Temperature programmed studies of Co on MCM-41 and SiO$_2$

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Abstract

High surface area MCM-41 with mesoporous structure and conventional SiO$_2$, containing micropores were used as support materials for Co$_2$(CO)$_8$ in a gas phase preparation of supported cobalt samples. Two different kinds of preparation methods were used: direct deposition, with continuous adsorption of cobalt carbonyl on to the support over an extended period of time; and a pulsing method with successive deposition/decarbonylation cycles. Since the reduced metal is usually the active phase in catalytic reactions, the aim of the preparation of heterogeneous catalysts is to produce samples in which the supported metal is easily reducible. The effects of the support materials, the gas phase deposition methods and decarbonylation atmospheres on the reactivity of the Co/SiO$_2$ and Co/MCM-41 samples toward oxygen and hydrogen treatments were compared. According to the results, reducibility of the samples decreased in the order: MCM-41 + pulsing method > SiO$_2$ + pulsing method > SiO$_2$ + direct method > MCM-41 + direct method. Oxygen/hydrogen consumptions of the samples decreased in the decarbonylation atmosphere inert > oxidising > reducing. Co/SiO$_2$ and Co/MCM-41 samples prepared via pulsing method indicated a good stability during oxidation/reduction treatments. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Cobalt; Silica; MCM-41; Temperature programmed treatments

1. Introduction

To increase its catalytic activity, cobalt has been supported on high surface area carriers to obtain a high metal dispersion. In hydrogenation reactions, for example in the Fischer–Tropsch synthesis, the active phase is metallic cobalt. Well-dispersed and reduced cobalt provides a high metal surface area available for the reaction. The catalyst precursor [1–4], the support [2,5–7], the preparation method [2–4,7–10] and the metal loading [4,7] have an influence on the reduction behaviour of cobalt catalysts.

Temperature programmed reduction (TPR) studies have been used extensively to characterise nitrate [1–3,5,6,10–15], acetate [1,2], acetylacetonate [3], chloride [1,2], sulphide [2] and carbonyl [16–19] based Co/SiO$_2$ catalysts. Sewell and coworkers [2,5,14] have used a combined TPR/TPO (temperature programmed oxidation) technique to determine the extent of cobalt reduction and to estimate the extent of cobalt-support species' formation. In general, oxidic and silicate species are formed during calcination and activation of the cobalt catalysts [1,3,6,8,11,14,20]. Reduction of the surface cobalt phases is difficult. However, Coulter and Sault [8] have reported that a certain amount of cobalt silicates is necessary for obtaining a highly dispersed cobalt catalyst.

In carbonyl based precursors, the metal is initially at a zero valence state. However, during thermal decomposition, the supported metal complex can be oxidised by a reaction with surface hydroxyl groups of the support and thus a zero-valence metal is not formed

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[21]. The release of CO and the formation of water, methane and CO_2 have been detected during the TPR treatment of cobalt carbonyl compounds supported on SiO_2 [16,18,19]. Niemelä et al. [16] have reported a better dispersion of the metallic species and a stronger adsorption of CO for $Co_2(CO)_8$ than for $Co_4(CO)_{12}$ based Co/SiO_2 catalysts prepared by impregnation.

In our previous studies, $Co_2(CO)_8$ has been deposited on SiO_2 and MCM-41 supports by vapour phase adsorption in order to avoid the effect of solvent [19,22]. Two different kinds of deposition methods were used; a direct method, in which the cobalt carbonyl precursor was deposited on to the support over an extended period of time, and a pulsing method comprising successive deposition and decarbonylation cycles. Mesoporous, high surface area MCM-41 material has shown a considerably greater ability to adsorb $Co_2(CO)_8$ molecules from gas phase compared to the conventional SiO_2 material containing micropores [22]. Furthermore, high cobalt dispersions have been previously obtained with the gas phase preparation methods [3,7].

Since the reactivity of the Co/SiO_2 catalysts is most often based on the reduced cobalt phases, e.g. the Fischer–Tropsch reaction, the reducibility of the supported cobalt species is among the most important factors in catalyst preparation. The aim of this study was to characterise the reactivity and stability of $Co_2(CO)_8$ based Co/SiO_2 and Co/MCM-41 samples toward oxygen and hydrogen treatments. Also, the effects of the SiO_2 and the MCM-41 supports, the direct and the pulsing methods and the decarbonylation atmosphere on the reducibility of the samples were given special consideration. Decarbonylation was carried out under inert (temperature programmed desorption, TPD), reducing (TPR) and oxidizing (TPO) atmospheres.

