Co/SiO_2 for Fischer–Tropsch synthesis: comparison among different preparation methods

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An extensive study of different preparation methods for Co/SiO_2 catalysts is reported in the present paper. In addition to the conventional impregnation, other more innovative methods are tested together with the sol–gel process, methods involving the use of ultrasound and of particular metal precursors or solvents. The prepared samples are fully characterized and tested in the CO hydrogenation.

KEY WORDS: Fischer–Tropsch synthesis; cobalt catalyst; preparation; ultrasound; sol–gel; characterization.

1. Introduction

Cobalt-based catalysts are highly investigated for Fischer–Tropsch synthesis (FT): they are highly active, selective for linear hydrocarbons, scarcely active for the competing water-gas shift reaction; their price is quite low, compared to noble metals [1].

Many authors have already studied the role of support. At atmospheric pressure and at low conversion, Reuel and Bartolomew [2] 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 of the methane and C_{5+} hydrocarbons selectivity can be neglected. According to these authors [3] the reaction is insensitive to the structure of cobalt, respectively, its dispersion. Therefore, high activity for FT synthesis is shown by cobalt catalysts with high reduction degree and high cobalt dispersion and the activities of Co catalysts may be predicted directly from Co dispersion values of the reduced catalysts measured by hydrogen chemisorption [4]. However, structural changes of cobalt catalysts during the reaction may result in significant decrease in the number of active sites, so that the catalysts show lower activities than the predicted values [5].

The chemical nature of the support, its surface-acid-base properties and its texture also play a very important role. For an acid support it was reported that the long residence time would favor the hydrogenolysis and hence the production of lighter products [6]. 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.* [7] 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.

Recent works reported the preparation of catalysts by mixed impregnation of cobalt (II) nitrate and cobalt (II) acetate that seems to be more easily reduced to the metallic state thanks for an H_2 spillover mechanism [8].

In the present work, an extensive study of seven different preparation methods for Co/SiO_2 catalysts is reported. In addition to the conventional impregnation, other more innovative methods are tested together with the sol–gel process, which is now largely used especially for the synthesis of silica gel [9,10]. This process would allow mastering the specific surface area, the porosity and particle size of the sample [11,12].

Ultrasound (US) irradiation as an energy source to induce various physical and chemical reactions has become an active area of research in recent years [13]. US is here used as preparation tool to enhance the cobalt dispersion as already reported in the past [14].

The possibility to use particular cobalt precursors (chloride, fluoride) was also taken into account.

The samples were tested as catalysts for the CO hydrogenation to give hydrocarbons (FT synthesis) in a bench scale fixed bed reactor and these data were correlated with the results obtained by the characterization analyses.

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2. Experimental

2.1. Sample preparation

Seven different preparation methods were used in this paper.

All the samples (5 wt% Co confirmed by ICP-AES measurements) were prepared using the same kind of silica (by Aldrich, surface area 520 m^2/g), except the one involving the sol–gel method.

Depending on the preparation method, the metal precursor was chosen among: $Co(NO_3)_2 \cdot 6H_2O$, $CoCl_2$, and CoF_3 [all Fluka products].

The first sample was prepared by the classical incipient wetness impregnation (sample named CS, "classical sample"). The support was impregnated with an aqueous solution of cobalt nitrate hexahydrate in a single step and then put into a vacuum oven at 353 K overnight.

The second method was the ammonia one as described by Barbier *et al.* [15] (sample named AS "ammonia sample"). The precursor was added to a suitable amount of water at room temperature and stirred by a magnetic rod; to prevent Co^{2+} oxidation dissolved oxygen was removed by boiling the water and the system was protected from air by an argon blanket. A solution of ammonia was poured in the solution bringing about the precipitation of $Co(OH)_2$ (this precipitate is dissolved by a large excess of ammonia). The support was then added to the solution and its pH reached an equilibrium value near 12 after stirring 1 h. After equilibrium, the system was stirred for one additional hour, then centrifuged and washed five times. Finally it was dried in a vacuum oven at 353 K overnight.

US was used for the third and fourth preparation methods to improve the metal dispersion [16,17].

In the third preparation (sample named CRUS "classical reduced with US sample"), the impregnation was performed as for CS, but before reducing the catalyst in flowing hydrogen, the sample was added to a solution of pure hydrazine at 353 K and here left under sonication (20 kHz) for 15 min as described in [16].

In the forth method (sample named USS "Ultrasound sample") the aqueous solution of cobalt nitrate was directly added to the silica under sonication (20 kHz) for 1 h at room temperature and then reduced in flowing hydrogen following the steps described for CS.

