# $Co/SiO_2$ sol–gel catalysts for Fischer–Tropsch synthesis

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Six catalysts with a different cobalt content were prepared following the sol–gel method. The samples were tested by the Fischer–Tropsch synthesis performed both at low and high temperature and pressure. All the catalytic performances are well correlated with the characterization results which highlighted the good metal distribution and the presence of a large amount of metallic cobalt (but not the whole) on the surface of both 10 and 30% Co catalysts. As a result, high CO conversions were observed with a particular sensitivity to the reaction pressure and also the limitation of the produced hydrocarbons fraction to $C_6$ or $C_9$ at low or high pressure, respectively.

**KEY WORDS:** cobalt-based catalyst; preparation; characterization; sol–gel; Fischer–Tropsch synthesis

## 1. Introduction

Cobalt-based catalysts are highly investigated for Fischer–Tropsch synthesis due to their high activity, selectivity for linear hydrocarbons, low activity for the competing water–gas shift reaction, and quite low price, compared to noble metals [1].

Many authors have already studied the role of the support. At atmospheric pressure and at low conversion, Reuel and Bartholomew [2] have reported, with 10 wt% Co supported catalysts, an increase in specific activity (at $P = 0.1$ MPa, $T = 498$ K, $H_2/CO = 2$) depending on the nature of the support in the following order: $Co/MgO < Co/C < Co/SiO_2 < Co/Al_2O_3 < Co/TiO_2$. However, the works of Iglesia *et al.* [3] at higher pressure ($P > 0.5$ MPa) and at high conversion indicate that the influence of the support on the specific activity and the methane and $C_{5+}$ hydrocarbons selectivity can be neglected. According to these authors [3] the reaction is insensitive to the structure of cobalt and is also independent of its dispersion.

However, the chemical nature of the support, its surface acid–base properties and its texture play a very important role. For an acid support it was reported that the long residence time would favour the hydrogenolysis and hence the production of lighter products [4]. Besides, the pore size and the acid properties can influence the metal–support interaction and lead to the formation of well defined phases as cobalt silicate, aluminate or lanthanate.

Moreover, the nature of the cobalt precursor has a large influence on the reducibility of cobalt and on its activity and selectivity. Niemela *et al.* [5] reported the following order in activity for 5% $Co/SiO_2$: $Co_2CO_8 > Co(NO_3)_2 > Co(CH_3COO)_2$, but cobalt(II) nitrate seems to be the best precursor for high activity and long chain hydrocarbon formation.

In the present work, an extensive study of the performance of catalysts prepared by the sol–gel process has been performed. The sol–gel process is now largely used especially for the synthesis of silica gel [6,7]. It would allow the specific surface area, the porosity and particle size of the sample to be controlled [8,9].

All the prepared samples have been fully characterized and tested in a bench-scale fixed-bed reactor.

## 2. Experimental

### 2.1. Sample preparation

Six different samples were prepared with 5, 10, 15, 20, 25 and 30 wt% of Co on $SiO_2$, named 5SG, 10SG, 15SG, 20SG, 25SG and 30SG, respectively.

The cobalt nitrate hexahydrate $[Co(NO_3)_2{\cdot}6H_2O]$, as Co precursor, was dissolved in a suitable amount of water and then tetramethyl orthosilicate (TMOS) was added under stirring. The homogeneous sol was transferred in a wide vessel for the evaporation of the solvent and the subsequent gelation. The obtained gel was dried in vacuum at room temperature, calcined in air at 573 K overnight and finally reduced in a microreactor by flowing hydrogen at 623 K for 12 h.

### 2.2. Catalyst characterization

#### 2.2.1. BET

The $N_2$ (99.9995% purity) adsorption isotherms were obtained by using a Sorptomatic 1900 apparatus (Fisons Instruments), by a static volumetric technique. The analysis was controlled by microcomputer processing using MILES-200 and MILEADP software for computations.

