The effect of steam treatment on MeO / Al_2O_3 model catalysts (Me = Ni, Co, Cu, Fe)

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To study the influence of steam on the solid state reaction between MeO (Me = Ni, Co, Cu or Fe) and Al_2O_3, MeO/α-Al_2O_3 and MeO/γ-Al_2O_3 model catalysts were kept in either N_2/20% O_2 or N_2/O_2/30% H_2O at 500–1000°C. The samples were subsequently analyzed with RBS and FTIR. Surprisingly, nickel, cobalt and copper volatilized when MeO/α-Al_2O_3 or $MeAl_2O_4$/α-Al_2O_3 samples were annealed in the presence of 0.3 atm steam at 1000°C. Especially copper was found to volatilize very rapidly in the presence of steam, even at a temperature as low as 800°C. FTIR spectra of steam-treated NiO/α-Al_2O_3 samples showed the incorporation of hydroxyl groups in the nickel oxide layer. This observation and an excellent agreement with thermochemical calculations support our conclusion that the volatile species are metal hydroxides. The solid state reaction of MeO with γ-Al_2O_3 was found to proceed at a much higher rate in the presence of 0.3 atm steam at 500–800°C, presnmably as a result of an enhanced surface mobility of Me and Al ions along the grain boundaries and the surfaces of the internal pores of the γ-Al_2O_3 support, when steam is present.

Keywords: volatilization; steam; transition metal hydroxides; NiO; Co_3O_4; CuO; Al_2O_3; Rutherford backscattering spectrometry (RBS); solid state reaction

1. Introduction

In many catalytic processes, and also in many catalyst preparation steps, the presence of steam is inevitable. Often steam is either a reactant or a reaction product. In the methane-steam reforming process, for example, relatively high steam partial pressures are applied, not only because steam is a reactant, but also to prevent excessive coking [1]. Since steam is produced during catalytic combustion, the catalyst must endure considerably high steam pressures at elevated temperatures (about 800°C, with spikes above 1000°C) [2]. Most catalysts are prepared from aqueous solutions, followed by drying and calcination. Because of the porosity of the catalyst support, the water is not removed completely during the drying procedure. Water is thus nearly always present during calcination. Furthermore, many catalysts are activated by reduction of oxidic precursors with hydrogen, producing additional water vapour.

Therefore, it is very important to establish the influence of steam on alumina-supported transition metal oxide catalysts. There are indications that steam could affect the reaction to aluminates substantially. Knijff [3] demonstrated that the reducibility of NiO/γ-Al_2O_3 catalysts depends strongly on the presence of water vapour before and during the reduction, which retards the reduction process and promotes the formation of nickel aluminate-like compounds, which ask for high reduction temperatures. Zielinski [4] reported similar results.

In order to investigate the influence of steam we annealed a number of MeO/Al_2O_3 samples (Me = Ni, Co, Cu, Fe) at 800–1000°C in a N_2/O_2 flow containing 30% steam. Both α-Al_2O_3 and γ-Al_2O_3 substrates were used. The samples were subsequently analyzed by Rutherford backscattering spectrometry (RBS) and Fourier transform infrared (FTIR) spectroscopy.

2. Experimental

2.1. Sample preparation

Polycrystalline α-Al_2O_3 substrates (obtained from Gimex, Geldermalsen, The Netherlands) were cleaned from adhering organic impurities by rinsing with acetone and a subsequent heat treatment in air at 1200°C for 48 h. Slices of γ-Al_2O_3 were prepared by pressing γ-Al_2O_3 powder (Al 4172, Engelhard, De Meern, The Netherlands) for 3 min at 590 MPa. The substrates were subsequently kept at 500°C for 3 h in a 100 ml/min 80% N_2/20% O_2 gas flow to remove most of the adsorbed water. Nickel, cobalt, iron and copper films (30–120 nm) were vacuum vapour-deposited onto these substrates from an α-Al_2O_3 crucible heated by a tungsten filament. The nickel, cobalt and iron films were oxidized to metal oxides at 750°C in a gas flow of 80% N_2/20% O_2. With

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the copper samples, the oxidation temperature was 500°C. The samples were subsequently annealed at temperatures ranging from 500 to 1000°C for various periods of time. Some samples were kept in a $N_2/O_2/30\%$ H_2O flow, while other samples were kept in 80% $N_2/$ 20% O_2.

The $N_2/O_2/30\%$ H_2O gas flow was produced by passing a 80% $N_2/20\%$ O_2 flow through a saturator containing distilled water. The samples that were treated in a steam-containing atmosphere were always heated up in dry N_2/O_2. When the final temperature was reached, the flow was switched to $N_2/O_2/30\%$ H_2O, and immediately before cooling down the flow was again switched to $N_2/$ O_2.

