

TPR Study on the Preparation of Impregnated Co/SiO₂ Catalysts

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During the preparation of impregnated cobalt on silica catalysts, different Co-species are formed and these can be detected by means of temperature programmed reduction (TPR). The impregnation step can be explained in terms of *interfacial coordination chemistry*. During the impregnation step, the precursor of surface cobalt silicate is formed by a reaction between surface silanol groups and aqueous cobalt complexes. Therefore, the choice of solvent used in the impregnation step, of the metal salt, and of the carrier is of great importance in the degree of reduction that can be achieved at normal reduction temperatures and catalyst dispersion. Decreasing the polarity of the solvent increases the amount of surface cobalt silicates in the catalyst since the interaction between silanol groups and the cobalt aquocomplex is favored. If the pH of the impregnation solution is above 5 (e.g., using cobalt acetate as the cobalt salt) more cobalt silicates are formed. Drying or low-temperature calcination destroys the precursor of the surface cobalt silicate. © 1996

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1. INTRODUCTION

Cobalt as a metal is a good catalyst for Fischer-Tropsch CO-hydrogenation, especially when high-chain-growth probability and low branching probability are required (1), and for the reductive amination of alcohols using ammonia (2). To expose as many metal atoms as possible to gaseous reactants the relatively precious metal cobalt is normally deposited on a high-surface-area carrier to obtain a high metal dispersion. Commonly used high-surface-area carriers are silica, alumina, and, to a smaller extent, carbon, titania, and magnesia.

Several methods can be used to deposit the metal on the surface of the carrier. These include precipitation, ion exchange, and impregnation. Due to its simplicity the most frequently used method in laboratories is incipient wetness impregnation, in which a metal salt dissolved usually in water, but sometimes in organic solvents (3–5), is added to the carrier in an amount equal to pore volume of the support. Subsequently, the solvent is removed and the precursor is reduced to obtain the active metal catalyst. A calcination step might be introduced after drying the precursor material.

Although it is in practice easy to prepare impregnated catalyst, this is actually a complex process, in which many individual steps might influence the final performance of the catalyst, i.e., metal precursor, solvent, carrier, aging time, drying time/temperature, and calcination temperature. Failure to control these parameters might lead to irreproducible catalyst preparation.

Temperature-programmed reduction (TPR) is a sensitive, but destructive, technique for detecting the "structure" of catalysts as has been shown for Co/Al₂O₃ (6). The reduction of unsupported cobalt oxide (Co₃O₄) is a two-stage process (7, 8), which could be ascribed to the successive reduction of Co₃O₄ to CoO to Co (9–11). After the preparation of precipitated Co on silica catalysts, Puskas *et al.* (12) observed the formation of cobalt species, which can be reduced only at elevated temperatures (exceeding 970 K). They indicated that these cobalt silicates were formed by a solid-solute reaction under slightly alkaline conditions using high-surface-area silica. Recently, Ming and Baker (13) reported on the influence of pH of the impregnation solution on the formation of cobalt silicates. At pH ≥ 5 they observed the reaction of cobalt ions with the surface of silica gel to form various cobalt silicates or hydrosilicates. Coulter and Sault (14) concluded that prolonged drying converted cobalt silicates into Co₃O₄. Rosynek and Polansky (15) studied the influence of the metal-starting material on the reduction of the Co/SiO₂ precursor. The catalyst formed from the chloride salt showed essentially the same behavior in TPR as observed for the unsupported cobalt chloride. In the case of nitrate and acetate precursors a number of peaks were observed in the TPR-spectra indicating the formation of various surface CoO_x and cobalt silicate species.

In this study we investigated the influence of different steps in the preparation of impregnated Co/SiO₂ catalysts by incipient wetness on the reducibility of the catalyst precursor and on the formation of cobalt silicates. Although the reduction of cobalt silicates is difficult it was shown that a certain amount of them is necessary for obtaining highly dispersed cobalt catalyst (14). This has also been shown for Ni/SiO₂, where nickel hydrosilicate species, which are more difficult to reduce, act as "anchors" for reduced nickel crystallites (16).

TABLE 1
Characteristics of the Used Silica Gels

	Surface area (m ² /g)	Mean pore diameter (Å)	Pore volume		pH of 5 wt% slurry in water (acc. to producer)
			Calculated (cm ³ /g)	Measured (cm ³ /g)	
Davisil, grade 646	300	150	2.25	2.3	7
Davisil, grade 636	480	60	1.44	1.5	6.5
Merck, grade 10181	675	40	1.35	1.4	—
May & Baker, lot 69554	750	21	0.75	0.9	—

2. EXPERIMENTAL

The catalysts were prepared by means of incipient wetness. The metal salts (Co(NO₃)₂ · 6H₂O; Co(CH₃COO)₂ · 4H₂O; CoCl₂ · 6H₂O; and CoSO₄ · 6H₂O) were dissolved in an appropriate volume of solvent (deionized water, methanol p.a., ethanol p.a., *n*-propanol p.a., *n*-butanol p.a., acetone p.a., tetrahydrofuran p.a., dimethylsulfoxide p.a., and dimethylformamide p.a.) and then added to the silica support ($d_p = 150\text{--}250\ \mu\text{m}$; for further details cf. Table 1). The catalyst precursor was aged for a certain time at room temperature and then subsequently dried in an oven. The resulting cobalt loading (in weight percentage Co) of some of the samples was checked by AA and was found to be within the error of measurement of the after preparation expected loading. The reference material Co₃O₄ was prepared by heating cobalt nitrate at 773 K for 3 h in air.

The TPR rig was constructed using stainless-steel tubing, fittings, and valves and contained a quartz microreactor. The gas streams (air or N₂ as calcining gas, a mixture of 5% H₂ in N₂ as reducing gas, and N₂ as a reference gas for the TCD) were fed with a mass flow controller. After the reactor the effluent was led via a 3A molecular sieve trap to remove the product water. The thermal conductivity of the exit gas was compared with the reference gas stream to determine the hydrogen concentration in the effluent gas. The catalyst precursor (ca. 0.15 g in the case of supported catalysts) was loaded into the quartz TPR cell and heated at 10 K/min up to the final calcination temperature in 60 ml (NTP)/min calcining gas (N₂ or air) and held at this temperature for 1 h. Subsequently the reactor was cooled to 373 K. Finally the precursor was reduced using a linear temperature program (10 K/min up to 1273 K) in 60 ml (NTP)/min reducing gas (5% H₂ in N₂). The *K*-value (17) was Ca. 100 s for the supported cobalt catalysts indicating that hydrogen depletion is avoided. The *P*-value (18) was ca. 17 K for these catalysts, thus indicating distortion of the profile due to the temperature-programmed reduction process to be minimal and resolution in multistep reduction processes to be maintained. The equivalent values were 150 s and 25 K, respectively, during the reduction of the unsupported Co₃O₄.

