

RESEARCH NOTE

On Cobalt Silicate Formation during High-Temperature Calcination of Impregnated Cobalt/Silica Catalysts

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In recently published papers (1–8) the influence of different preparation processes of impregnated Co/SiO₂ catalysts on the formation of various CoO_x and cobalt–silica species and their subsequent reduction with hydrogen have been investigated. Among the numerous factors, the influence of the support type and the cobalt salt used for impregnation on reduction of resulting cobalt precursors was studied. Special attention was paid to the influence of subsequent steps of catalysts preparation like ageing time, drying temperature and time, calcination atmosphere (high vacuum, inert gas) and temperature on the resulting catalyst phase compositions (1–3). Puskas *et al.* (4) observed the cobalt silicate formation in precipitated Co on silica catalysts, which can be reduced only at elevated temperatures (above 970 K). Recently, Ming and Baker (3) reported on the influence of pH of the impregnation solution on the formation of cobalt silicates in cobalt–silica gel catalysts. Coulter and Sault (2) observed the cobalt silicate formation in Co/SiO₂ catalyst under ultra-high vacuum conditions at relatively low temperatures. They have shown that a certain amount of cobalt silicate is necessary for obtaining highly dispersed cobalt catalysts. On the other hand, the formation of surface cobalt silicate during preliminary steps of catalyst preparation, or even during reduction, is considered as a reason for partial reduction of the total cobalt present at the temperatures normally used, i.e., up to 773 K. Results by van Steen *et al.* (1) clearly show that calcination in flowing nitrogen in the temperature region of 1073–1273 K has a great influence on the resulting hydrogen consumption peak lying at 1170 K, which was ascribed to a solid-state reaction between cobalt compounds and silica support with the formation of surface cobalt silicate species. Although the cobalt orthosilicate formation by direct heating of cobalt oxides and silica is already known (9, 10), the structural and morphological data on the formation of cobalt silicate in dispersed Co/SiO₂ systems are rather scarce (3, 7).

In this study, by using X-ray powder diffraction (XRD) and high-resolution transmission electron microscopy (HRTEM) we investigated the influence of high-temperature calcination in both inert and oxidative atmospheres on the phase composition of impregnated Co/SiO₂ catalysts prepared by incipient wetness and on the reducibility of such catalyst precursors. The influence of the support (silica with both low- and high-surface area) and metal salt used (cobalt nitrate and cobalt acetate) also has been investigated.

Two types of silicas, Rhone–Poulenc XOA-400 ($S=390\text{ m}^2/\text{g}$, pore volume $1.25\text{ cm}^3/\text{g}$, mean pore diameter 100 \AA) and XOB-15 ($S=26\text{ m}^2/\text{g}$, pore volume $0.3\text{ cm}^3/\text{g}$, mean pore diameter 2000 \AA)—according to the manufacturer's data—were incipient-wetness impregnated with aqueous solutions of cobalt acetate (XOB-15) or cobalt nitrate (XOB-15 and XOA-400). The cobalt salts were used as supplied by the manufacturer without any further purification or analysis. For convenience, these samples are denoted in the paper as Co(Ac)SiO₂-26, Co(N)SiO₂-26, and Co(N)SiO₂-390, respectively. Then, the precursors were dried in air at room temperature (295 K) for 48 h, next for 20 h in a vacuum desiccator over P₂O₅, and finally one half of each, additionally in an oven in air at 410 K for 20 h. These precursors were used for experiment without any further thermal treatments. The precursor sample (500–900 mg) was placed at room temperature into quartz tube (24 mm ID) in argon, oxygen, or hydrogen flow (40 cm³/min) and after purging (20 min) the sample was heated (5°C/min) to the required temperature and then was maintained for 18 or 4 h (cf. figure captions). After cooling to room temperature it was removed without passivation, or any other treatments. The hydrogen used for reduction (99.99% purity) was purified by passing over Pd/asbestos catalyst and next P₂O₅, KOH, and zeolite traps. Cobalt contents (reduced basis), determined by the atomic absorption method, were 8.5 wt% [(Co(N)SiO₂-390)], 6.3 wt% [(Co(N)SiO₂-26)],