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### 2.2.2. $H_2$ chemisorption

Metal dispersions ($D_M$) were measured by single-introduction–back-sorption coupled methods on the basis of irreversibly adsorbed hydrogen, as described elsewhere [10,11]. The measure was performed at 373 K as pointed out by Bartholomew *et al.* [2,12]. Dispersion percentage ($D$%) was calculated according to the equation [13]

$$D\% = \frac{X}{190.3Wf}, \qquad (1)$$

where $X$ is the total $H_2$ uptake in micromoles per gram of catalyst, $W$ the weight percentage of cobalt, and $f$ the fraction of cobalt reduced to the metal determined from XPS analysis. In this way, with the introduction of reduction degree $f$, the unreduced cobalt was not included in the calculation of $D$%.

### 2.2.3. TPR

The experiments were performed using a TPR/O (Thermo Quest Italia). The samples were initially dried under nitrogen at 393 K for 1 h. After cooling to room temperature, a reducing gas mixture (10 vol% $H_2/N_2$) was introduced at a flow rate of 30 ml/min. The temperature was increased to 973 K at a rate of 10 K/min. The $H_2$ consumption was detected by a TCD (thermal conductivity detector) and recorded as function of temperature.

### 2.2.4. XPS

XPS measurements were performed in an M-Probe Instrument (SSI) equipped with a monochromatic Al K$\alpha$ source (1486.6 eV) with a spot size of 200 × 750 $\mu$m and a pass energy of 25 eV, providing a resolution for 0.74 eV. Si 2p 103.3 eV was used as internal reference.

Co 2p region was fitted assuming a theoretical value of 2 for the ratio Co 2p$_{3/2}$ and 2p$_{1/2}$ [14]. The quantitative data were accurately checked and reproduced several times (at least ten times for each sample) and the data reported in table 1 and figure 1 can be estimated to be ±1% thanks to a severe confidence in spectral decomposition. Metallic cobalt is easily distinguished from oxidized cobalt because of the large difference in binding energy (BE). In contrast, the slight difference in BE between $Co_3O_4$ and $Co^{2+}$ species (CoO and cobalt silicate) makes getting a clear assignment very difficult except for the difference of $\Delta E$ (15.0 eV for $Co_3O_4$, 15.7 eV for $Co^{2+}$ species) [15,16].

XPS measurements were performed on all the catalysts after the reduction performed *in situ* into the reaction chamber directly connected to the vacuum system of the spectrometer allowing the samples to be transferred into the measurement chamber without exposure to air, but also *ex situ*. In fact it was important to observe the behavior of the surface after the re-exposure of the reduced samples to the atmosphere because this allows the surface passivation, *i.e.*, the reoxidation of the metallic atoms while it has no influence on the existing Co oxides.

On all the samples the reducing treatments, both *in situ* and *ex situ*, were performed by flowing pure hydrogen at 623 K for 12 h.

Table 1

| Sample | BET surface area (m$^2$/g) | XPS | | | | |
|---|---|---|---|---|---|---|
| | | Surface atomic Co/Si | *Ex situ* reduction | | *In situ* reduction | |
| 5SG | 513 | 0.01 | $Co^{2+}$ | 100% | $Co^{2+}$ | 100% |
| 10SG | 458 | 0.19 | $Co_3O_4$ | 66% | $Co^0$ | 69% |
| | | | $Co^{2+}$ | 33% | $Co^{2+}$ | 31% |
| 15SG | 430 | 0.05 | $Co_3O_4$ | 29% | $Co^0$ | 31% |
| | | | $Co^{2+}$ | 71% | $Co^{2+}$ | 69% |
| 20SG | 305 | 0.08 | $Co_3O_4$ | 30% | $Co^0$ | 33% |
| | | | $Co^{2+}$ | 70% | $Co^{2+}$ | 67% |
| 25SG | 189 | 0.06 | $Co_3O_4$ | 25% | $Co^0$ | 39% |
| | | | $Co^{2+}$ | 75% | $Co^{2+}$ | 61% |
| 30SG | 160 | 0.21 | $Co_3O_4$ | 53% | $Co^0$ | 61% |
| | | | $Co^{2+}$ | 47% | $Co^{2+}$ | 39% |