From the concentration versus temperature curve assuming constant total flow the hydrogen consumption was cal-

culated. The change in flow due to the trapping of reduction water hardly influences the total flow in our mode of operation. The integration of the individual peaks in the TPR-spectra was done from valley to valley, so that the hydrogen consumption ascribed to the reduction of a certain species can only be a rough estimate.

3. RESULTS

pH During the Impregnation Step

In the impregnation step a quantity of the impregnation solution, corresponding to the pore volume of the carrier, is added to the silica. To measure the pH during the impregnation small amounts of silica were added to an aqueous 1.09 M Co-solution. As a baseline case, silica was added to deionized water. Figure 1 shows the change in pH as a function of the amount of silica added to the different solutions. At infinite mass addition of silica to deionized water, a pH corresponding to the isoelectric point of the solid is expected (19). This is reported for silica gel to be between pH 1 and 2.2 (20, 21). The observed value is different, which might be explained by leaching of impurities out of the silica (21, 22). The pH of the aqueous cobalt nitrate and cobalt

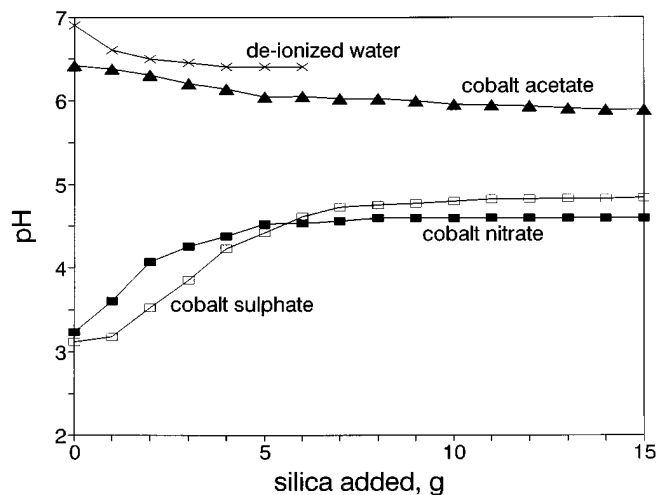


FIG. 1. pH of 1.09 M Co-solutions as a function of the amount of silica gel (Merck, grade 10181, surface area 675 m²/g) added.

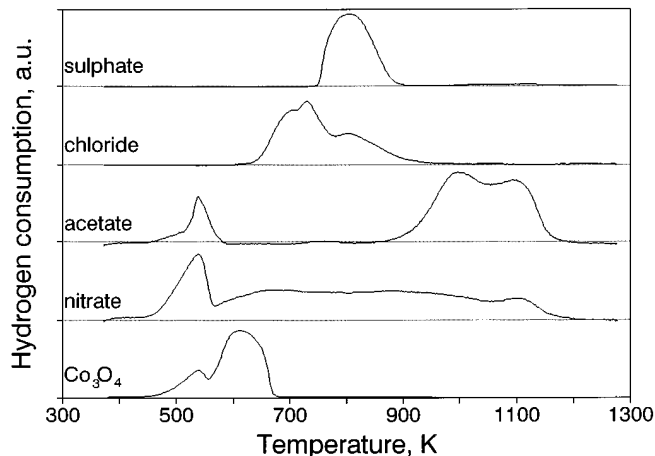


FIG. 2. Influence of the anion on the reduction spectrum of impregnated 9 wt% Co/SiO₂-catalysts and TPR-spectrum of Co₃O₄. Reducing gas, 60 ml(NTP)/min 5% H₂ in N₂; temperature-programming rate 10 K/min, $m_{\text{cat}} \approx 0.15$ g; impregnated catalysts prepared using silica gel (Merck grade 10181, surface area 675 m²/g), water as solvent, aged for 1 h, dried at 373 K for 24 h, calcined in air at 673 K for 1 h.

sulphate solution increases from the initial value of 3 to 4.6, respectively 4.9, upon the addition of silica. The pH of the aqueous cobalt acetate solution decreases from 6.2 to 5.2 upon silica addition. The limiting value of the pH is different for the different cobalt salts used. This might be ascribed to both the difference in the ability of the salts for leaching impurities in silica and the adsorption of cobalt ions on the silica surface. The difference in the limiting pH value will result in a difference in the amount of cobalt ions adsorbed on the silica surface, i.e., the largest amount starting from the acetate.

Influence of Metal Salt on the Reduction

Different metal salts have been reported to have a remarkable influence on the dispersion obtained and on the

reducibility of the catalyst (15, 23). Figure 2 shows the TPR-spectra of Co₃O₄ and impregnated Co/SiO₂ catalysts starting from different metal salts (nitrate, acetate, chloride, and sulphate). The spectra for the catalysts starting from cobalt nitrate, acetate, and chloride are qualitatively similar to those published by Rosynek and Polansky (15). The spectra of cobalt catalysts starting from chloride or sulphate are essentially the same as for the unsupported metal salt showing negligible interaction between the support and the salt. Also the hydrogen consumption for the impregnated catalysts starting from chloride or sulphate corresponds to that of the unsupported metal salt (in the case of cobalt sulphate the high hydrogen consumption of 4.8 indicates the almost complete reductive decomposition of the sulphate anion). In the case of the nitrate or acetate precursor, however, a number of peaks can be seen in the TPR-spectra indicating the formation of different cobalt species during the preparation steps. The TPR-spectra of the nitrate and the acetate precursors are very similar, with only the intensities of the peaks differing markedly. The spectrum consists of low-temperature peaks at ca. 560 and 620 K, a broad diffuse hydrogen consumption between 770 and 1020 K, a broad high-temperature peak between 1020 K and 1120 K, and a relatively sharp peak at ca. 1170 K. The broad peaks indicate the existence of several species reducing at approximately the same temperature, whereas the sharp peaks indicate the existence of a single species.