and 9.1 wt% [(Co(Ac)SiO₂-26)]. Phase composition of catalyst samples during thermal treatment (calcination in Ar, O₂, reduction in H₂) was determined using a Siemens D5000 X-ray powder diffractometer (CuK α radiation; $\lambda = 0.154$ nm). Microscopic observations were performed with a Philips CM20 Super Twin transmission electron microscope (resolution 0.14 nm, accelerating voltage 200 kV). All XRD and TEM experiments were done *ex situ*, and precursor or catalyst samples were handled in air. Only the samples for magnetic measurements were degassed (673 K, 10⁻⁵ Torr, 4 h) and sealed off under vacuum without any contact with air.

In Fig. 1 the diffraction patterns of the precursors calcined in argon flow at different temperatures are shown. Presented results indicate that calcination of both precursors containing NO₃⁻ and CH₃COO⁻ anions at temperatures higher than 1083 K leads to the formation of orthorhombic cobalt orthosilicate (11). It also can be easily observed by eye, as the precursor changes the color from pink or black to violet-blue (for NO₃⁻) or violet-pink (for CH₃COO⁻). The difference in the color could result from a different degree of ordering of the orthosilicate formed as well as from its dispersion (10). The cobalt orthosilicate formation proceeds in the cases of both room-temperature dried precursors and oven-dried (410 K) ones. In the latter case, after drying in air at 410 K, the formation of CoO and/or Co₃O₄ was detected by electron microscopy. At the temp-

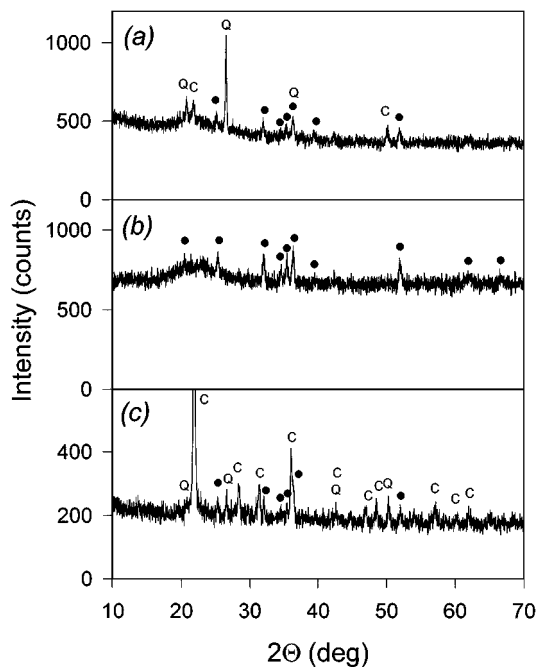


FIG. 1. XRD diagrams of cobalt precursors calcined in argon: (a) Co(Ac)SiO₂-26, 18 h, 1083 K; (b) Co(N)SiO₂-390, 18 h, 1103 K; (c) Co(Ac)SiO₂-26, 18 h, 1213 K. (●) Co₂SiO₄, (Q) α -quartz, (C) cristobalite.

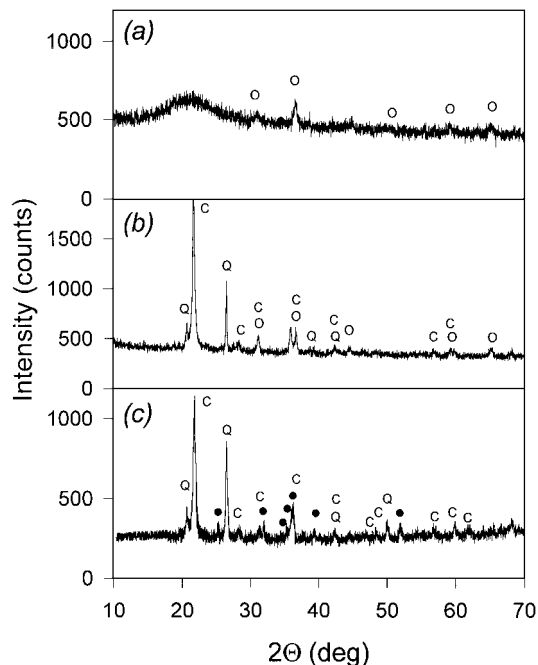


FIG. 2. XRD diagrams of cobalt precursors calcined in oxygen: (a) Co(Ac)SiO₂-26, 16 h, 773 K; (b) Co(N)SiO₂-26, 16 h, 1123 K; (c) Co(Ac)SiO₂-26, 18 h, 1213 K. (●) Co₂SiO₄, (O) Co₃O₄, (Q) α -quartz, (C) cristobalite.