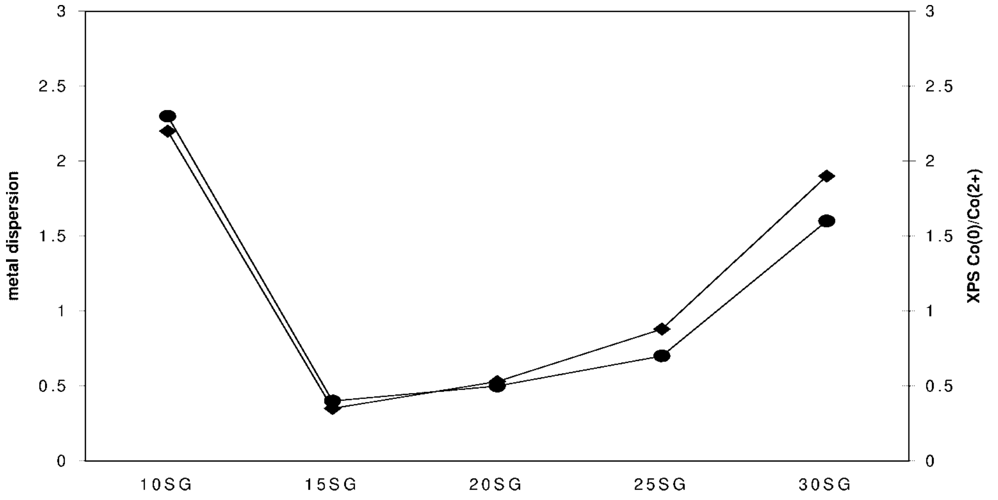

Figure 1. Metal dispersion (%) by $H_2$ chemisorption (◆) and $Co^0/Co^{2+}$ atomic ratio by XPS (●) for all the investigated samples.

### 2.3. Catalytic tests

Reaction tests were performed in a stainless-steel tubular reactor, inside coated with copper, especially designed for FTS of hydrocarbons ($C_n$: $n < 15$), described elsewhere [17]. 1 g of fresh catalyst, packed into the reactor body, was activated in flowing $H_2$ (12 l/h) at 623 K, 800 kPa for 12 h. The reaction was carried out with a mixture of high purity CO and $H_2$ (SIAD); the $H_2$/CO ratio of the inlet mixture was 2. All the catalysts were studied for 72 h at a space velocity (SV) of $9.0 \times 10^{-2}$ mmol-CO/(mmol-Co s), 500–2000 kPa and at 473–548 K; the hydrocarbon products were analyzed on-line by gas-chromatography [17].

Since CO was the only detectable reagent, the mass balance calculation was based on carbon, presuming that the amount entering the reactor is equal to that exiting. Therefore, conversion was easily calculated by considering the total number of unreacted moles of CO by the number of moles of carbon-containing species found at the exit.

## 3. Results and discussion

Table 1 lists the BET surface area for all the prepared samples: it is interesting to observe the rapid decrease of the surface area at increasing metal loading.

A different trend was observed studying the metal dispersion: the obtained values are always very low for all the samples, and a maximum was observed for both 10SG and 30SG (figure 1). It should be remembered that the unreduced cobalt was not introduced into the calculation of $D$% and, therefore, the reported data really refer to the atoms active from the catalytic point of view.

On the same figure (figure 1), the $Co^0/Co^{2+}$ ratio, obtained by XPS measurement after the *in situ* reduction, is reported. The trend is similar with the best results always shown by 10SG and 30SG.

The 5SG values were not reported because the amount of hydrogen chemisorbed was too low for a reliable measurement to be made and the surface cobalt detected by XPS was completely unreduced.

XPS measurements were performed on all the catalysts after the reduction both *ex situ* and *in situ*. No metallic Co was found on the passivated samples; on the contrary a complete Co reduction was never observed on any *in situ* reduced catalyst (table 1), as already observed by Backman *et al.* [18].

It is important to observe the complete disappearance of $Co_3O_4$ species after the reduction *in situ*; by contrast the $Co^{2+}$ species (CoO, but also cobalt silicate) are still present. As it is quite easy to reduce CoO to metallic Co [19], it seems allowable to conclude that the unreduced species are due to cobalt silicate [18].

The surface ratio between Co and Si was also calculated (table 1). Very small amounts of surface cobalt were detected, as if the metal was enclosed into the support, except for 10SG and 30SG: these two samples strangely showed a quite high and similar Co/Si ratio notwithstanding the large difference of their active metal content. Besides they showed the highest amount of metallic Co on the surface (69 and 61%, respectively).

