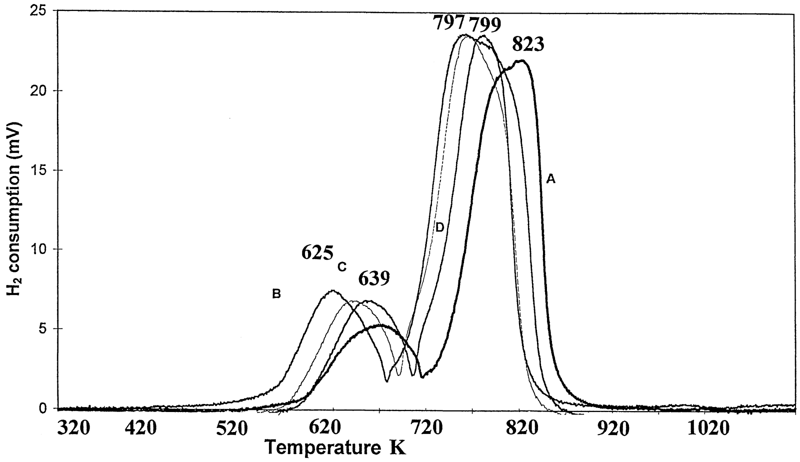

Fig. 7. TPR specra of: (A) Co/TiO_2; (B) $H_2O/Co/TiO_2$; (C) 200 ppm $S/Co/TiO_2$; (D) 2000 ppm $S/Co/TiO_2$.

Fig. 7. All four catalysts studied have two reduction peaks below 823 K, corresponding to the two-step reduction of Co_3O_4, first to CoO and then to Co^0 [17]. Fig. 7 shows that the aqueous loading procedure *decreases* the reduction temperatures for both reduction steps (for example, the difference between the peak temperatures of the second reduction step, for the cobalt on titania and water treated catalysts, is approximately 25 K). Increasing the concentration of sulfur on the surface of the catalysts from 200 to 2000 ppm results in an *increase* in the reduction temperatures of each peak relative to those of the water treated catalyst. The same trend was also observed for the catalysts prepared by loading sulfur before cobalt (results not shown here).

Co/SiO_2 catalysts produced the TPR spectra shown in Fig. 8. The first two peaks (below 693 K) correspond to the two-step reduction of Co_3O_4 to Co, while the two peaks at higher temperatures correspond to reducible cobalt silicates [17]. The high temperature peak (above 873 K) appears to be most affected by the sulfur, with a decrease in intensity being observed with an increase in sulfur concentration.

4. Conclusion

DRIFTS and TPR studies were performed over Co/TiO_2 and Co/SiO_2 F–T catalysts which had been loaded with different concentrations of sulfur from different sulfur sources prior to calcination and reduc-

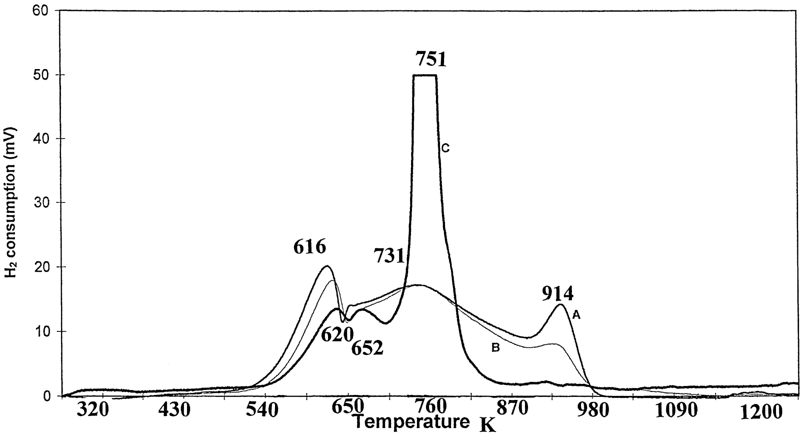

Fig. 8. TPR spectra of: (A) Co/SiO_2; (B) 1000 ppm $S/Co/SiO_2$; (C) 2000 ppm $S/Co/SiO_2$.

tion. The IR data indicate that sulfur inhibits CO adsorption onto the surface of Co catalysts for all sulfur concentrations studied (100–2000 ppm) possibly due to (i) site blockage and (ii) inhibited reduction of the catalysts. Sulfur also affects the TiO_2- and SiO_2-supported catalysts during the F–T reaction. The in situ F–T reactions, monitored by DRIFTS, further suggest that low concentrations of sulfur (100 ppm) on the TiO_2-supported cobalt catalysts *improves* catalyst activity. Preliminary results indicate that lower reduction temperatures *combined* with less CO adsorption favor the formation of hydrocarbons on the surface of the supported Co catalysts as monitored by DRIFTS.

Studies are currently underway to correlate FTIR peak intensities from DRIFTS monitored F–T reactions with catalyst activity obtained from reactor studies.

Acknowledgements

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