Influence of Silica Source

Puskas *et al.* (12) stated that high-surface-area silica would favor the formation of cobalt silicates. Four different silicas, whose characteristics are given in Table 1, were used for preparing impregnated Co/SiO₂ catalysts using an aqueous cobalt nitrate impregnation solution. The TPR-spectra of these catalysts are given in Fig. 3a and a quantitative estimate of the hydrogen consumed by the reduction of different cobalt species as a function of the surface area of this

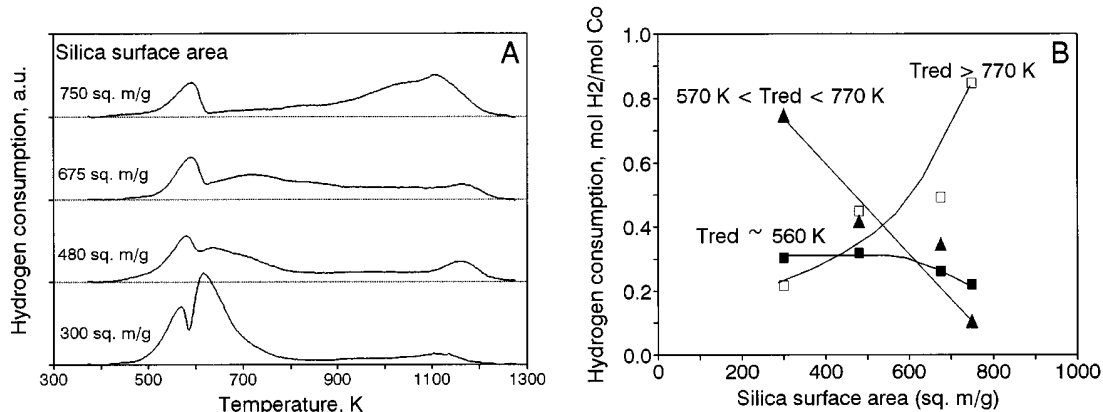


FIG. 3. Influence of silica gel surface area on the reduction of impregnated 9 wt% Co/SiO₂-catalysts. Reducing gas, 60 ml(NTP)/min 5% H₂ in N₂; temperature-programming rate 10 K/min, $m_{\text{cat}} \approx 0.15$ g; impregnated catalysts prepared using Co(NO₃)₂·6H₂O, water as solvent, aged for 1 h, dried at 373 K for 24 h, calcined in air at 673 K for 1 h.

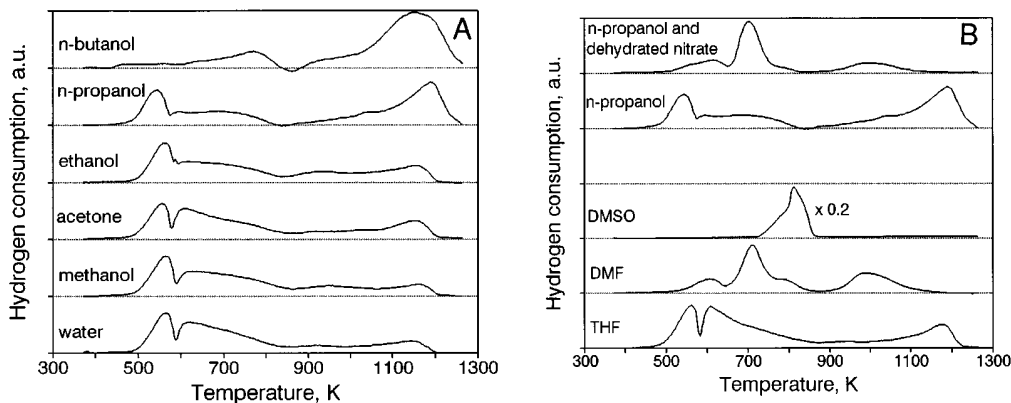


FIG. 4. Influence of solvent on the reduction of impregnated 9 wt% Co/SiO₂-catalysts. Reducing gas, 60 ml(NTP)/min 5% H₂ in N₂; temperature-programming rate 10 K/min, $m_{\text{cat}} \approx 0.15$ g; impregnated catalysts prepared using Co(NO₃)₂ 6H₂O, silica gel (Davisil grade 646, surface area 300 m²/g), aged for 1 h, dried at 373 K for 16 h, calcined in N₂ at 673 K for 1 h.

material is given in Fig. 3b. The different cobalt species are for reasons of convenience subdivided into cobalt species reduced at ca. 560 K, species reduced between 570 and 770 K, and species that require higher reduction temperatures (>770 K). The main features of the TPR-spectrum of the four impregnated catalysts using silicas with different surface areas are similar. The first peak is at about the same temperature (560 K), but the amount of hydrogen consumed, as calculated from this peak, decreased from 0.28 to 0.2 mol H₂/mol Co. The second region (between 620 and 770 K) shows a remarkable decrease in intensity going from the low-surface-area silica to the high-surface-area silica and the hydrogen consumption decreases from 0.78 to 0.2 mol H₂/mol Co, whereas the intensity of the high-temperature peak (at ca. 1170 K) shows a strong increase (from 0.2 to 0.76 mol H₂/mol Co). The Co-concentration in the impregnation increased from 0.66 mol/liter for silica with a surface area of 300 m²/g to 1.69 mol/liter for silica with a surface area of 750 m²/g. Silica gel has approximately a constant number of silanol groups per unit surface area (5/nm²) (24–27) and therefore it might be postulated that both the relative increase in the number of silanol groups and the increase in Co-concentration in the impregnation solution might cause an increase in the formation of cobalt species, which can only be reduced at high temperatures. This assumes that the interaction between cobalt in the impregnation solution and silanol groups leads to the formation of these species. Consequently, the species reduced between 570 and 770 K were formed to a lesser extent. Also the formation of the species reduced at 560 K would be less favored, but its formation is less affected by using high-surface-area silicas.