eratures applied (1083–1123 K) one could observe also a partial recrystallization of the low-surface area silica support to α -quartz (12) and at higher temperatures (~ 1213 K) to cristobalite (13). Comparing the intensity of the XRD peaks of silica support not impregnated but calcined in the same way (not shown here) and cobalt acetate-impregnated silica, one could note the inhibition influence of cobalt salts and/or cobalt silicate formation on the recrystallization of the low-surface-area support to cristobalite. The transformation of cobalt precursors to cobalt orthosilicate in the case of high-surface-area silica Co(N)SiO₂-390 proceeds at a temperature slightly higher (~ 20 K) than in the case of low-surface-area silica. A recrystallization of this support to α -quartz was not observed at the temperature applied.

In Fig. 2 the diffraction diagrams of the precursor calcined in flowing oxygen are shown. During calcination at 773 K for 16 h in the case of both precursors (NO₃⁻, CH₃COO⁻) the formation of well-crystallized Co₃O₄ (14) is observed. There are minor discrepancies found in comparison with the results of Rosynek and Polansky (5), where in the case of a cobalt acetate precursor the Co₃O₄ peaks were hardly visible. Co(Ac)SiO₂-26 samples calcined in oxygen at 1123 K, i.e., in the temperature region in which argon atmosphere Co₂SiO₄ is formed, still give Co₃O₄ patterns with the presence of α -quartz and cristobalite. On the other hand, calcination of the acetate and nitrate precursors at 1213 K for 4 h is sufficient to form cobalt orthosilicate. In the case of

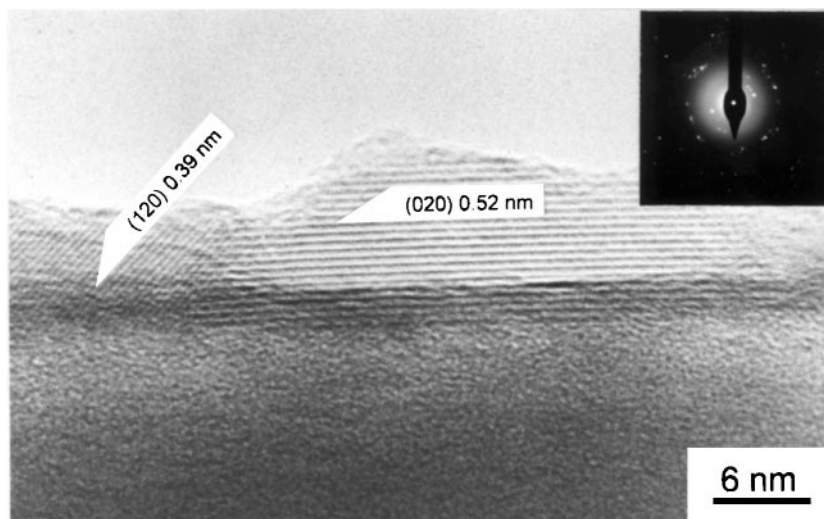


FIG. 3. HRTEM micrograph of $\text{Co}(\text{Ac})\text{SiO}_2\text{-26}$ calcined in argon, 18 h, 1213 K. Well-ordered region having interplanar distances of 0.515 nm identified as Co_2SiO_4 .

Co acetate precursor the temperature of 1193 K is sufficient to form Co_2SiO_4 .