2.2. Analysis

RBS was performed with 2.87 MeV He^+ ions. The incident beam was parallel to the surface normal, and the detector was positioned at a scattering angle of 170°.

FTIR spectra were recorded in transmission mode on a Digilab FTS-40 spectrometer equipped with a liquid nitrogen-cooled HgCdTe detector. The resolution was 8 cm^{-1}. Before and during the measurements the sample holder compartment was purged with nitrogen. A reference spectrum, which was taken from a bare, cleaned alumina substrate, was subtracted from the measured spectrum. The spectra were analyzed by subtracting a third order polynomial background in the region of the absorption features and subsequent numerical integration of the remaining peak.

3. Results

3.1. RBS of α-Al_2O_3-supported model catalysts

In fig. 1 the RBS spectra of two NiO/α-Al_2O_3 samples kept at 1000°C for 168 h are compared. One sample was treated in dry N_2/O_2, while the second sample was exposed to a N_2/O_2 gas flow containing 30% steam. A remarkable collapse of the nickel peak was evident in the latter case, indicating that a considerable amount of nickel had disappeared. This surprising phenomenon obscured any possible effect of steam on the simultaneously proceeding solid state reaction between NiO and α-Al_2O_3. The most obvious explanation is that steam causes volatilization of nickel.

To check this hypothesis, an experiment was performed with a clean α-Al_2O_3 slice above a NiO/α-Al_2O_3 sample. The sample and the slice were separated from each other by two platinum wires (Ø 0.25 mm), as shown in fig. 2. After treatment at 1000°C for 70 h in $N_2/O_2/$ 30% H_2O, the bottom side of the top α-Al_2O_3 slice was analyzed with RBS (fig. 3). The experiment was repeated with a dry N_2/O_2 gas flow.

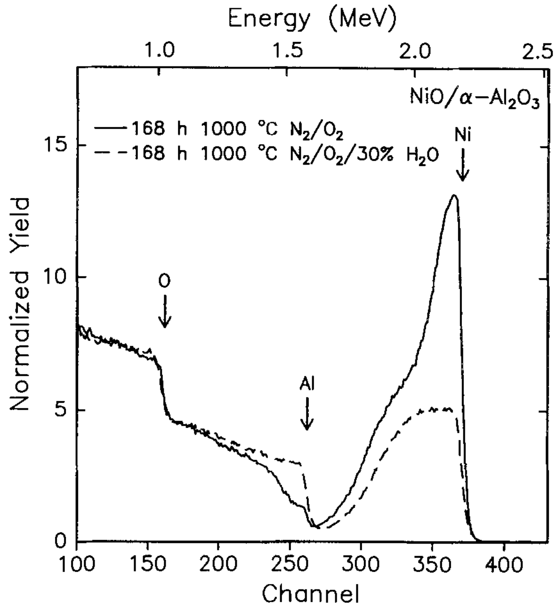

Fig. 1. RBS spectra of NiO/α-Al_2O_3 samples kept at 1000°C for 168 h in N_2/O_2 and $N_2/O_2/30\%$ H_2O gas mixtures. The thickness of the deposited Ni layers was about 120 nm.

Clearly, in the presence of steam some nickel was deposited onto the slice, whereas the slice remained unloaded when steam was absent. Because no relation was found between the amount of nickel detected and the distance to the nearest platinum wire, we exclude the possibility that some nickel had reached the upper slice by diffusion over the surface of the platinum wires. We thus conclude that some nickel species, formed under the influence of steam, disappeared from the NiO/α-Al_2O_3 sample into the vapour phase.

Similar results as shown in fig. 3 were obtained when the NiO/α-Al_2O_3 sample had been replaced by a sample where the NiO already had reacted completely to $NiAl_2O_4$, or by pressed tablets of NiO or $NiAl_2O_4$ powder. Both $NiAl_2O_4$ and NiO are hence susceptible to reaction to a volatile nickel species in the presence of steam at 1000°C. This process appeared to proceed somewhat slower in the case of $NiAl_2O_4$.

Cobalt oxide was also found to volatilize at 1000°C in the presence of 0.3 atm steam (fig. 4), but not as

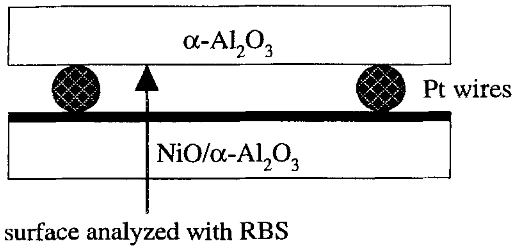

Fig. 2. Experimental arrangement during the annealing of α-Al_2O_3/Pt-wires/NiO/α-Al_2O_3 for 70 h at 1000°C in $N_2/O_2/30\%$ H_2O. The gas flow direction was parallel to the platinnm wires.