Effect of Impregnation Solvent

Some authors have used organic solvents to obtain highly dispersed supported metal catalysts (3–5). Therefore, a

number of solvents were used in the impregnation step in the catalyst preparation. The TPR-spectra of these catalysts are shown in Fig. 4. Using water, *n*-alcohols, acetone, or THF resulted in similar TPR-spectra, in which the main features are the same although the abundance of the various species differs. Using solvents like DMSO and DMF resulted in quite different TPR-spectra.

Catalysts made using DMSO as a solvent exhibit only one main region of hydrogen consumption (at ca. 770 K) and the hydrogen consumption was quite high (H₂/Co = 3.2 mol/mol) indicating not only the reduction of the cobalt ions, but also the reductive decomposition of other species. DMSO is a chelating solvent, which replaces water as a ligand turning the cobalt aquocomplex into a cobalt DMSO complex, which is apparently not destroyed upon calcination in nitrogen at 673 K, hence explaining the high hydrogen to cobalt ratio. This affects the formation of the different cobalt species severely thus indicating the necessity of water ligands for the formation of these species.

To confirm the role of the water ligand in the cobalt complex on the reduction behavior of impregnated catalyst, a sample was prepared using 90% dehydrated cobalt nitrate, prepared by heating the cobalt salt at 373 K for 3 h, and using *n*-propanol as a solvent (see Fig. 4b). The reduction spectrum of this catalyst compared to the catalyst made using Co(NO₃)₂ 6H₂O and *n*-propanol as a solvent shows a remarkable difference. The catalyst starting with hydrated cobalt nitrate has quite a large amount of cobalt species, which can only be reduced at ca. 1170 K, whereas the sample starting from dehydrated cobalt nitrate exhibits a major hydrogen consumption peak at ca. 700 K.

The TPR-spectrum obtained from the catalyst using DMF as a solvent is quite similar to the spectrum obtained from the sample starting from the dehydrated cobalt nitrate using *n*-propanol as a solvent and also the amount of hydrogen consumed for the reduction is similar (1.14 mol H₂/mol Co for sample using DMF as a solvent versus 1.12 mol

H₂/mol Co for sample starting from dehydrated cobalt nitrate using *n*-propanol as a solvent). This might be explained by a partial reduction of the number of water ligands, which reduces the interaction with the silica surface thereby reducing the number of different species formed.

Use of solvents that result in similar TPR-spectra and that hence can be assumed to form the same species on the catalyst surface was accompanied by a shift in the relative abundance of the different cobalt complexes bonded to the silica surface. A correlation between the polarity index of solvents according to Snyder (28) and the amount of hydrogen consumed to reduce the different species formed using water or *n*-alcohols as a solvent could be established (see Fig. 5). Decreasing the polarity of the solvent caused an increase in the interaction between the cobalt complex in the solution and the silica gel surface forming more species that are reduced at elevated temperatures (>770 K). The amount of the species that are reduced at the low temperature of ca. 560 K are hardly influenced by the polarity of the solvent, so long as an excessive amount of species that can only be reduced at high temperatures is not formed (e.g., with *n*-butanol or *n*-propanol as a solvent). Using acetone or THF as a solvent resulted in the same TPR-spectra as using water as a solvent. A better parameter to correlate the different solvents with the formation of the different species might be the ability of the solvents to form hydrogen bridges with the surface silanol groups. The influence of the polarity or ability to form hydrogen bridges of the solvent might be explained by an enrichment of the cobalt aquocomplexes in the vicinity of the silica gel surface thus forming a boundary layer with a relatively high cobalt complex concentration, which enhances the probability of the

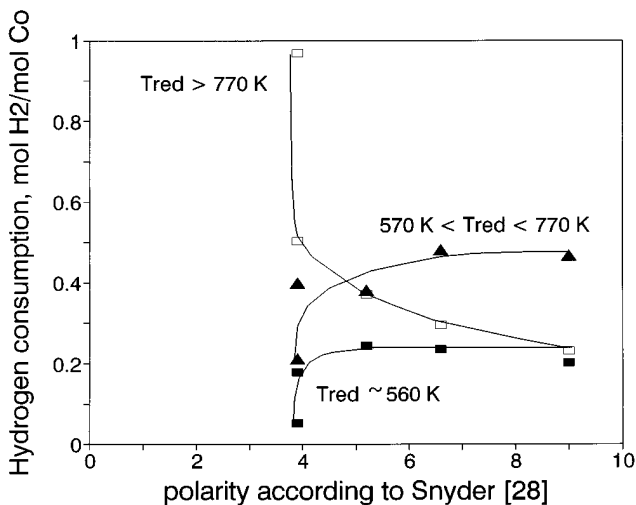


FIG. 5. Hydrogen consumption during TPR for several cobalt species as a function of the polarity of the solvent (solvent water or *n*-alcohols) according to Snyder (28). Impregnated catalysts prepared using Co(NO₃)₂·6H₂O, silica gel (Davisil grade 646, surface area 300 m²/g), aged for 1 h, dried at 373 K for 16 h, calcined in N₂ at 673 K for 1 h.

formation of the precursor of species that can only be reduced at temperatures greater than 770 K.

Solutions of cobalt salts in water are acidic. To study the influence of pH of the aqueous impregnation solvent, cobalt nitrate was dissolved in diluted HNO₃ solutions. In the range between 10⁻⁵ and 10⁻³ N HNO₃ hardly any influence on the reducibility of the impregnated cobalt catalysts could be detected. The TPR-spectrum of the catalyst prepared with an impregnation solution of 0.01 and 0.1 N HNO₃ showed a somewhat lower high-temperature reduction peak at ca. 1170 K.

Influence of Aging Time

After the impregnation of the silica with aqueous cobalt nitrate solution, the solid was aged for a certain time at room temperature. Reproducible TPR-spectra within the error of measurement (H₂, consumed/Co = 1.19 mol/mol ± 3%) could be obtained irrespective of aging time (between 0 and 96 h) thus indicating no influence of aging time on the formation of the different cobalt species and on the reducibility of the impregnated catalysts.

