CoSi particles on silica support as a highly active and selective catalyst for naphthalene hydrogenation†

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CoSi particles on a silica support, synthesized by metal organic chemical vapor deposition (MOCVD) of $Co(SiCl_3)(CO)_4$ as a precursor at atmospheric pressure and moderate temperature in a fluidized bed reactor, show high catalytic activity and selectivity in naphthalene hydrogenation.

Aromatics in fuels not only lower the quality and produce undesired exhaust emissions, but also have potentially hazardous and carcinogenic effects.[1] This has led to a strong interest in catalytic materials different from the classically supported metal sulfide and noble metal catalysts. Metal carbides and nitrides are initially highly active, but are easily poisoned by a small amount of sulfur.[2] Thermochemical calculations have indicated that metal silicides can tolerate much higher H_2S concentrations than the corresponding carbides and nitrides.[3] Therefore, we explored the possibility of using metal silicides as novel catalysts for the deep hydrogenation of aromatics.

Metal silicides are important in microelectronics as ohmic contacts and interconnections in CMOS transistors because of their good electrical conductivity, high chemical inertness and thermal stability.[4] However, to the best of our knowledge, few reports have been published on metal silicides as catalysts,[5–9] although they are the active phase in the hydrodehalogenation of silicon tetrachloride.[10] Recently, palladium silicide in Pd/SiO_2 was reported to exhibit a much higher selectivity than Pd/SiO_2 in the hydrogenation of phenylacetylene, but to have the same specific activity.[7] It was also reported that the amorphous $Pd_{81}Si_{29}$ alloy prepared by melt spinning was suitable for the semihydrogenation of propargylic alcohol and exhibited a TOF more than 50 times higher than Pd/SiO_2.[9] Unfortunately, preparation methods for silicides inherited from the microelectronic industry result in low surface area. The controlled synthesis of well-dispersed metal silicides still remains an important challenge for catalytic applications. MOCVD has been shown to be a powerful method for generating highly dispersed catalysts in a controlled and reproducible manner.[11] Here, we firstly report metal organic chemical vapor deposition (MOCVD) of $Co(SiCl_3)(CO)_4$ as a single source precursor to highly dispersed CoSi nanoparticles on a silica support at atmospheric pressure and moderate temperature in a fluidized bed reactor. The resulting material exhibits excellent activity in hydrogenation of naphthalene and may find additional applications in petroleum processes and in the synthesis of fine chemicals.

The organometallic precursor $Co(SiCl_3)(CO)_4$ was synthesized from $Co_2(CO)_8$ and $SiHCl_3$ following a modified procedure from the literature,[12] as confirmed by IR and NMR (ESI† Fig. S1–S2). The final yellow crystalline product was obtained with a yield of about 60%. $Co(SiCl_3)(CO)_4$ was chosen as the precursor because it combines the precise stoichiometry of Si and Co with high vapor pressure and stability in moist air at low temperature. The CoSi deposition onto the silica support (668 m^2/g) was achieved by a two-step chemical vapor deposition of $Co(SiCl_3)(CO)_4$ in a fluidized-bed reactor. Prior to CoSi deposition, the silica was calcined in air at 500 °C to remove adsorbed water, which promotes hydrolysis of the precursor. The precursor was sublimed and adsorbed at 65 °C in argon as carrier gas. The adsorbed precursor was treated at 300 °C in H_2 at atmospheric pressure. Argon treatment resulted in the formation of blue $CoCl_2/SiO_2$ (further confirmed by the fact that the sample turned brownish red with water), while the H_2 treatment led to a stable black sample.

Surface area, porosity and average pore size of $CoSi/SiO_2$ with 7.0, 13.5 and 17.1 wt% CoSi loading, as determined by N_2 physisorption, showed a decreasing trend with increasing CoSi loading, indicating that CoSi fills and blocks a fraction of the silica pores (ESI† Table S1). However, the X-ray diffraction patterns only revealed a broad SiO_2 diffraction peak at about 23.4° and did not show any diffraction peaks of CoSi or metallic Co, indicating that the CoSi particles were too small to be detected by XRD (Fig. 1). The same phenomenon was observed in supported metal nitrides and carbides with similar loading.[13]

The crystalline nature and particle size of the $CoSi/SiO_2$ samples were confirmed by transmission electron microscopy (TEM) measurements. The TEM image in Fig. 2(a) shows that uniform nanostructured CoSi particles with a size of about 1–2 nm are evenly dispersed on the silica, which is in good agreement with the XRD results. And the size of the CoSi particle increases with increased loading as shown in Fig. S3 in the ESI.† The high-resolution TEM image in Fig. 2(b) further confirms the formation of a CoSi phase of about 2 nm size. The observed lattice spacing of 0.314 nm matches well with the reported value of the 110 plane in the CoSi structure (JCPDS PDF65-3296). The EDX spectrum from the HRTEM further