2. Experimental

2.1. Reagents

Dicobalt octacarbonyl ($Co_2(CO)_8$) was supplied by Fluka Chemie AG and used without further purification. The silica was GRACE SILICA S 432 ($S_{BET} = 320\,m^2/g$, pH $= 7$ and particle size 250–500 μm, manufacturer's values) supplied by Grace Davison. The mesoporous high surface area MCM-41 mate-

rial ($S_{BET} = 1041\,m^2/g$) was synthesised according to the procedure of Beck et al. [23] The detailed description of preparation and characterisation of the MCM-41 material is reported in our previous publication [22]. MCM-41 was preheated at 300°C and SiO_2 at 500°C under vacuum for 10 h in order to remove physisorbed water and to control the number of OH species on the surface. After the vacuum treatment, the supports were stored in a glovebox under nitrogen atmospheres.

Nitrogen (99.999%), CO (99.997%), hydrogen (99.999%) argon (99.9999%), helium (99.9999%) oxygen (99.999%) and 10% H_2/Ar were used as carrier gases during sample preparation and in the temperature programmed experiments. CO was supplied by Fluka and the other gases by AGA.

2.2. Preparation of the samples

Deposition of the $Co_2(CO)_8$ on SiO_2 and MCM-41 supports was carried out in a fluidised bed reactor, which was designed for controlled experiments at low temperatures [19,24]. All handling of the pretreated support materials and carbonyl precursor was done without exposure to air or moisture. CO flowed through the sublimation chamber (45°C), transporting the vaporised carbonyl compound into the fluidised bed reactor (50°C), where $Co_2(CO)_8$ was adsorbed on the support surface. In the direct method, the maximum deposition time was 25 h for Co(CO)/MCM and 20 h for Co(CO)/SiO_2 samples. In the pulsing method, successive deposition and decarbonylation cycles was used to increase the cobalt content on the support. Deposition of cobalt carbonyl on the supports was done under the same preparation conditions as in the direct deposition method followed by the decarbonylation treatment at 150°C in a stream of N_2 for 5 h. The Co/SiO_2 and Co/MCM samples used in this study are presented in Table 1.

2.3. Characterisation of samples

TPD, TPR, TPO and oxygen pulse chemisorption measurements were carried out in an ASAP 2910 analyser equipped with a thermal conductivity detector (TCD). The outlet of the TPD analyser was connected to a HP 5971 quadrupole mass spectrometer and to a Galaxy 6020 Fourier Transform infrared spectrometer

Table 1
Co/SiO$_2$ and Co/MCM samples used in this study

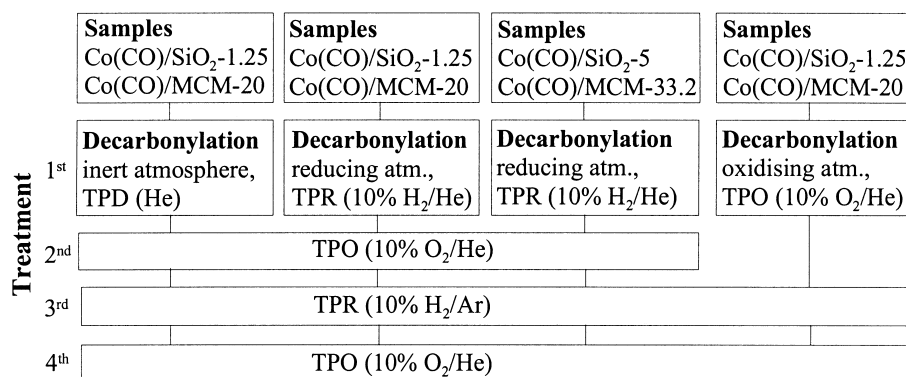| Abbreviation	Deposition method	Decarbonylation treatment[a]	Cobalt wt.%
Co(CO)/SiO$_2$-1.25	Direct	No	1.25
Co(CO)/SiO$_2$-1.75	Direct	No	1.75
Co/SiO$_2$-5	Pulsing	Yes	5
Co(CO)/MCM-17.3	Direct	No	17.3
Co(CO)/MCM-18	Direct	No	18
Co(CO)/MCM-20	Direct	No	20
Co/MCM-33.2	Pulsing	Yes	33.2