Influence of Drying Temperature and Drying Time

After silica was impregnated with an aqueous cobalt nitrate solution and the catalyst precursor was aged at room temperature, the samples were dried in an oven in an air atmosphere. Increasing drying time caused a decrease in the amount of cobalt species that are reduced at high temperatures and an increase in the amount of species reduced between 570 and 870 K (Fig. 6a). Increasing drying temperature resulted in the same effect (Fig. 6b). Therefore, it can be concluded that precursors of cobalt species, which are only reduced at temperatures up to 1170 K, can be destroyed by a low-temperature drying process, which was also reported recently by Coulter and Sault (14). A semilogarithmic plot of the amount of hydrogen consumed ascribed to the high-temperature peak (at ca. 1170 K) versus drying time (Fig. 7) shows that the kinetics of the destruction of these species could be described by an irreversible first-order reaction with respect to these species, assuming that the amount of hydrogen needed for reduction is directly proportional to the amount of these species:

$$-r_{\text{cobalt species}, T_{\text{red}} \approx 1170 \text{ K}} = 43 \cdot e^{-47 \times 10^3 / RT} \cdot C_{\text{Co-species}} \text{ mol Co-species/s.}$$

Influence of Calcination Temperature

After drying the catalyst precursor (starting from cobalt nitrate), the samples were calcined in nitrogen at different calcination temperatures. The TPR-spectra and the amount of hydrogen ascribed to the different peaks as a function of calcination temperature are shown in Fig. 8. Several peaks were evaluated: the low-temperature peak between 450 and

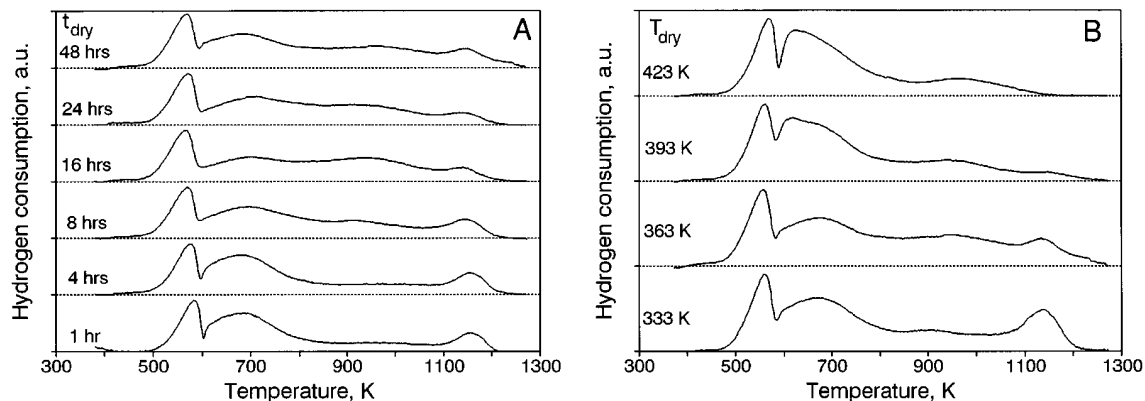


FIG. 6. Influence of drying on the reduction of impregnated 9 wt% Co/SiO₂-catalysts. Reducing gas, 60 ml(NTP)/min 5% H₂ in N₂; temperature-programming rate 10 K/min, $m_{\text{cat}} \approx 0.15$ g; impregnated catalysts prepared using CO(NO₃)₂ 6 H₂O, silica gel (Davisil grade 636, surface area 480 m²/g), water as a solvent, aged for 1 h, dried, calcined in N₂ at 673 K for 1 h.

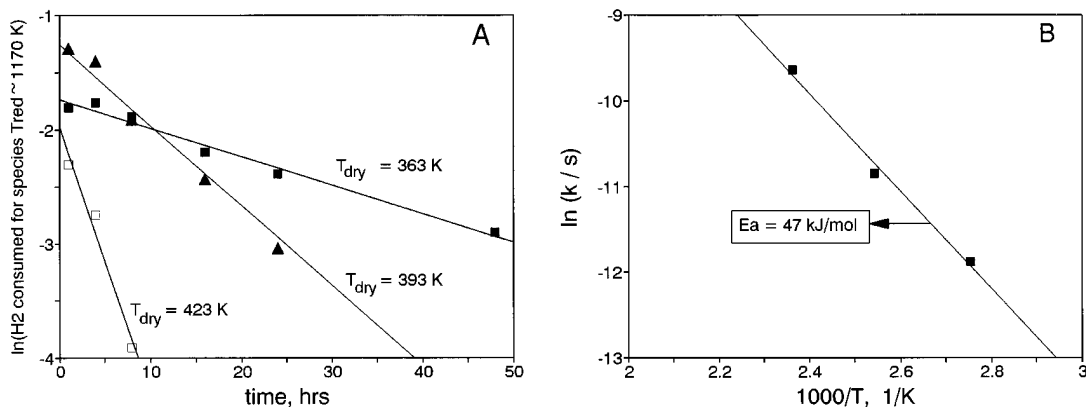


FIG. 7. Kinetic evaluation of the destruction of the cobalt species reduced at ca. 1170 K. Impregnated catalysts prepared using CO(NO₃)₂ 6H₂O, silica gel (Davisil grade 636, surface area 480 m²/g), water as a solvent, aged for 1 h, dried, calcined in N₂ at 673 K for 1 h.

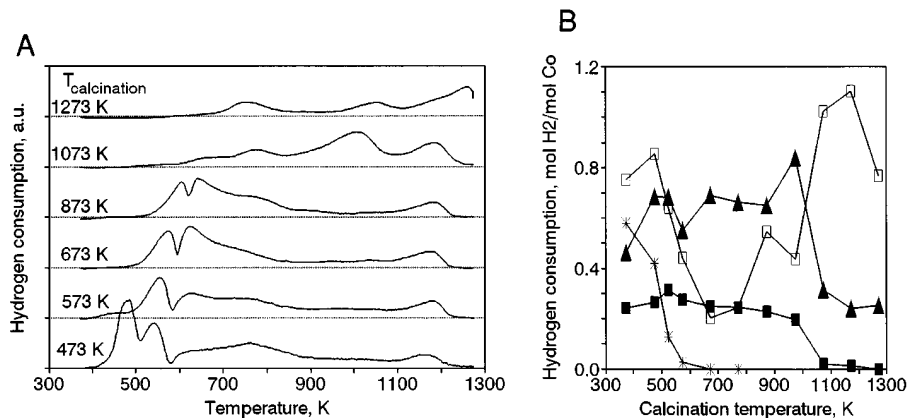


FIG. 8. Influence of calcination on the reduction of impregnated 9 wt% Co/SiO₂-catalysts. Reducing gas, 60 ml(NTP)/min 5% H₂ in N₂; temperature-programming rate 10 K/min, $m_{\text{cat}} \approx 0.15$ g; impregnated catalysts prepared using Co(NO₃)₂ 6H₂O, silica gel (Davisil grade 636, surface area 480 m²/g), water as a solvent, aged for 1 h, dried at 373 K for 16 h, calcined in N₂ for 1 h. (*) Tred, 450–510 K; (■) Tred, 540–560 K; (▲) Tred, 570–770 K; (□) Tred >770 K.