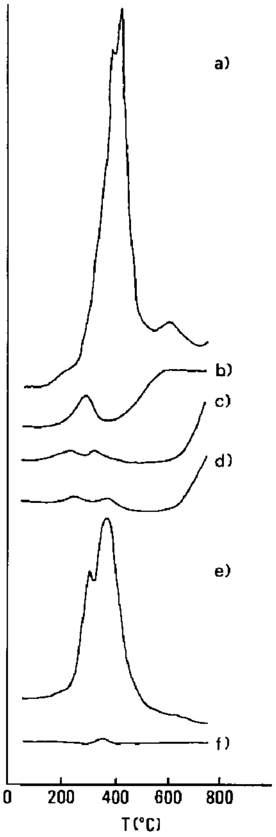

Figure 2. TPR 700 °C spectra of the following samples: (a) 30SG, (b) 25SG, (c) 20SG, (d) 15SG, (e) 10SG and (f) 5SG.

All these results are also confirmed by TPR analyses (figure 2): 10SG and 30 SG showed the largest amount of hydrogen consumption at temperatures within 473 and 723 K with two very close peaks of high intensity.

The cobalt-based catalyst usually exhibits two main peaks [16,20–23]; the first peak is essentially due to the reduction of $Co_3O_4$ to $Co^{2+}$, while the latter one is due to the reduction to $Co^0$ of CoO, which are not interacting with the support. For $Co^{2+}$ atoms which are interacting with the support, a broad peak at higher temperature appears (peak not present on unsupported $Co_3O_4$) [22].

All other catalysts showed negligible hydrogen consumption as though samples with a very low metal content were analyzed: it is possible to observe very small peaks and the beginning of a quite large hydrogen consumption at temperatures over 973 K where the reduction of cobalt silicate is justified.

All the characterization data give a strong explanation to the different performance of these catalysts tested in the Fischer–Tropsch synthesis.

No activity was shown by 5SG, as already reported by Okabe *et al.* [24]. In such a catalyst most of the Co particles might be occluded in the $SiO_2$ matrix and the activation is very difficult. The negligible amount of chemisorbed $H_2$ on the catalyst and the absence of surface metallic cobalt shown by XPS and TPR measurements correspond to its complete lack of activity in each reaction condition. By contrast, all the other samples showed very interesting CO conversion (see figure 3), even under the mildest condition (500 kPa and 473 K). The catalyst activity increased a lot reaching a quite complete conversion (~95%) for the sample 30SG at 2000 kPa and 548 K.

It is important to underline the 10SG behavior: as expected, considering the characterization results (amount of metallic cobalt at the surface and metal dispersion), this catalyst showed a very good activity comparable to the sample with the largest metal amount (30SG) and much higher than the catalysts with a cobalt content between 15 and 25%. For 15SG and 20SG, it is even necessary to perform the reaction at high temperature and high pressure to obtain a proper CO conversion.

However, it was not so profitable to work at too high temperature because, from the selectivity point of view, a particular sensitivity of all these catalysts to this parameter was observed. In fact, the increase in temperature caused an increase of the $CO_2$ production as the competing water–gas shift reaction could be promoted (for example taking into account the 30SG sample, the $CO_2$ quantity raised from 1.3 to 1.8 to 32.5% in the three tested conditions).

Finally, it is necessary to stress that the production of hydrocarbons is limited to the $C_6$ fraction when the reaction is performed in mild conditions, and to the $C_9$ fraction when it is performed at high pressure and temperature. This behavior was already observed by the authors but only using a zeolitic support like ETS-10 [25]: the limitation to the production of hydrocarbons below a certain fraction was explained taking into account the possible "cage-effect" of the support structure. Obviously, in this case this limitation, that occurs only with this kind of catalysts prepared by the sol–gel