Sample 5 (named SGS "sol–gel sample") was prepared *via* sol–gel: cobalt nitrate hexahydrate was dissolved in dry THF, then TMOS and water were added and the homogeneous sol was transferred in a vessel suitable for the evaporation of the solvent and the gelation. The obtained gel was then dried in vacuo at room temperature [18].

For the sample 6 (named SIS "sol immobilization sample") the sol immobilization technique was used [19]. An aqueous $CoCl_2$ solution (200 mg/mL) was prepared. To this, under vigorous stirring, the Polyvinyl Pirrolidone (PVP) was added (2 wt% solution). Then, drop wise, a 0.1 M freshly prepared solution of $NaBH_4$. The sol was immobilized by simply dipping the support in the metal dispersion. After 1 h the slurry was filtered. Before use, the catalyst was thoroughly washed with distilled water and dried at 343 K for 5 h in air.

Sample 7 (named FS, "fluoride sample") was prepared using CoF_3 as metal precursor [20]. The fluoride precursor was added to a solvent (diglyme, 2-methoxyethyl ether) and the mixture was heated at 373 K for 30 min in a glass flask equipped with a cooling column. After dissolution of the cobalt fluoride, the silica was added and stirring was maintained at 373 K for 2 h. The solid phase was filtered and dried in a vacuum oven at 393 K overnight.

All the dried samples underwent a calcination-reduction treatment in a stream of pure flowing hydrogen (99.99% purity grade), at 648 K for 16 h (flow rate = 150 mL H_2/min, $P = 0.8$ MPa). The reduction schedule included a temperature ramp of 3 K/min (from room temperature) with half-hour holds at 373 K to facilitate the water removal and at 473 K to ensure controlled nitrate decomposition (when cobalt nitrate was used).

2.2. Catalyst characterization

2.2.1. BET

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

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 [21,22]. The samples were pre-treated at 623 K for 4 h in flowing H_2 (30 mL/min), outgassed at the same temperature for 16 h. H_2-uptake was performed at 398 K.

2.2.3. TPR

The experiments were performed using a TPR/O (ThermoQuest 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 thermal conductivity detector (TCD) and recorded as function of temperature.

2.2.4. XRD

The analyses were collected using a Philips PW1710 vertical goniometric diffractometer using a Ni-filtered Cu-$K_{\alpha 1}$ radiation. The analyses were performed on the samples after the reductive calcination treatment. Moreover all the samples were recalcined at 1173 K for 4 h and then reanalyzed.

2.3. Catalytic test

Reaction tests were performed in a stainless steel tubular reactor, inside coated with copper, especially designed for FT synthesis of hydrocarbons (C_n: $n < 15$), described elsewhere [23]. 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. The catalysts (always 1 g of fresh sample for each run) were tested four days long at 548 K, 0.5 MPa and a space velocity (SV) of 9.0×10^{-2} mmolCO/(mmolCo·s); hydrocarbons products were analyzed on-line by gas-chromatography. Since CO is the only detectable reagent, the mass balance calculation is based on carbon, presuming that the amount entering the reactor is equal to the exiting. Therefore conversion is easily calculated by considering the total number of non-reacted CO moles by the number of moles of carbon-containing species found at the exit.

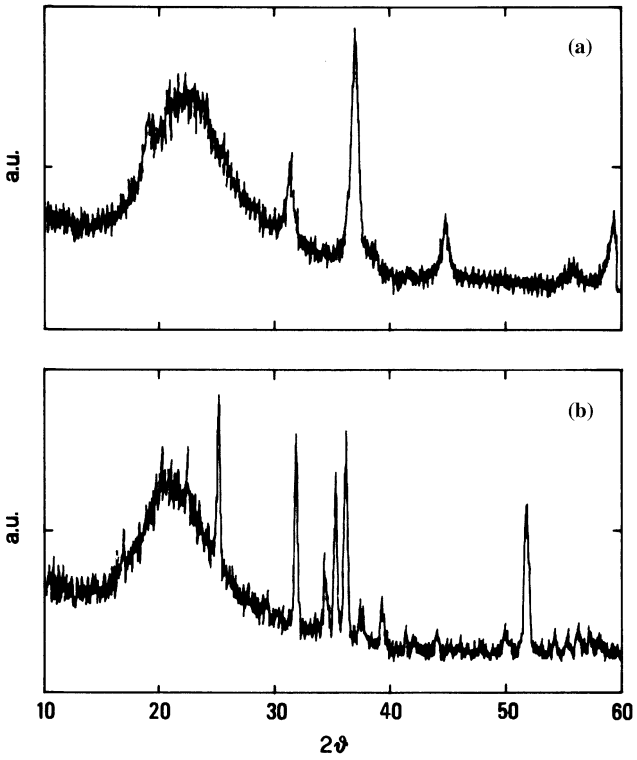

Figure 1. X-ray diffraction patterns of the (a) CS after the reductive calcination treatment at 648 K for 16 h and (b) of the same sample after subsequent calcination at 1173 K for 4 h.