510 K, the peak between 540 and 560 K, the peak with a maximum between 920 and 1070 K, and the high-temperature peak at 1140–1190 K. The area between 570 and 770 K was evaluated as one single area due to the bad peak separation, although this area consists of at least two peaks. At the low calcination temperatures (up to 573 K) a peak between 450 and 510 K is observed in the reduction spectra. The amount of species, which can be reduced at 540–560 K, did not change much (H_2 , consumed/Co = 0.24–0.27 mol/mol) if the amount of species reduced at high temperatures is not excessively large. When the calcination temperature is increased to 873 K, the amount of cobalt species, which are reduced at temperatures larger than 770 K, decreases. This might be ascribed to the same process as was observed during drying of the catalyst. Increasing the calcination temperature further causes an increase in the amount of both species. However, the amount of species, which are reduced between 920 and 1070 K, seems to pass through a maximum. The high calcination temperature might cause solid-state reaction between surface cobalt species and silica.

Influence of Calcination Atmosphere

For catalysts starting from the nitrate precursor no major influence of the calcination atmosphere on the TPR-spectrum was observed at a calcination temperature of 673 K, since the thermal decomposition of the nitrate leads to NO_2 , which is itself a strong oxidizing agent. However, the amount of hydrogen consumed for the reduction of the species reduced at ca. 560 K decreased slightly from 0.28 to 0.24 mol H_2 /mol Co.

4. DISCUSSION

Peak Assignment

The TPR-spectrum of impregnated cobalt on silica catalysts starting from cobalt nitrate or acetate consists of a number of distinct maxima (450–510 K, 540–560 K, 570–770 K, 920–1070 K, 1170 K). The appearance of distinct, different maxima in the TPR-spectra indicates the reduction of at least five different species. Close inspection of the TPR-spectra might reveal more different species, which would then have similar reduction behavior.

An urgent question, however, which must be addressed first, is whether all cobalt species can be reduced up to 1273 K. If the stoichiometry of reduction is well established, the H_2 /Co ratio could be used. However, this ratio varies between 1 and 1.3 mol H_2 /mol Co, which was also observed for the reduction of CO/Al_2O_3 (6). Therefore, a temperature-programmed reduction/oxidation cycle was performed to determine the extent of reduction (29). After the temperature-programmed reduction up to 1273 K was completed, the sample was kept at this temperature for 20 min, after which it was cooled down to 323 K. Subsequently, the sample was oxidized in a 2% O_2 in He stream

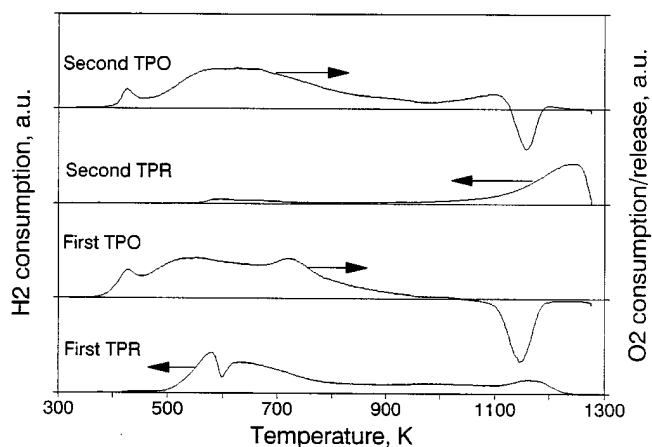


FIG. 9. TPR/TPO-cycle of impregnated 9 wt% Co/SiO₂-catalyst. Reduction in 60 ml(NTP)/min 5% H₂ in N₂, temperature-programming rate 10 K/min, $m_{cat} = 0.232$ g; oxidation in 60 ml(NTP)/min 2% O₂ in He, temperature-programming rate 10 K/min, $m_{cat} = 0.232$ g; impregnated catalysts prepared using $Co(NO_3)_2 \cdot 6H_2O$, silica gel (Davisil grade 636, surface area 480 m²/g), water as a solvent, aged for 1 h, dried at 373 K for 16 h, calcined in N₂ at 673 K for 1 h.

by increasing the temperature at 10 K/min up to 1273 K. This temperature-programmed reduction/oxidation cycle was then repeated. The spectra obtained are given in Fig. 9 and the quantitative evaluation of this experiment is given in Table 2. During the first temperature-programmed oxidation, cobalt is oxidized to Co_3O_4 at temperatures below 970 K, the oxygen consumption can be measured, and, assuming that the reaction occurring is $Co \rightarrow Co_3O_4$, the amount of cobalt can be calculated. The oxygen release at

TABLE 2

Hydrogen Consumption and Oxygen Consumption/Release during TPR/TPO Cycle of Impregnated 9 wt% Co/SiO₂ Catalyst

		Amount of Co (mmol)	H_2/Co^a (mol/mol)
Mass of catalyst (g)		0.232	0.286
First TPR	H_2 consumption, mmol	0.364	1.20
First TPO	O_2 consumption, mmol	0.200	0.296
	O_2 release, mmol	0.051	0.308
Second TPR	H_2 consumption, mmol	0.307	1.01
Second TPO	O_2 consumption, mmol	0.188	0.282
	O_2 release, mmol	0.018	0.106 ^b

Note. Reduction in 60 ml(NTP)/min 5% H₂ in N₂, temperature-programming rate 10 K/min from 373 K till 1273 K; oxidation in 60 ml(NTP)/min 2% O₂ in He, temperature-programming rate 10 K/min from 323 K till 1273 K; impregnated catalysts prepared using $Co(NO_3)_2 \cdot 6H_2O$, silica gel (Davisil grade 636, surface area 480 m²/g), water as a solvent, aged for 1 h, dried at 373 K for 16 h, calcined in N₂ at 673 K for 1 h.