[a] Decarbonylation at 150°C under nitrogen flow.

with an MCT (mercury-cadmium-tellurium) detector. The spectral resolution for the gas phase IR spectra was $2 \, cm^{-1}$. This arrangement allowed the study of desorbed species and reaction products. Samples and temperature programmed treatments are presented in Schemes 1 and 2. A maximum reduction and oxidation temperature of 500°C was chosen in order to minimise sintering and because of the pretreatment of the SiO$_2$ at 500°C and the MCM-41 at 300°C (MCM-41 was calcined at 540°C in air) [22]. Formation of the non-reducible surface cobalt phases may also be possible at high temperatures.
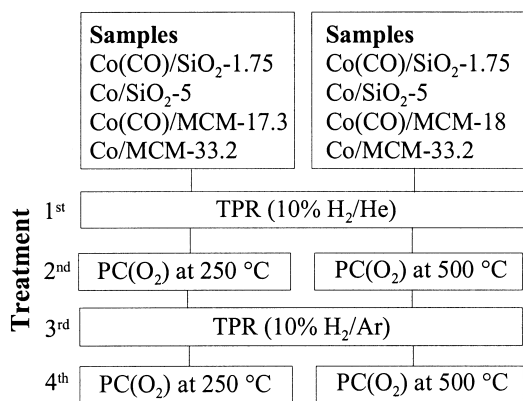
The samples presented in Scheme 1 were loaded inertly into the sample holder and flushed with helium at room temperature for 30 min. The first experiment for all the samples was decarbonylation under different gas atmospheres. TPD experiments were performed under helium flow, TPR experiments under 10% hydrogen/helium flow and TPO experiments under 10% oxygen/helium flow. In all studies, a $40 \, ml \, min^{-1}$ flow

rate, $10°C \, min^{-1}$ heating rate and temperature ramp from 25 to 500°C was applied. After decarbonylation, samples were cooled under helium flow. The second experiment was TPO under 10% oxygen/helium flow with a $40 \, ml \, min^{-1}$ flow rate, $10°C \, min^{-1}$ heating rate and temperature ramp from 30 to 500°C. The temperature was kept at 500°C for 10 min and then the samples were cooled under Ar flow. The third experiment was the TPR treatment which was carried out under 10% hydrogen/argon gas mixture, where $10 \, ml \, min^{-1}$ flow rate, $10°C \, min^{-1}$ heating rate and temperature ramp from 30 to 500°C were applied. Additionally, the samples were kept at 500°C for 10 min and cooled under helium flow. The fourth experiment was TPO with the same parameters as in the previous TPO treatment.

Samples in TPR and oxygen pulse chemisorption PC(O$_2$) studies are presented in Scheme 2. A 10% hydrogen/helium flow and a 10% hydrogen/argon flow were used in the first and second reduction treatments, respectively. The above mentioned flow and heating

Scheme 1.

Samples	Samples
Co(CO)/SiO$_2$-1.75	Co(CO)/SiO$_2$-1.75
Co/SiO$_2$-5	Co/SiO$_2$-5
Co(CO)/MCM-17.3	Co(CO)/MCM-18
Co/MCM-33.2	Co/MCM-33.2

Treatment

1st	TPR (10% H$_2$/He)	
2nd	PC(O$_2$) at 250 °C	PC(O$_2$) at 500 °C
3rd	TPR (10% H$_2$/Ar)	
4th	PC(O$_2$) at 250 °C	PC(O$_2$) at 500 °C

Scheme 2.

rates as well as temperature ramps were used in TPR also. In the oxygen pulse chemisorption studies, oxygen was pulsed under helium flow at 250 and 500°C. The amount of hydrogen and oxygen taken up were determined by reference to a calibration of known volume of the gases.

Cobalt content was determined by an ACAX 300 energy dispersive X-ray fluorescence (EDXRF) spectrometer equipped with a solid-state Si(Li) detector [19]. The resolution of the EDXRF device was 0.15 keV, and Cd (109) radioisotope was used as the source of radiation.