3. Results and discussion

Many authors have already remarked the possibility for Co atoms to react with the support molecules to give irreversible spinels. This behavior was intensively investigated for Co/Al_2O_3 [24 and references therein], but it is possible to observe a similar phenomenon using SiO_2 as support.

Figure 1 shows the XRD spectra obtained for the CS sample before and after the recalcination treatment at 1173 K (as reported in Section 2). The large difference between the two spectra is evident. In particular, in figure 1b the appearance of new, intense bands due to the formation of Co-spinel species can be noticed.

For this reason, it was chosen to prepare the catalysts using preparation methods, which only required mild conditions. Moreover, the final calcinations were performed in the presence of hydrogen (reductive calcinations) to prevent the formation of such species.

Data on metal dispersion and surface area are summarized in table 1. It is possible to observe an interesting change of the BET surface area of the support when the samples are treated with US. It is well known [25] how the ultrasonic waves can severely modify the surface of solid materials due to local very high temperature and pressure. Moreover, a large difference in D_M data changing the catalysts preparation method was observed (table 1).

Table 1
Characterization data

Sample	Co wt%	Surface area (m^2/g)	Metal dispersion D_M (%)
SiO_2	–	520	–
CS	5	504	1.46
AS	5	324	0.85
CRUS	5	442	0.97
USS	5	280	2.66
SG	5	498	0
SIS	5	453	0.21
FS	5	489	0

TPR profiles are reported in figure 2. It is important to observe the differences among the curves given by each catalyst and to stress at which temperature it is possible to observe the reduction of the cobalt atoms, reduction that can be quantified (table 2).

USS is the sample that shows the highest amount of hydrogen consumption in the lowest temperature range (just around 623 K). And it is the catalyst that shows the large amount of metal atoms at the lowest temperature coupled to the high metal dispersion (see table 1).

CO conversion (a mean value on four working days) and selectivities for all the catalysts are reported in table 2.

No activity was shown by SGS as already reported in [26]. Neither a pre-activation of the sample in air for one

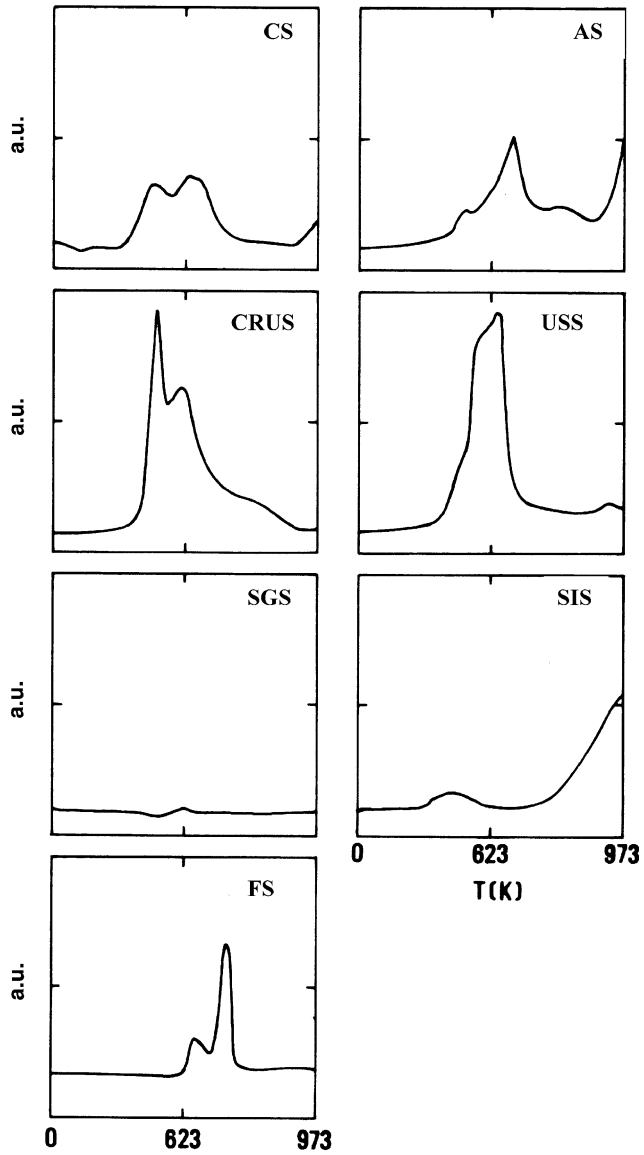

Figure 2. TPR patterns of the investigated samples.

night at 573 K gave any positive results (see table 3). In such a catalyst most of the Co particles are occluded in the SiO_2 matrix and the activation is very difficult. The negligible amount of chemisorbed H_2 on the catalyst corresponds to its low activity. This result is also in agreement with the TPR analysis, which shows no hydrogen consumption and thus no reduction of the cobalt sites (figure 2).