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† Electronic supplementary information (ESI) available: IR and NMR of organometallic precursor $Co(SiCl_3)(CO)_4$, TEM images and EDX spectra of $CoSi/SiO_2$ with 7.0, 13.5 and 17.1 wt% CoSi loading, and surface area, porosity and average pore size of $CoSi/SiO_2$ with 7.0, 13.5 and 17.1 wt% CoSi loading. See DOI: 10.1039/b820519a

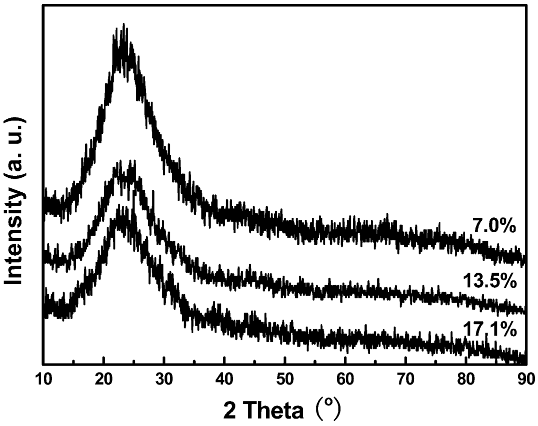

Fig. 1 X-Ray diffraction patterns of CoSi/SiO_2 with 7.0, 13.5 and 17.1 wt% CoSi loading from MOCVD.

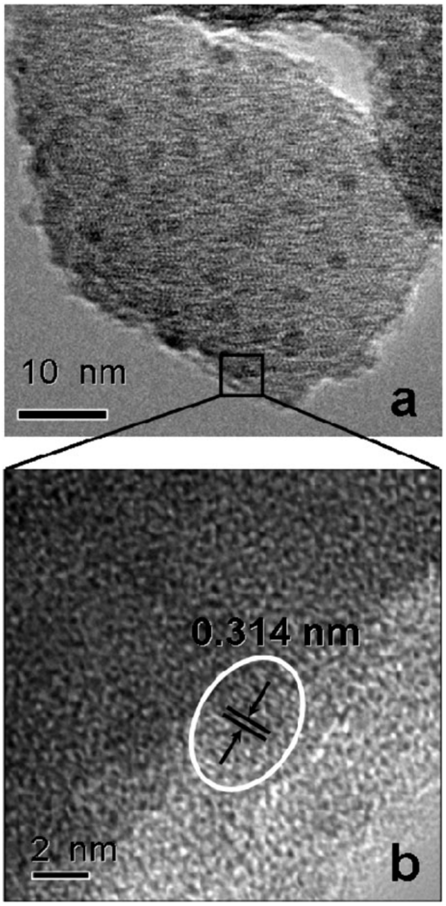

Fig. 2 TEM (a) and HRTEM (b) images of CoSi/SiO_2 with 17.1 wt% CoSi loading from MOCVD.

confirms the formation of CoSi composed of Si and Co elements.

Temperature programmed reduction and desorption (TPR and TPD) are powerful tools for characterising supported catalysts. For comparison, Co_3O_4/SiO_2 and Co/SiO_2 samples with the same metallic cobalt loading were also prepared by impregnation. Fig. 3(a) shows H_2-TPR profiles of different loading of CoSi/SiO_2 and Co_3O_4/SiO_2 samples. For the Co_3O_4/SiO_2 sample, two peaks were observed around 348 and 646 °C, which have been attributed to the reduction of Co_3O_4 to CoO and of CoO to metallic cobalt.[14] For the CoSi/SiO_2 samples, a high temperature peak at 852 °C is attributed to the liberation of Si due to CoSi decomposition in hydrogen. The peak shifts to the lower temperature with increased CoSi loading, probably due to the interactions between CoSi and SiO_2 becoming weak. For the passivated CoSi/SiO_2 sample, one low temperature peak was observed at 303 °C, which can be tentatively assigned to the reaction of oxygen species adsorbed on CoSi with H_2. The results are similar to those of the TPR of nitrides.[15] Clearly, the CoSi/SiO_2 sample presents a reduction behavior that is completely different from that of Co_3O_4/SiO_2. Fig. 3(b) shows the H_2-TPD profiles of the different loading of CoSi/SiO_2 and Co/SiO_2 samples. The profile of 13.5% CoSi/SiO_2 exhibited two desorption peaks at 92 and 647 °C. The peak at low temperature could be due to the desorption of weakly chemisorbed H_2 due to the different H–Co surface sites on silica.[16] While the one observed at high temperature could arise from strongly chemisorbed H_2, which could be related to the presence of the active hydrogenation sites in the surface of CoSi. Obviously, the profiles for 7.0% and 17.1% CoSi/SiO_2 are very similar to 13.5% CoSi/SiO_2 except for peak intensity, which is related to the particle size of CoSi and the interaction between CoSi and SiO_2. However, the profile of Co/SiO_2 exhibited only one weak desorption peak at 92 °C, due to desorption of H_2. The results further confirmed the formation