3. Results and discussion

3.1. Decarbonylation treatments

Decarbonylation of the samples (Scheme 1, 1st treatment) was studied under different gas atmospheres using temperature programmed treatments. Partial decomposition of carbonyl compound was detected under helium flow at 25°C: a small amount of CO and CO$_2$ molecules desorbed, when the carrier gas (CO) used during deposition was replaced by He. The sample also changed colour. Additionally, from the freshly made samples, but not from aged brown-coloured samples, small amounts of CO and CO$_2$ molecules were desorbed at 50–60°C during TPD, TPR and TPO studies. Co$_4$(CO)$_{12}$ is reported to form readily through the thermal decomposition of Co$_2$(CO)$_8$ at about 50°C under inert atmosphere. These findings and previously reported studies

[16,19,25] support the conclusion that the conversion of Co$_2$(CO)$_8$ to Co$_4$(CO)$_{12}$ occurs completely before total decarbonylation. Similar results were obtained for Co(CO)/SiO$_2$-1.25.

Maximum desorption of CO during decarbonylation under inert and reducing atmospheres occurred at 120°C for the CO(CO)/SiO$_2$-1.25 sample (not shown) and at 140°C for the Co(CO)/MCM-20 sample (Fig. 1a). The higher desorption temperature for the MCM-41 supported sample was probably due to the mesoporous structure of this carrier and the higher metal loading. Small amounts of CO$_2$ were detected at about 200°C. TPD and TPR profiles of the samples were closely similar. One difference was the larger proportion of CO$_2$ and the formation of methane (150–250°C) during decarbonylation under reducing atmosphere. Methane was probably formed through the hydrogenation of still intact carbonyl groups or the carbonaceous residues left on the support surface.

In TPO studies, large amounts of CO and CO$_2$ were released soon after the sample contacted with oxygen. During the temperature ramp, only very small amounts of CO were desorbed at about 50°C, and maximum release of CO$_2$ occurred at 200°C. TPR studies of pulsed Co/MCM-33.2 and Co/SiO$_2$-5 samples indicated the formation of small amounts of CO$_2$ at about 120–200°C. Release of water was not detected owing to the cold trap installed before the analysing equipment.

3.2. Treatments of decarbonylate samples

3.2.1. Oxidation treatments

Oxidation of Co(CO)/SiO$_2$-1.25 and Co(CO)/MCM-20 samples decarbonylated under inert and reducing atmospheres (Fig. 2a, b, e and f), began below 100°C and, in the case of the Co(CO)/MCM-20 sample (Fig. 2e and f) continued up to 300°C. No meaningful differences between the shapes of the curves were detected. Oxidation of the Co/SiO$_2$-5 and Co/MCM-33.2 samples (Fig. 2d and h), prepared via pulsing method, occurred at higher temperatures than oxidation of the samples prepared via direct method. Furthermore, the TPO profile of Co/MCM-33.2 sample (Fig. 2h) indicate the sequential oxidation of metallic cobalt, first to CoO and then to Co$_3$O$_4$, described by Sewell et al. [5].
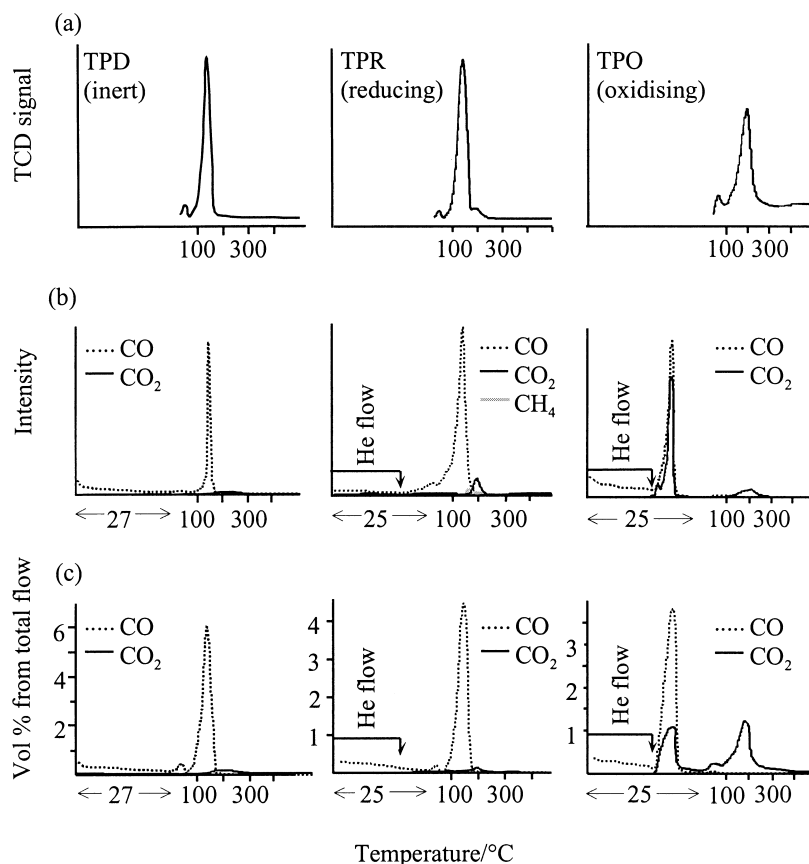
Fig. 1. Decarbonylation of the Co/MCM-20 samples under inert, reducing and oxidising atmospheres. (a) TPD, TPR and TPO profiles and analysis of desorbed species according to (b) mass spectrometric and (c) IR spectroscopic measurements.