^a Amount of cobalt based on average of the weighted amount and the amount determined at the first TPO experiment.

^b Low value caused by bad separation between area of oxygen consumption and oxygen release.

1040 K is due to the thermal reduction of Co₃O₄ to CoO and the amount can be related to the amount of cobalt that has been oxidized to Co₃O₄. After the experiment the sample was weighed and the amount of cobalt was calculated assuming all cobalt to be present as CoO. The values obtained correspond very well, viz. 0.298 mmol Co ± 4%. The deviation calculated from the oxygen release during the second TPO can be ascribed to the poor separation between oxygen consumption and oxygen release. Thus it can be concluded that, after the TPR experiments up to 1273 K, all cobalt ions are reduced.

The maximum at 510 K only occurs for catalyst precursors starting from cobalt nitrate that have been calcined below 523–573 K. At higher calcination temperatures nitrate has been thermally decomposed (30). Therefore the reduction peak at 510 K is ascribed to the reductive decomposition of residual nitrate. The reductive decomposition of the nitrate might even lead to the observation of a negative peak in the TPR-spectrum (29, 30). This can happen, if the exit lines are cold enough to allow the dimerization of the product NO₂ to N₂O₄, which has a higher thermal conductivity than hydrogen (31). Therefore, the first peak in the TPR-spectrum of impregnated Co/SiO₂ catalysts synthesized using nitrate salt is ascribed to the reductive decomposition of the nitrate ion.

For the catalysts starting from cobalt nitrate the amount of hydrogen ascribed to the reduction of the second maximum at 560 K was between 0.2 and 0.29 mol H₂ consumed per mol of Co, if the amount of cobalt species that are reduced at high temperatures is not excessive. The total hydrogen consumption, exclusively the hydrogen needed for the reductive decomposition of the nitrate ion, varied between 1.0 and 1.3 mol H₂/mol Co. Arnoldy and Moulijn (6) also observed rather low ratios of H₂ consumption to cobalt for the reduction of Co/Al₂O₃ (between 0.9 and 1.2), although their first peak accounted for up to 33% of the total hydrogen consumption. They ascribed this peak to the one-step reduction of Co₃O₄ to metallic Co. Okamoto *et al.* (23) ascribed the first peak to small Co₃O₄ particles and the subsequent reduction peak maximum to larger particles, thus indicating a bimodal distribution of this compound. Unsupported Co₃O₄ exhibits two peaks (see Fig. 1), where the hydrogen consumption ascribed to the first peak is approximately 25% of the total hydrogen consumption (9, 10). This indicates that the reduction of this oxide is a two-step process (Co₃O₄ → CoO → Co), which has been proven using XPS (11). The XRD-spectra of impregnated Co/SiO₂ catalysts show broad peaks, which can be ascribed to small Co₃O₄ particles (15, 23, 32). It might be argued that, because the diffusional limitation during a TPR-experiment with smaller particles is less severe, the peak separation observed for the unsupported material (with relatively large crystals) would not diminish by reducing particle size, but should be enhanced. It is therefore concluded that the peak

at 540–560 K is due to the reduction of trivalent to divalent cobalt. However, not all trivalent cobalt is present in this form of Co₃O₄, because the corresponding hydrogen consumption for the subsequent reduction of CoO to Co is not observed in the reduction of one single species.

The broad peak/area between 570 and 770 K must be ascribed to at least two different species with maxima at ca. 620 K and at ca. 700 K. The maximum at 623 K corresponds to the second maximum in the reduction of Co₃O₄ and can therefore be attributed to the reduction of divalent cobalt with hardly any interaction with the carrier to metallic cobalt. The species reducing at slightly higher temperatures may have a somewhat stronger interaction with the silica gel surface.

Species that can be reduced only at temperatures higher than 770 K have a stronger interaction with the support. Under normal reduction conditions (up to 770 K) they cannot be reduced and they are therefore probably inactive in metal-catalyzed reactions.

Between 770 K and 1070 K a broad hydrogen consumption peak can be observed, which must be ascribed to the reduction of several different cobalt species. In a separate experiment a catalyst was prepared starting with Ludox HS 40, a colloidal silica solution, as silica source to which cobalt nitrate was added. Upon addition of the cobalt salt a blue precipitate was formed and the reduction of this sample after calcination at 673 K in air showed several maxima between 870 and 1070 K. The colloidal silica source contains many silanol groups, which might react with cobalt ions in the solution forming cobalt hydrosilicate. The hydrogen consumption during TPR of supported Co/SiO₂ between 770 and 1070 K is therefore tentatively ascribed to the reduction of cobalt hydrosilicates.

The peak with a maximum at ca. 1170 K is sharp and therefore belongs to one species. Oxidizing the sample at 1273 K leads to the formation of this species (see Fig. 9), whose reduction requires 1.0 mol H₂/mol Co (See Table 2; second TPR) thus indicating the reduction of divalent cobalt. Starting from an impregnated Co/SiO₂ catalyst that was calcined at 1273 K in air and contained, according to XPS-measurements, Co²⁺, Ming and Baker (13) also observed a single peak at ca. 1173 K in the TPR-spectrum. Under these conditions the formation of orthocobalt silicate by a solid-state reaction between CoO and SiO₂ is well known (33) (from the observed H₂/Co ratio, the formation of cobalt silicide during high-temperature reduction can be excluded (34)). From this circumstantial evidence the peak at 1170 K might now be ascribed to the reduction of surface cobalt silicate species.