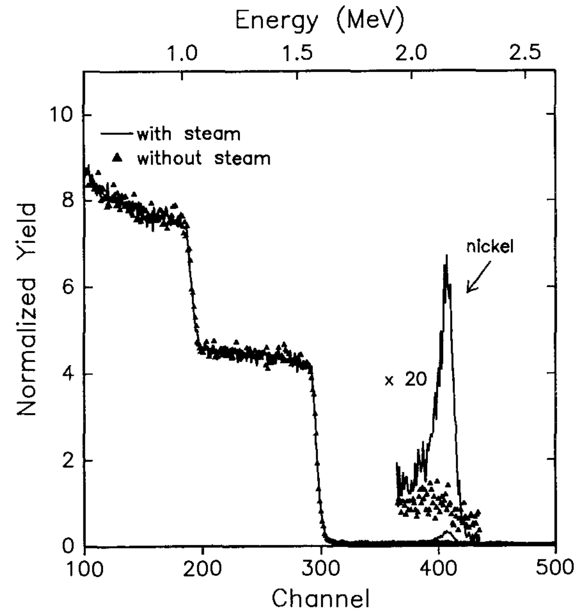

Fig. 3. RBS spectra of the bottom side of the upper α-Al_2O_3 slice (see fig. 2) after annealing at 1000°C for 70 h in N_2/O_2 and N_2/O_2/30% H_2O gas mixtures. (The yield in the Ni surface energy region is also shown after multiplication by 20.)

rapidly as nickel oxide. The RBS spectrum shows that the remaining cobalt oxide had completely reacted to $CoAl_2O_4$, which was also observed with the cobalt oxide layer on the sample treated in dry N_2/O_2. This is in agreement with the results reported previously [5,6], and with the characteristic intense blue colour of the thermally treated samples.

Disappearance of iron atoms from Fe_2O_3/α-Al_2O_3 samples that were kept at 1000°C for 70 h in N_2/O_2/30% H_2O could not be detected (fig. 5).

Copper oxide, on the other hand, volatilized very rapidly in the presence of steam at 1000°C (fig. 6). After 20 h virtually no copper was left on a sample onto which 30 nm copper had originally been deposited. The appearance of a reddish-brown deposit downstream at the cold end of the reactor confirmed that the copper species was indeed transported through the vapour phase due to the presence of steam.

The experiments described above were repeated at 800°C (except for the Fe_2O_3/α-Al_2O_3 samples). After 168 h annealing at this temperature no detectable loss of nickel or cobalt atoms from NiO/α-Al_2O_3 (fig. 7) and Co_3O_4/α-Al_2O_3 samples (not shown) was observed. Furthermore, in experiments as represented in fig. 2, no deposition of Ni or Co species onto the top alumina slice was detected after 168 h annealing at 800°C in N_2/O_2/30% H_2O.

Fig. 8 reveals that copper oxide, on the other hand, still volatilizes rapidly at 800°C in the presence of 0.3 atm steam. The RBS spectrum of the steam-treated sample shown in this figure is taken at the centre of the sample, which had remained brown. Near the edges, however, the sample had assumed a white colour, viz. that of polycrystalline alumina, which implies that the copper had disappeared from these sample areas. The distribution of the remaining copper atoms was confined to the centre of the sample. This was confirmed by recording RBS spectra from various spots of the same sample. Apparently, the volatilization of copper proceeded in a way similar to the process of a puddle drying up from a flat surface. The surface mobility of copper

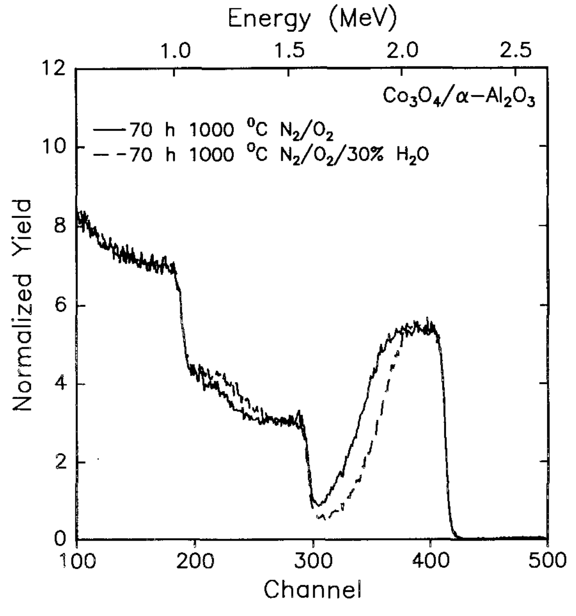

Fig. 4. RBS spectra of Co_3O_4/α-Al_2O_3 samples kept at 1000°C for 70 h in N_2/O_2 and N_2/O_2/30% H_2O gas mixtures. The thickness of the deposited Co layers was about 100 nm.