As well as in the case of the first TPO curves, the second TPO curves have several similarities between the samples decarbonylated under inert and reducing atmospheres (Fig. 2a, b, d–f and h). Comparison of these profiles to the first TPO profile reveals that the oxidation temperature maxima are higher in all cases except for the pulsed Co/MCM-33.2 (Fig. 2h).

3.2.2. Reduction treatment

After oxidation, the samples were treated with temperature programmed reduction (TPR). The TPR profiles of the pulsed samples (Fig. 2d and h) correspond to the two-stage reduction of Co_3O_4 via CoO to metallic cobalt [6,13,14]. Although the corresponding peaks are seen in the TPR curves of $Co(CO)/SiO_2$-1.25 and Co(CO)/MCM-20 decarbonylated under inert and reducing atmospheres (Fig. 2a, b, e and f), the ratio of

the peak areas is not the same as in the TPR curves of the pulsed samples (Fig. 2d and h). In the directly prepared samples, the first reduction peak at about 250–280°C is the strongest. The difference in ratios of the peak areas may be an indication of incomplete reduction of cobalt oxide species and/or the existence of non-reducible cobalt support species. Furthermore, the peak areas of the second reduction peaks are smaller for samples decarbonylated under reducing (Fig. 2b and f) than under inert atmospheres (Fig. 2a and e).

Two distinct reduction peaks have been observed in the TPR profile of unsupported bulk Co_3O_4 [13]. Co_3O_4 reduces via CoO to metallic cobalt under 500°C [6,14]. Reduction profiles of supported cobalt oxides are not so clear due to the differences caused by the metal dispersion, the particle size and the interaction between the support and metal oxide species
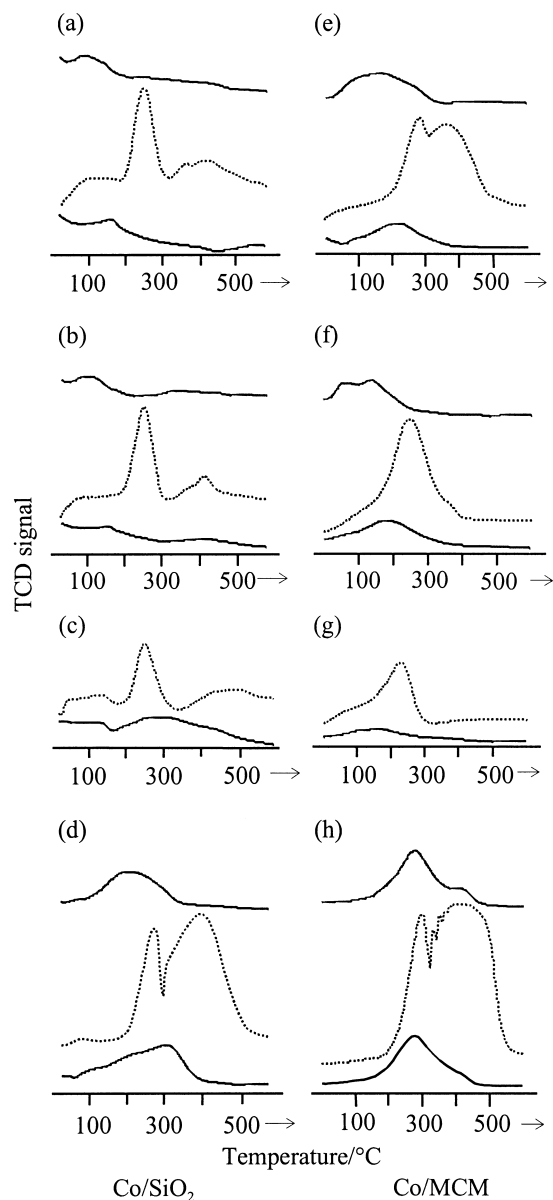
Fig. 2. TPO-TPR-TPO studies of Co/SiO$_2$-1.25 and Co/MCM-20.0 samples after decarbonylation under (a) and (e) inert, (b) and (f) reducing and (c) and (g) oxidising atmospheres and TPO-TPR-TPO studies of pulsed Co/SiO$_2$-5.0 and Co/MCM-33.2 samples after decarbonylation under (d) and (h) reducing atmosphere; (—) TPO and (···) TPR treatment.