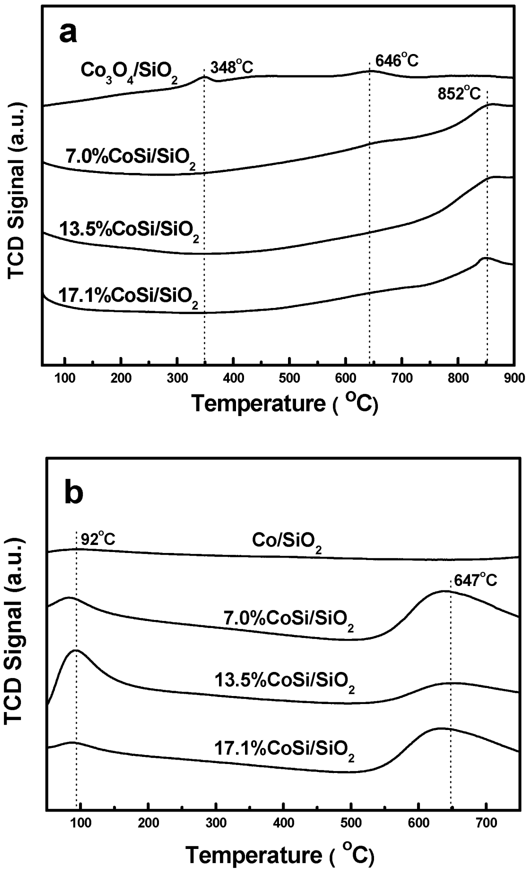

Fig. 3 H_2-TPR profiles (a) of CoSi/SiO_2 and Co_3O_4/SiO_2, and H_2-TPD profiles (b) of CoSi/SiO_2 and Co/SiO_2.

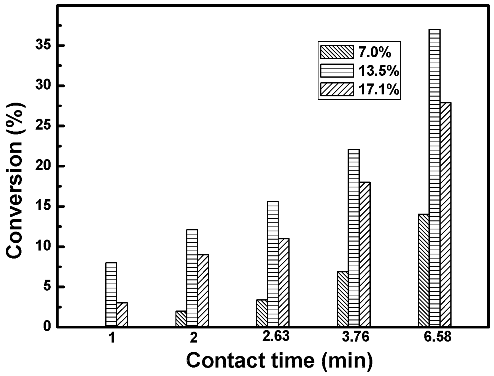

Fig. 4 Conversion of naphthalene using different loading CoSi catalysts.

of highly dispersed CoSi on silica, which is totally different from the Co/SiO_2 sample.

The hydrogenation activities of CoSi/SiO_2 and Co/SiO_2 catalysts were tested in the hydrogenation of naphthalene at 340 °C and 4.0 MPa. The passivated catalysts (0.2 g, diluted with 2.0 g SiC) were activated *in situ* with H_2 at 400 °C and 0.1 MPa for 4 h. The reaction was carried out in a continuous fixed-bed reactor. The liquid reactant was composed of 1 mol% undecane (as internal standard for GC analysis), 5 mol% naphthalene reactant, and varying amounts of decane (as solvent). The reaction product was analyzed by off-line gas chromatography with an OV-101 capillary column and a flame ionization detector. Product identification was performed with an Agilent 6890 gas chromatograph equipped with a HP-5MS capillary column and an Agilent 5973 mass selective detector.

The hydrogenation of naphthalene over CoSi/SiO_2 occurred in two steps: the conversion to tetralin, followed by the formation of decalin. The conversion of naphthalene increased with an increase in contact time from 0 to 6.6 min (Fig. 4). Among the three catalysts, the 13.5% CoSi/SiO_2 showed the highest conversion, which shows good consistency with the H_2-TPD results. The results can be explained by the size effect of the CoSi particle and the interactions between CoSi and SiO_2. The selectivities of the products showed that naphthalene hydrogenation to tetralin is the main reaction (100% selectivity to tetralin) and further hydrogenation of tetralin did not take place at a low contact time (3.76 min), indicating that the hydrogenation of tetralin is a rate-controlled step over the CoSi/SiO_2. However, no product was detected over the Co/SiO_2 catalyst under the same reaction conditions. This shows that the CoSi/SiO_2 catalyst is much more active than the Co/SiO_2 catalyst. The results show that CoSi/SiO_2 is a promising catalyst for semihydrogenation, which can be very important in the synthesis of fine chemicals.

In conclusion, highly dispersed CoSi particles on a silica support have been synthesized by MOCVD of $Co(SiCl_3)(CO)_4$ as a precursor at atmospheric pressure and moderate temperature in a fluidized bed reactor. The results show that the resulting CoSi particles with a size of about 2 nm were highly dispersed on the silica support and have H_2 reduction and desorption properties completely different from those of Co_3O_4/SiO_2 or Co/SiO_2. The CoSi/SiO_2 sample showed a catalytic activity and selectivity to tetralin superior to those of a Co/SiO_2 catalyst in the hydrogenation of naphthalene. The results indicate that metal silicides are novel promising catalysts in the hydrogenation of aromatics and may find application in petroleum processes and in the synthesis of fine chemicals.

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