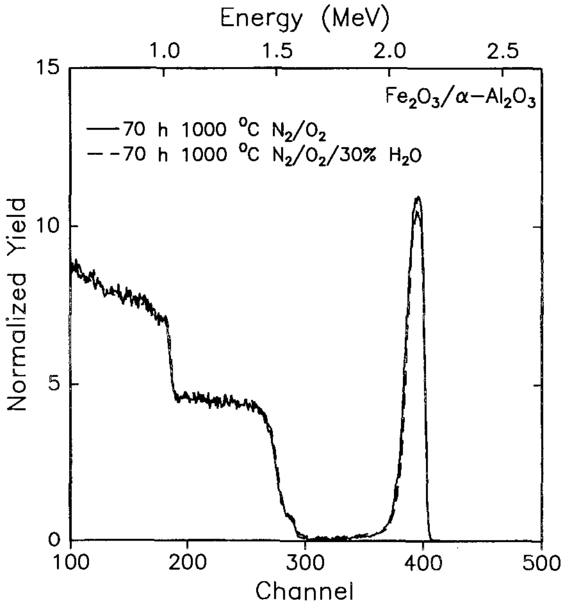

Fig. 5. RBS spectra of Fe_2O_3/α-Al_2O_3 samples kept at 1000°C for 70 h in N_2/O_2 and N_2/O_2/30% H_2O gas mixtures. The thickness of the deposited Fe layers was about 45 nm.

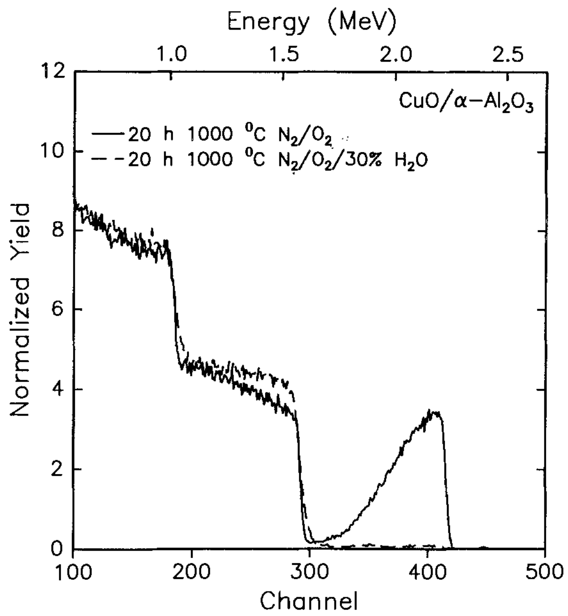

Fig. 6. RBS spectra of $CuO/\alpha\text{-}Al_2O_3$ samples kept at 1000°C for 20 h in N_2/O_2 and $N_2/O_2/30\%$ H_2O gas mixtures. The thickness of the deposited Cu layers was about 35 nm.

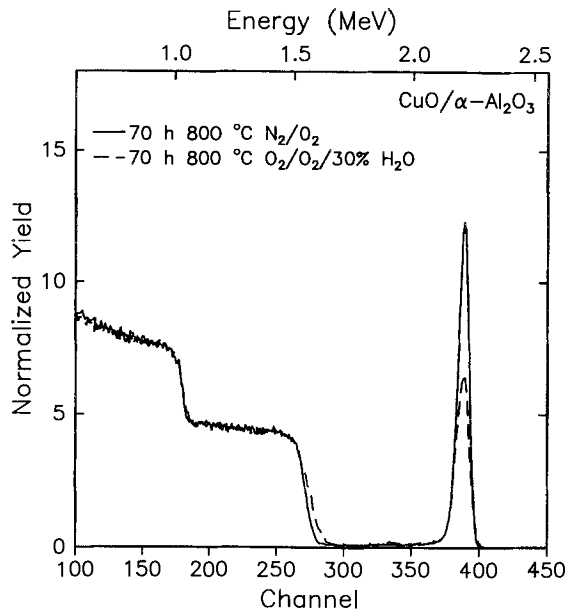

Fig. 8. RBS spectra of $CuO/\alpha\text{-}Al_2O_3$ samples kept at 800°C for 70 h in N_2/O_2 and $N_2/O_2/30\%$ H_2O. The thickness of the deposited Cu layers was about 30 nm.

species must have been rather high during steam treatment.