[11]. The existence of several peaks in the TPR profile is an indication of differently reducible cobalt species on the support surface. Reduction of cobalt species at temperatures higher than 500°C indicate

the stronger interaction of cobalt with the surface. In contrast, reducibility at lower temperatures than those of bulk cobalt oxide is due to the particle size of the cobalt oxide and to the electronic interaction between the cobalt and the support [5].

3.2.3. Oxygen and hydrogen uptakes

The differences in samples prepared by direct and pulsing methods and in samples decarbonylated under different gas atmospheres are clearly seen in the oxygen and hydrogen uptakes of Co/MCM samples (Fig. 3). The consumption of gas per cobalt atom was greater for the directly prepared samples decarbonylated under inert atmosphere than for those decarbonylated under reducing atmosphere. This indicates a better oxidation/reduction ability for the samples decarbonylated under inert atmosphere. Redox properties also were better for samples decarbonylated under oxidising atmosphere. From these findings, cobalt was concluded to react with the MCM-41 support more strongly during decarbonylation under hydrogen than under inert or oxidising atmospheres. The oxygen consumption of the Co/MCM sample decarbonylated under reducing atmosphere was the same in the first and second TPO treatments, which indicated a stable situation on the surface of the sample.

The oxygen/hydrogen uptake per cobalt was about five times as great for the pulsed Co/MCM-33.2 sample as for the samples prepared via direct method. The fact that the cobalt atoms in the pulsed sample were
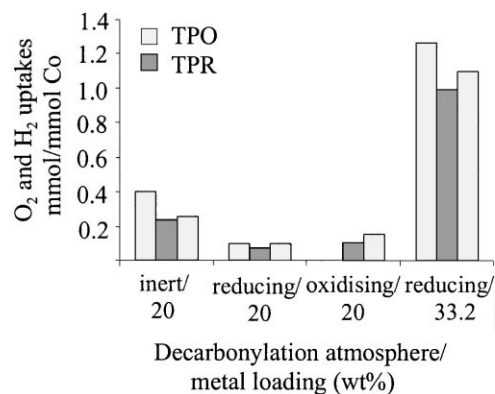

Fig. 3. Oxygen and hydrogen consumptions of Co/MCM-20 and pulsed Co/MCM-33.2 samples in TPO-TPR-TPO experiments after decarbonylation under inert, reducing and oxidising treatments.
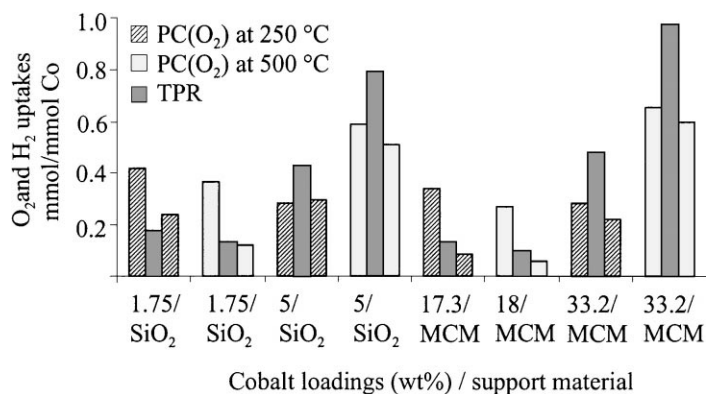
Fig. 4. Oxygen and hydrogen consumptions of Co/SiO$_2$ and Co/MCM samples with different metal loadings in PC(O$_2$)-TPR-PC(O$_2$) experiments.