FS showed a very similar behavior: magnetic measurements reported by Barbier *et al.* [20] have already shown that the precursor of this sample was less reducible than the usual cobalt nitrate hexhydrate. No H_2-uptake was detected for such a sample (table 1) and the TPR profile shows a net consumption of hydrogen, but at temperatures higher than 623 K (figure 2, table 2). Therefore, in our experimental conditions, the cobalt was absolutely not reduced at metal state. On the contrary it is possible to observe some interesting data for SIS. Good CO conversion coupled with a quite low methane production (considering the catalytic test was carried on at 0.5 MPa) (table 3). In this case, the TPR

Table 3
Activities and selectivities of catalysts

Sample	CO conversion[a] (%)	CH_4 (%)	C_{2+}[b] (%)	$C_{4=}/C_4$ (%)	iso C_4/nC_4 (%)
CS	58	52	40	3.8	0.12
AS	84	40	55	2.2	0.19
CRUS	54	89	9	0.5	1.12
USS	87	32	61	0.2	0.04
SG	0	0	0	0	0
SG att[b]	0	0	0	0	0
SIS	39	39	55	0.9	0.11
FS	0.6	36	–	–	–

[a]Mean value on 4 days.
[b]Sample pre-activated in air at 573 K for one night.

Table 2
Reducibilities of catalyst sample

Sample	Reducibility (%)		
	(RT[a]–673 K)	(673–973 K)	Overall (RT–973 K)
CS	25.6	34.6	60.2
AS	15.4	53.9	69.3
CRUS	45.4	26.8	72.2
USS	59.1	15.9	75.0
SG	n.a. [b]	n.a.	n.a.
SIS	12.3	32.1	44.4
FS	1.1	25.6	26.7

[a]Room temperature.
[b]Not available.

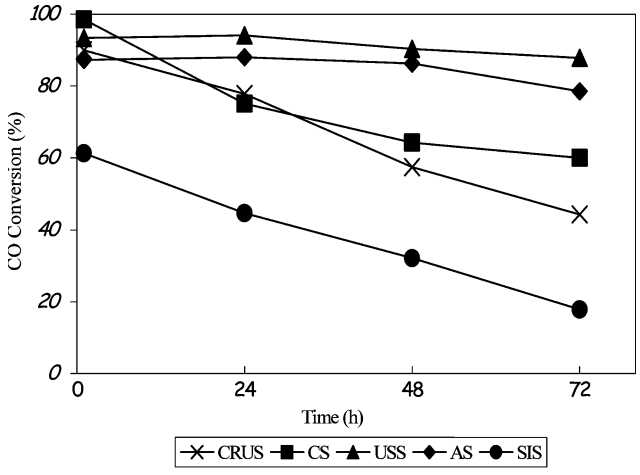

Figure 3. CO conversion versus time ($T = 548$ K, $P = 5$ bar, $H_2/CO = 2$).

profile showed the reduction of the cobalt atoms happened just at about 623 K, but only for a part of the total active phase. The large part of the atoms is only reduced at very high temperature (table 2).

As expected by the characterization data, USS showed the best catalytic performance with both the best CO conversion and the lowest CH_4 production.

This sample also shows the lowest decrease of CO conversion versus time (figure 1). On the contrary both CRUS and CS deactivate rapidly with a loss in the conversion $>35\%$ in only four working days.

4. Conclusions

The preparation method of a Co/SiO_2 catalyst plays a fundamental role in its future catalytic performance. Interesting differences were observed whether as CO conversion, selectivity and deactivation trend.

The sample prepared using US during the first step of the preparation (USS) is the best catalyst showing the highest CO conversion coupled with the lowest C_1 production and a good stability. The characterization data have underlined that this catalyst showed the highest D_M coupled with the lowest BET surface area, but, first of all, the highest amount of hydrogen consumption in the lowest temperature range (just around 623 K that is the temperature of the reduction treatment before the FT reaction) in comparison to all the other samples.

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