3.2. *Infrared spectroscopy of steam-treated NiO/ α-Al2O3 samples*

The FTIR spectra of the steam-treated $NiO/\alpha\text{-}Al_2O_3$ samples are shown in fig. 9. A very broad O–H stretching band with maximum intensity at about 3600

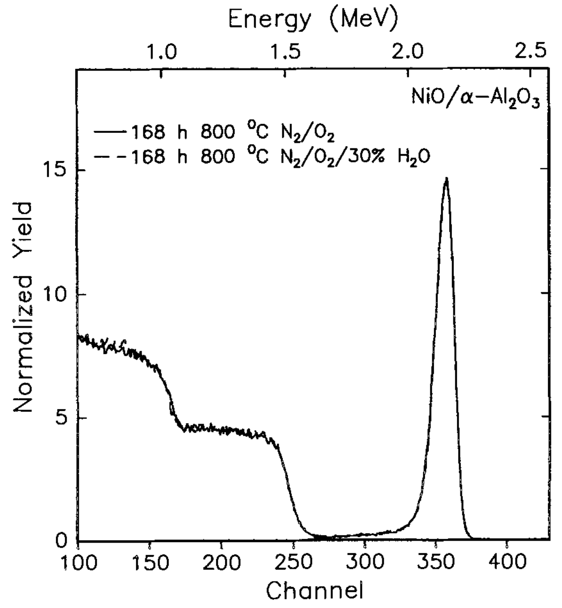

Fig. 7. RBS spectra of $NiO/\alpha\text{-}Al_2O_3$ samples kept at 800°C for 168 h in N_2/O_2 and $N_2/O_2/30\%$ H_2O. The thickness of the Ni layers was about 60 nm.

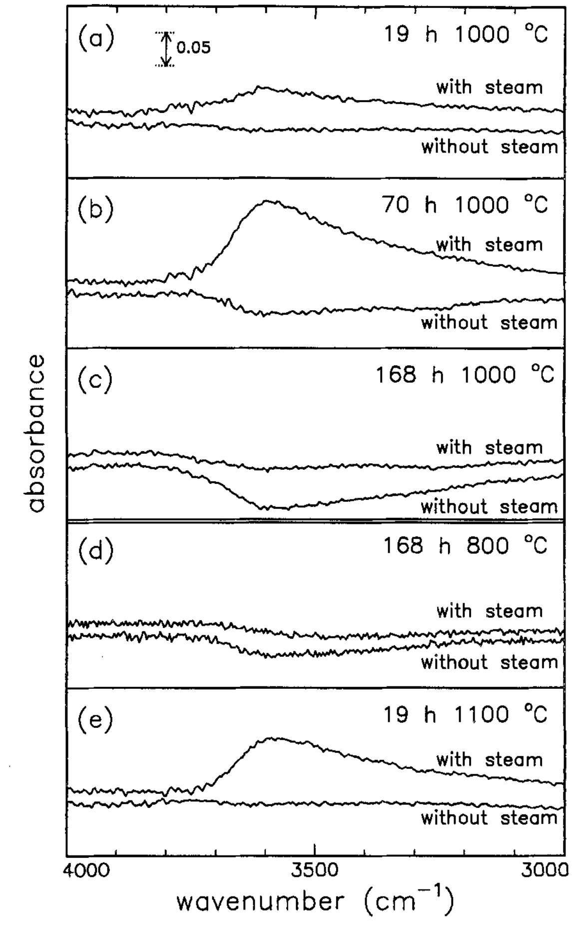

Fig. 9. FTIR spectra of $NiO/\alpha\text{-}Al_2O_3$ samples after annealing in $N_2/O_2/30\%$ H_2O and dry N_2/O_2. (a) 19 h 1000°C, (b) 70 h 1000°C, (c) 168 h 1000°C, (d) 168 h 800°C, (e) 19 h 1100°C. The thickness of the deposited Ni layers was about 120 nm.

cm^{-1} developed upon annealing at 1000°C in $N_2/O_2/30\% H_2O$. On the other hand, a negative peak, indicative of removal of OH groups compared to the reference Al_2O_3 spectra, is visible after annealing in dry N_2/O_2. The intensity of the negative band increased with annealing time. Apparently, the α-Al_2O_3 reference sample, which was like all samples transported through the ambient to the spectrometer after annealing, contained some hydroxyl groups. The NiO/α-Al_2O_3 samples also contained O–H groups, probably at the NiO/α-Al_2O_3 interface, which were slowly removed during annealing at 1000°C in dry N_2/O_2. During annealing at 1000°C in $N_2/O_2/30\% H_2O$, however, hydroxyl groups are incorporated. From the strong increase of the O–H stretching band after 70 h annealing compared to the sample kept for 19 h at 1000°C in $N_2/O_2/30\% H_2O$ we conclude that the amount of hydroxyl groups present after 19 h does not represent a saturation concentration. Therefore the uptake of OH is considered to be a slow process. After 168 h at 1000°C, however, the intensity of the O–H band had strongly decreased. From fig. 1 it is clear that a large fraction of the nickel atoms of this sample had already disappeared into the vapour phase. Obviously, the hydroxyl groups are associated with the nickel oxide/nickel aluminate overlayers, and not with the alumina support. When the amount of nickel atoms decreases, less hydroxyl groups can be accommodated.