more easily oxidised and reduced may be an indication of the different strengths of interaction of the cobalt species with the silica surface in samples prepared via direct and pulsing deposition methods.

3.3. Oxygen pulse chemisorption/reduction treatments

Reducing/oxygen pulse chemisorption treatments (TPR-PC(O$_2$)-TPR-PC(O$_2$)) (Scheme 2) were carried out to examine the effect of oxidation temperature on the redox behaviour of the SiO$_2$ and MCM-41 supported cobalt samples. The effect of the support material and gas phase preparation methods on the reducibility of the supported cobalt species was compared. Samples were decarbonylated in the first TPR treatment and two different oxidation temperatures, 250 and 500°C, were used. Oxygen and hydrogen consumptions are presented in Fig. 4.

Oxygen consumption of samples Co/SiO$_2$-1.75 and Co/MCM-17.3 was higher at 250 than at 500°C, probably due to the stronger interaction of cobalt with the silica surface at higher temperatures. After reduction, oxygen uptake of the samples collapsed, probably due to the insufficient oxidation temperature since, according to the TPO profiles (Fig. 2b and f), samples prepared by direct method were oxidised at higher temperatures after reduction treatment. Another reason could be the too low reduction temperature and insufficient time to reduce all oxidised cobalt species

on the surface. Cobalt silicate species require hydrogen treatment of at least 700°C, for example [20].

For samples prepared via pulsing method, oxidation temperature of 250°C is far too low. PC(O$_2$) treatment at 500 rather than 250°C doubled the oxygen consumption per cobalt. Reduction properties of supported cobalt species were considerably better for pulsed samples than for samples prepared by direct deposition method, perhaps because of weaker interaction of cobalt species with silica surface sites. Another possible explanation is hydrogen spillover from the reduced cobalt phase to the difficult-to-reduce cobalt phase. Hydrogen spillover is a phenomenon that is thought to lead to increased reducibility of the sample [3,20]. Furthermore, oxygen uptakes in the first and second PC(O$_2$) treatments at 500°C were nearly the same, indicating the higher stability of cobalt species in pulsed samples than in samples prepared via direct deposition. After direct deposition, the reducibility of cobalt species was a little better on SiO$_2$ than on MCM-41 support, but in the case of pulsed samples the situation was the opposite.

4. Conclusions

In this study, we have compared the effects of SiO$_2$ and MCM-41 supports, as well as the effect of direct and pulsing gas phase deposition methods, on reactivity of the Co/MCM and Co/SiO$_2$ samples toward oxygen and hydrogen treatments. SiO$_2$ is a conventional silica material containing micropores and

MCM-41 is a high surface area material with unidimensional mesoporous stucture. Decarbonylation of the samples was done under inert, reducing and oxidising atmospheres. The aim of the study was also to find a way to produce silica supported cobalt samples which are easily reduced. In catalytic reactions, reduced cobalt is usually the catalytically active phase.

Comparison of the results reveals that samples in which $Co_2(CO)_8$ was deposited on MCM-41 support via a pulsing method are most easily oxidised and reduced. Reactivity of the samples toward oxygen/hydrogen uptake decreased in the order: MCM-41 + pulsing method > SiO_2 + pulsing method > SiO_2+direct method > MCM-41+ direct method. Reactivity of decarbonylated Co/MCM samples toward oxygen/hydrogen treatments decreased in the order of decarbonylation atmosphere: inert > oxidising > reducing. During temperature programmed treatments, pulsed Co/SiO_2 and Co/MCM-41 samples demonstrated good stability of the active cobalt phase.

Acknowledgements

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