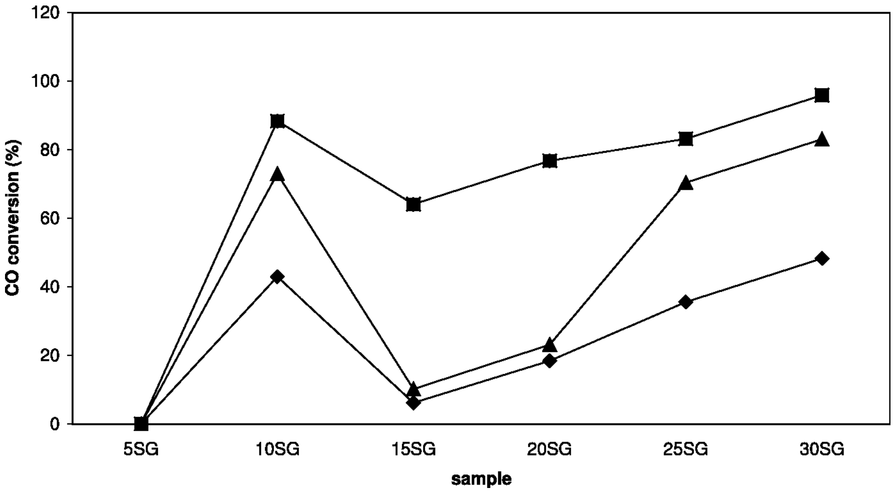

Figure 3. Mean CO conversion value for the investigated catalysts for reaction performed at: (■) 2000 kPa and 548 K; (▲) 2000 kPa and 473 K, (◆) 500 kPa and 473 K.

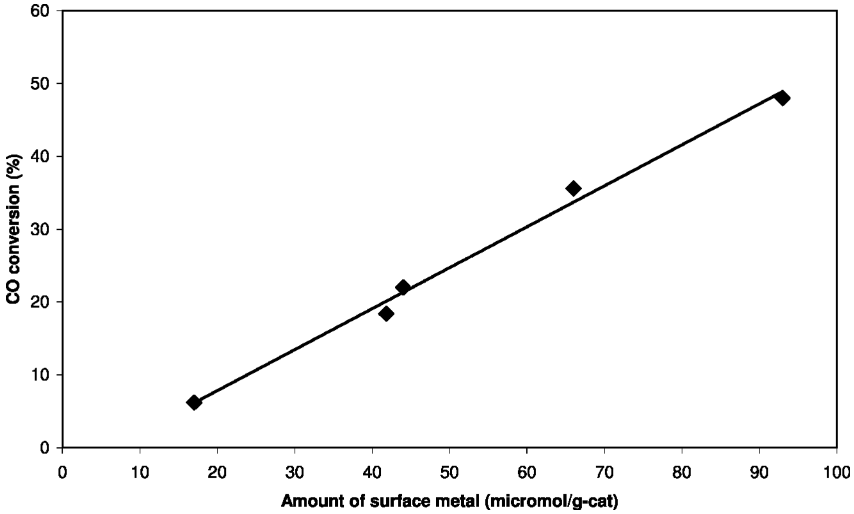

Figure 4. The relation of CO conversion with surface metal Co amount. Reaction conditions: $T = 473$ K, $P = 500$ kPa.

method [26], cannot be ascribed to this effect, but a suitable explanation was not found at present.

Apart from the real cobalt content, but taking only into account the amount of surface metal cobalt, it was finally demonstrated that the CO conversion increased linearly with increasing the amount of surface metal, as shown in figure 4, where the relation of CO conversion with surface metal Co amount was reported (reaction conditions: $T = 473$ K, $P = 500$ kPa).

This result indicates that even on this kind of support the CO hydrogenation on cobalt catalyst was a structure-insensitive reaction, as already reported by Iglesia *et al.* [3].

## 4. Conclusions

An excellent correlation between characterization data and catalytic performances were found for a series of Co-based catalysts prepared by the sol–gel method. Good conversions were obtained for 10 and 30% (wt%) Co while all the catalysts prepared with intermediate metal loading showed lower conversion. This behavior was well explained taking into account the real amount of disposed metallic cobalt on the samples surface.

A particular sensitivity to the reaction pressure and the limitation of the produced hydrocarbons fraction to $C_6$ or $C_9$ at low or high pressure, respectively, were also observed.

Further investigations are planned in order to fully understand the unexpected behavior of 10SG, in contrast with samples with a higher cobalt amount.

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