Influence of the Preparation Variables of Impregnated Co/SiO₂ on Its Reduction

The impregnation procedure can be described by the concept of *interfacial coordination chemistry* (35). This is

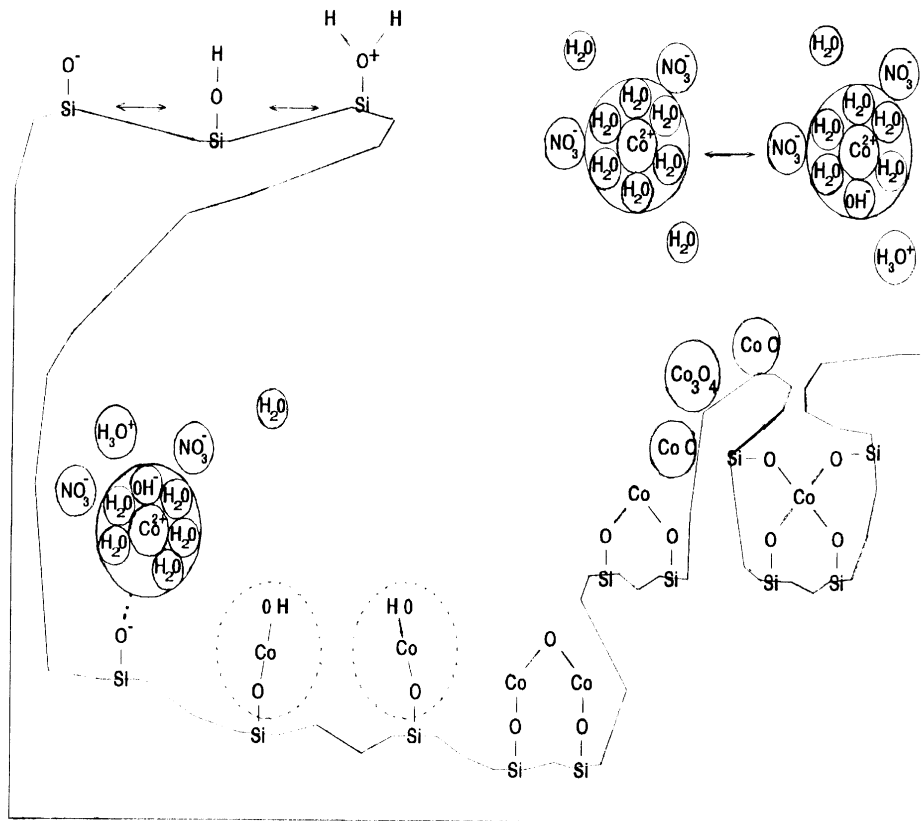


FIG. 10. Interaction between cobalt nitrate and silica gel surface during impregnation according to the concept of *interfacial coordination chemistry* (35).

illustrated in Fig. 10 for the interaction between silica gel surface and cobalt nitrate. In a nonchelating solution the cobalt ion is surrounded by water ligands originating from the starting cobalt salt. This species can interact with surface silanol groups and form a surface cobalt complex. If the water is replaced as a ligand, the interaction vanishes, indicating the necessity of water ligands for the formation of these surface complexes. The need for silanol groups to participate in this reaction is substantiated by the observed increase in the amount of hydrogen needed for the reduction of the surface cobalt silicates with increasing surface area of the silica.

Silanol groups act as an amphoteric material and, depending on the pH of the impregnation solution, exist as SiOH , SiO^- or SiOH_2^+ -species. The relative amount of these species at the silica surface is a function of the pH. At pH higher than the isoelectric point of silica (pH 1–2.2 (20, 21)) a surplus of negative charge is present on the silica surface. The adsorption of transition-metal complexes on inorganic oxides can be explained in terms of electrostatic interaction between the polarized surface, which is a function of pH, and the counterions (36). Another possible route to forming strongly bonded cobalt to the silica surface is the oxolation reaction (35). On the basis of our results it

cannot be concluded beyond doubt which of the above interactions prevails during the preparation of impregnated Co/SiO_2 catalysts.

The influence of the anion can also be explained in terms of the pH of the impregnation solution. Their pH using strong acidic cobalt salts (nitrate, sulphate, and chloride) is low and is increasing to approximately 4.4–4.7 in the process of pore filling. This yields a medium amount of the precursor of the surface cobalt silicate, for the zeta-potential in the region between pH of 2.5 and 5 is not a strong function of pH indicating an approximately constant amount of negative-charged SiO^- groups in this pH region (37). The zeta-potential strongly decreases above ca. pH 5. The solution of the acetate precursor is initially higher than this value and also after the addition of the silica gel to this solution. Therefore, more cobalt complexes in the solution formed from the acetate can interact with dissociated silanol groups and thus starting from the acetate might lead to a higher amount of surface cobalt silicate.

The solvent used in the impregnation step is of great importance. It is known that, with silanol groups, water forms a glassy layer of immobilized water (38, 39) due to the formation of hydrogen bridges. If solvents that are less able to form these hydrogen bridges are used, the silanol group

can form these bonds with the water ligands of the cobalt complex. This might lead to an enhanced possibility for the formation of the precursor of surface cobalt silicate.

The precursor of the surface cobalt silicates can be destroyed by a mild temperature treatment. The decomposition of the precursor of surface cobalt silicate starting from the chloride or sulphate might favor the formation of the original salt. With the nitrate and acetate salts the thermal destruction of the precursor of the surface cobalt silicate might yield cobalt hydroxide, which is subsequently transformed to CoO/Co₃O₄.

5. CONCLUSION

With temperature-programmed reduction up to 1273 K, the existence of all different cobalt species on the silica surface can be observed and their formation as a function of the variables in the preparation of these catalysts can be studied.

The preparation of impregnated catalysts is a complex process. The chemistry, which occurs in the impregnation solution, is of great importance and can be visualized in terms of the concept of *interfacial coordination chemistry* (35) (see Fig. 10). Dissolved cobalt nitrate is coordinated with water and hydroxyl groups. In the second layer nitrate ions are present. The aqueous cobalt complexes can react with surface silanol groups. This reaction is dependent on the number of SiO-species, which is a function of the pH of the impregnation solution. The formation of the strongly bonded cobalt species is enhanced using solvents that are less amenable to the formation of hydrogen bonds with silanol groups. During drying and calcination up to 673 K the strongly bonded cobalt species are destroyed.

The formation of surface cobalt silicate is enhanced by using metal salts that are decomposed during thermal treatment, having a high pH in the impregnation solution, using high-surface-area silica, using a less polar solvent for the impregnation, and applying low-drying/calcination temperatures during a short time. By varying drying temperature and/or drying time the resulting amount of surface cobalt silicates can be directed. This might be an important tool for maximizing the dispersion of supported cobalt catalysts.

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