Note that the samples were cooled down in dry N_2/O_2 after annealing in $N_2/O_2/30\% H_2O$. Consequently, the hydroxyl groups are incorporated at 1000°C. From the infrared spectra of the samples kept in $N_2/O_2/30\% H_2O$ at 800, 1000 and 1100°C it becomes clear that the tendency to incorporate hydroxyl groups increases with temperature. This is quite remarkable, because entropy will favour the formation of gaseous H_2O. The formation of bulk nickel hydroxide is very unlikely at such a high temperature. Furthermore, the broad features of the O–H stretching band indicate the presence of disorderly incorporated hydroxyl groups, not of a bulk hydroxide.

3.3. RBS of γ-Al_2O_3-supported model catalysts

In section 3.1 it was demonstrated that the volatilization of transition metal atoms (Me) obscured any possible effect of steam on the simultaneously occurring solid state reaction between MeO and α-Al_2O_3. γ-Al_2O_3, however, exhibits a much larger reactivity towards the transition metal oxides [5,6] than α-Al_2O_3. Therefore lower annealing temperatures can be applied to achieve sufficiently high reaction rates. At these temperatures, steam-induced volatilization of the metal atoms does not play an important role yet. Consequently it should be possible to measure exclusively the effect of steam on the solid state reaction between the oxides, as will be demonstrated below.

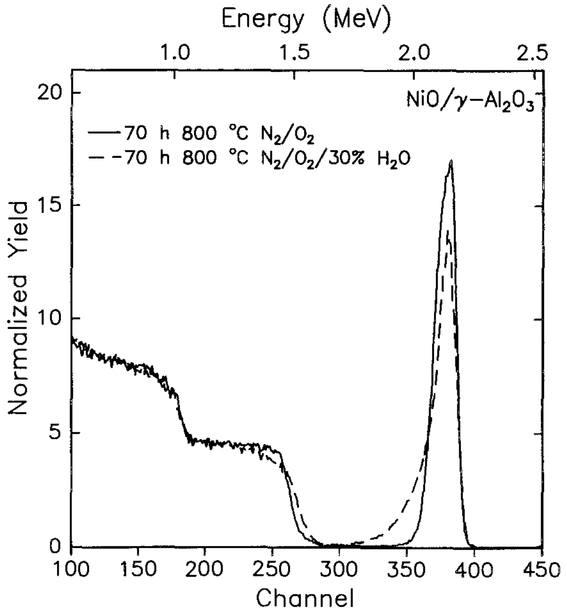

Fig. 10. RBS spectra of NiO/γ-Al_2O_3 samples kept at 800°C for 70 h in N_2/O_2 and $N_2/O_2/30\% H_2O$ gas mixtures. The thickness of the deposited Ni layers was about 55 nm.

Figs. 10 and 11 show the RBS spectra of NiO/γ-Al_2O_3 and Co_3O_4/γ-Al_2O_3 samples, respectively, after annealing in N_2/O_2 and $N_2/O_2/30\% H_2O$ for 70 h at 800°C. Obviously, in both cases the reaction of the overlayers with γ-Al_2O_3 was enhanced in the presence of 0.3 atm steam. At the low energy side in the RBS spectrum of the nickel peak of the steam-treated sample (fig. 10), a long tail is visible towards lower energies. This implies that a fraction of the nickel atoms penetrated rather deeply into the substrate, presumably along the γ-Al_2O_3 grain boundaries and the internal surface of the pores [6].

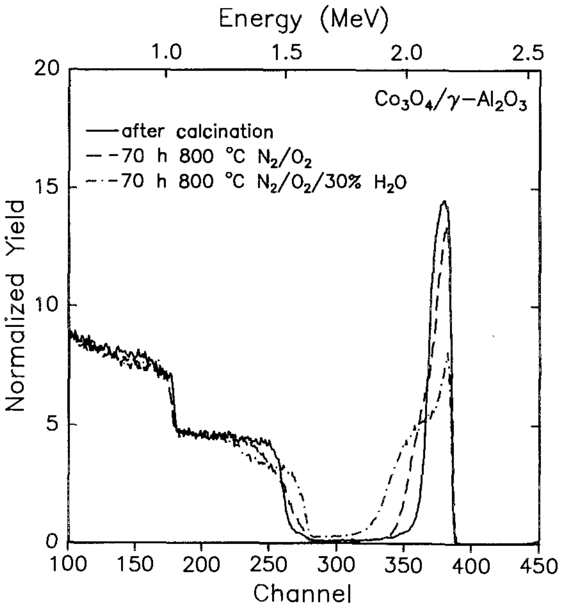

Fig. 11. RBS spectra of Co_3O_4/γ-Al_2O_3 samples kept at 800°C for 70 h in N_2/O_2 and $N_2/O_2/30\% H_2O$ gas mixtures. The thickness of the deposited Co layers was about 55 nm.