HRTEM micrograph (Fig. 3) and selected area diffraction (SAD) photo (inset) also confirm the presence of well-crystallized thin films of cobalt orthosilicate lying on the amorphous support. In Fig. 4 an area of the $\text{Co}(\text{Ac})\text{SiO}_2\text{-26}$ precursor calcined in argon at 973 K for 16 h is shown. Microdiffraction (Fig. 4a) reveals the presence of Co_3O_4 (14) or cubic Co_2SiO_4 (15). As was shown by Nguyen *et al.* (16), it is difficult to distinguish between these compounds by TEM methods. Nevertheless, crystalline regions having interplanar spacings of 0.515 nm, typical of orthorhombic Co_2SiO_4 , are also visible (Fig. 4b). This confirms that during calcination at lower temperatures also some quantities of Co_2SiO_4 , undetectable by XRD, are formed.

During XRD experiments and careful TEM inspection we have not observed the formation of anything other than α -polymorph of cobalt orthosilicate. β - and γ -polymorphs, although existing under normal pressure at room temperature, could be synthesized under high pressure (68–81 kbar) at high temperatures (1123–1693 K) (17). However, Nguyen *et al.* (16) reported cubic γ - Co_2SiO_4 formation under vacuum condition at 1073 K. Also cobalt metasilicate (9) as well as cobalt orthopyroxene ($\text{Co}_2\text{Si}_2\text{O}_6$) (18) were not detected. Cobalt orthopyroxene is stable only under high pressure (18, 19). Dalmon (20) has tried to synthesize cobalt metasilicate starting from stoichiometric mixture of CoO and SiO_2 (230 m^2/g) in air and under vacuum in the temperature range of 1073–1773 K, but he observed only orthorhombic Co_2SiO_4 formation. Therefore we claim

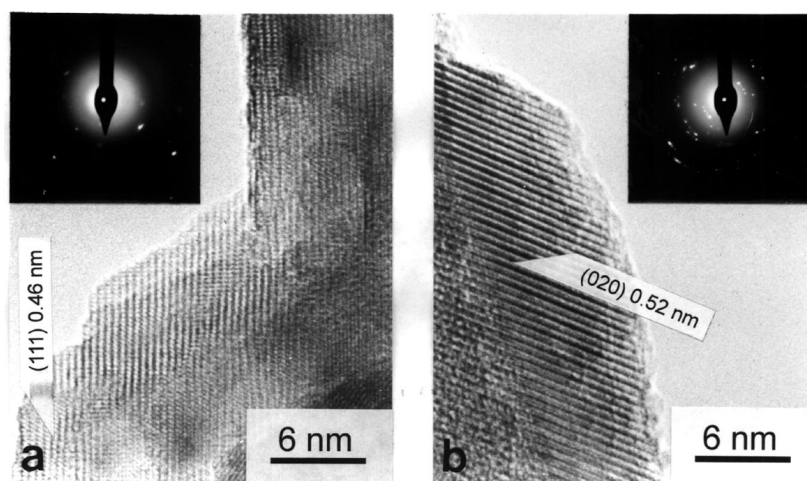


FIG. 4. HREM showing two different areas of $\text{Co}(\text{Ac})\text{SiO}_2\text{-26}$ calcined in argon, 18 h, 973 K; (a) Co_3O_4 or cubic Co_2SiO_4 ; (b) orthorhombic Co_2SiO_4 .

that under normal experimental conditions at the temperatures applied the orthorhombic Co_2SiO_4 is the more stable phase.

It is known (10) that the formation of cobalt orthosilicate proceeds by direct solid–solid reaction between CoO and SiO_2 according to the scheme $2\text{CoO} + \text{SiO}_2 \Rightarrow \text{Co}_2\text{SiO}_4$. One can suppose that the thermal decomposition of Co_3O_4 to CoO before the cobalt orthosilicate formation is necessary for this reaction to take place. Also, during the precursor calcination in slightly reducing or inert atmosphere the decomposition of the cobalt salts may proceed only to CoO and, as a consequence, facilitate occurrence of this reaction. Such conditions can exist during calcination of cobalt acetate precursor in flowing argon. Different temperatures of Co_3O_4 decomposition are reported, but 1183 K seems to be commonly accepted (10). From our results one can note the great influence of the calcination atmosphere on formation of orthorhombic cobalt orthosilicate. The decomposition of Co_3O_4 in flowing argon probably proceeds at 1073 K with simultaneous reaction of formed CoO with the support, whereas in oxygen such decomposition takes place at 1193 K. Higher temperatures of Co_3O_4 decomposition in oxygen atmosphere can be explained by assuming that the equilibrium reaction for the decomposition is shifted in oxygen toward Co_3O_4 formation.