The same phenomenon proceeded in CuO/γ-Al$_2$O$_3$ samples at temperatures as low as 500°C (fig. 12). A long tail at the low energy edge of the copper peak is present after annealing a CuO/γ-Al$_2$O$_3$ sample for 20 h at 500°C in N$_2$/O$_2$/30% H$_2$O. If such a sample is kept at 500°C in N$_2$/O$_2$, a much less pronounced low-energy tail of the copper peak appears. Yet a small tail is visible, which reflects the high reactivity of copper oxide with γ-Al$_2$O$_3$.

The importance of the presence of steam is emphasized once more in fig. 13. Both RBS spectra displayed in this figure are taken from NiO/γ-Al$_2$O$_3$ samples calcined at 500°C for 12 h and subsequently kept at 900°C for 70 h in N$_2$/O$_2$, but the samples were not treated simultaneously. The γ-Al$_2$O$_3$ substrate of one sample was precalcined at 500°C as usual, but the substrate of the other sample was not calcined before deposition of the nickel layer. In the latter case, the water adsorbed by the γ-Al$_2$O$_3$ was thus released during calcination at 500°C, which was proven by the appearance of a considerable amount of condensed water at the cold end of the reactor. Probably, steam pressures in the order of 1 atm were reached locally within the pore system of the sample. Apparently, the release of water had a very strong influence on the nickel oxide–alumina interaction, since the RBS spectra of the two samples are very different; the nickel atoms penetrated much deeper into the substrate with the γ-Al$_2$O$_3$ substrate that was not precalcined.

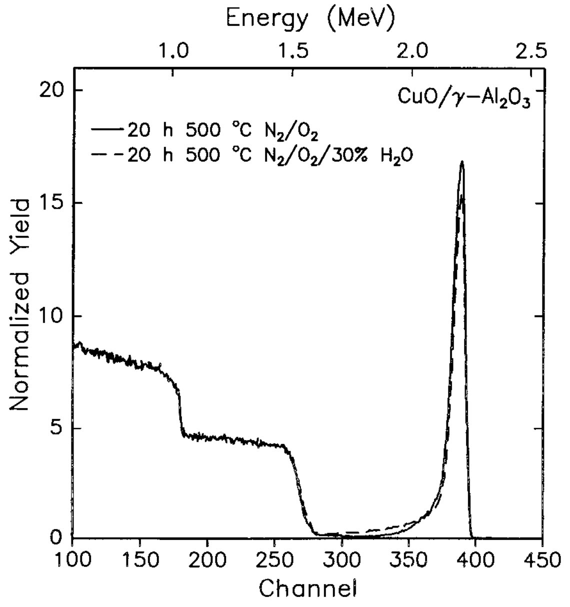

Fig. 12. RBS spectra of CuO/γ-Al$_2$O$_3$ samples kept at 500°C for 20 h in N$_2$/O$_2$ and N$_2$/O$_2$/30% H$_2$O gas mixtures. The thickness of the deposited Cu layers was about 40 nm.

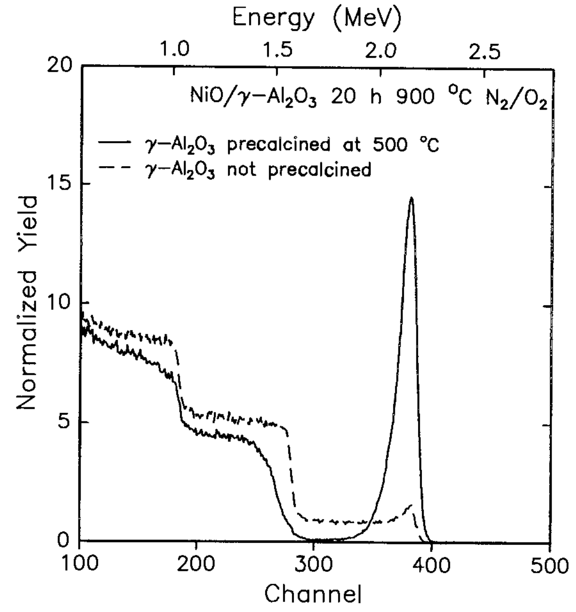

Fig. 13. RBS spectra of NiO/γ-Al$_2$O$_3$ samples kept at 900°C for 20 h in N$_2$/O$_2$. The thickness of the deposited Ni layers was about 55 nm. (a) γ-Al$_2$O$_3$ calcined for 3 h at 500°C before vapour-deposition of Ni (as usual). (b) γ-Al$_2$O$_3$ not calcined for 3 h at 500°C before vapour-deposition of Ni.