In Fig. 5 two diffraction patterns of $\text{Co}(\text{Ac})/\text{SiO}_2$ -26, previously calcined at 1093 K for 16 h in an argon stream and reduced with hydrogen, are shown. From the intensity of Co peaks (fcc phase only) (21) one can observe the increasing reduction degree of cobalt with the reduction temperature and growth of the cobalt particles formed. Interestingly, the cobalt silicate, or at least some cobalt silicate species, formed at 1093 K is partially reduced even at 873 K. This also was confirmed by TEM observations.

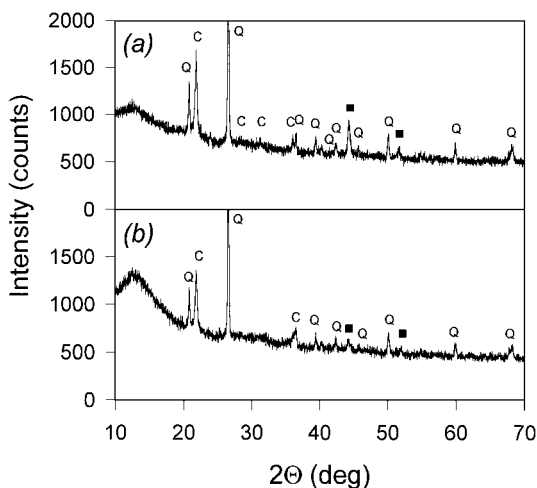


FIG. 5. XRD pattern of precalcined (Ar, 18 h, 1093 K) $\text{Co}(\text{Ac})/\text{SiO}_2$ -26, reduced in hydrogen. (a) 16 h, 1173 K; (b) 16 h, 873 K. (■) fcc-Co, (Q) α -quartz, (C) crystalbite.

Due to exposure on air during the specimen handling and XRD experiment, some parts of smaller Co particles could be oxidized (22) and escape XRD detection due to small crystalite size or small population. In the case of samples reduced at 1173 K (for 16 h) the mean diameter of cobalt particles was estimated to be 40 nm, i.e., more than twice as large as in the case of noncalcined precursors (23). Reduction degrees of the $\text{Co}(\text{N})\text{SiO}_2$ -390 and $\text{Co}(\text{Ac})\text{SiO}_2$ -26 samples estimated by our magnetization measurements have shown that in the reliability limits of the method, the cobalt species are completely reduced during the reduction at 1173 K, which confirms the results given in (1). Further investigations of catalytic activity as well as its adsorptive and chemisorptive properties are underway.

Summarizing, we can state the following:

(1) During the calcination of cobalt acetate- and cobalt nitrate-impregnated low-surface-area silica in argon or nitrogen at $T > 1083$ K the orthorhombic Co_2SiO_4 is formed, which is accompanied with partial recrystallization of the support to α -quartz or to crystalbite. Impregnated precursors of high-surface-area silica need a temperature slightly higher for the cobalt orthosilicate formation than low-surface-area precursors.

(2) The calcination of $\text{Co}(\text{Ac})\text{SiO}_2$ -26 precursors in argon atmosphere at 973 K also leads to a partial formation of orthorhombic Co_2SiO_4 . Simultaneously Co_3O_4 or cubic Co_2SiO_4 is formed.

(3) Calcination of cobalt/silica precursors in oxygen at 1213 K also leads to Co_2SiO_4 formation. At lower temperatures (773–1123 K), Co_3O_4 formation is observed.

(4) Reduction of Co_2SiO_4 formed during calcination at 1093 K begins at a lower temperature (873 K) although the degrees of the reduction are rather small, while at 1173 K total reduction of cobalt can be achieved.

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