4. Discussion

In section 3.1 it has been shown that nickel, cobalt and copper atoms volatilized when the corresponding α-Al$_2$O$_3$-supported metal oxides were kept in a N$_2$/O$_2$/30% H$_2$O flow at 1000°C. With Fe$_2$O$_3$/α-Al$_2$O$_3$ samples, volatilization of Fe atoms at 1000°C could not be detected. Especially copper evaporated very rapidly; even at 800°C Cu atoms disappeared rather fast from CuO/α-Al$_2$O$_3$ samples upon steam treatment. At this temperature, Ni and Co did not volatilize at a noticeable rate. Thus we found that the tendency to evaporate in a steam-containing atmosphere follows the sequence:

$$\text{iron oxide} \ll \text{cobalt oxide} < \text{nickel oxide} \ll \text{copper oxide}\,.$$

In a previous study [6] we showed that the reaction of a thin copper oxide layer with α-Al$_2$O$_3$ leads to an extraordinary disintegration of the sample surface, which results in a substantial enlargement of the surface area. It is not unlikely that an increase of the surface area of the sample contributed to the enhanced tendency of copper species to volatilize, but this effect alone cannot sufficiently explain the extremely high volatility of copper oxide in the presence of steam as compared to the other transition metal oxides.

Now the question arises about the nature of the volatile species. Infrared spectra of NiO/α-Al$_2$O$_3$ samples (section 3.2) revealed that steam treatment at high temperatures led to the incorporation of disorderly oriented hydroxyl groups in the nickel oxide layer. At 800°C, when there is no significant volatilization of nickel species, a very small number of hydroxyl groups is incorporated into the nickel oxide, whereas after annealing at 1000°C in N$_2$/O$_2$/30% H$_2$O a considerable amount of hydroxyl groups in the overlayer was detected, together with a substantial loss of nickel atoms. This correlation between the volatilization of nickel species and the tendency to form Ni–OH groups in the NiO layer, despite the fact that entropy favours the formation of gaseous H_2O at thus high temperatures, supports the assumption that the volatile species is a hydroxide, $Ni(OH)_2$. With copper oxide and cobalt oxide overlayers, the volatile compounds would be $Cu(OH)_2$ and CuOH, and $Co(OH)_2$, respectively.

The formation of volatile transition metal hydroxides at high temperatures, such as $MoO_2(OH)_2$, out of oxides in the presence of water vapour has been reported [7], but very little can be found in literature on volatile hydroxides of nickel, cobalt or copper. Formation of $Ni(OH)_2$ under extreme conditions (2100 atm H_2O at 500°C) has been mentioned [8], but no experimental data are known concerning the formation of such compounds under conditions similar to those applied in this work. However, McCarty and co-workers [9] predicted on the basis of thermochemical calculations, using measured and estimated values for the enthalpy of formation of gaseous metal hydroxides and oxyhydroxides, that the steam and oxygen levels encountered in the high-temperature combustion environment could significantly elevate concentrations of metal containing vapours over a wide variety of metal oxides. For example, Al_2O_3, SiO_2, and NiO in 0.5 atm O_2 at 1227°C were calculated to have a volatility increased by eight, six and four orders of magnitude, respectively, when 0.5 atm steam was added. The total vapour pressure of metal compounds at 1227°C in 0.5 atm O_2 and 0.5 atm H_2O was calculated to follow the sequence:

$$Al_2O_3 < Pd < Fe_2O_3 < Pt < MnO < CoO < NiO < CuO < Na_2O < K_2O .$$

For alumina, iron oxide, cobalt oxide, nickel oxide, and copper oxide the total vapour pressures are 5.2×10^{-8}, 3.3×10^{-7}, 9.9×10^{-6}, 1.1×10^{-5}, and 3.7×10^{-3} atm, respectively. The higher volatility was caused principally by the formation of $Al(OH)_3$, $Fe(OH)_2$, $Co(OH)_2$, $Ni(OH)_2$, and both CuOH (2.1×10^{-3} atm) and $Cu(OH)_2$ (1.7×10^{-3} atm) species, respectively. For some oxides, such as SiO_2, the main gaseous species is not a hydroxide but an oxyhydroxide ($SiO(OH)_2$). Note that the volatility of copper oxide is exceeded only by that of the alkali oxides. At 927°C the total equilibrium vapour pressure of copper hydroxides in 0.5 atm H_2O/0.5 atm O_2 is still as high as 1.8×10^{-4} atm.

Our results are in excellent agreement with the predictions of McCarty and coworkers. The very high volatility of copper oxide predicted by McCarty and the relatively low tendency of iron oxide to volatilize are confirmed by the observations dealt with in this study. The difference between the calculated metal hydroxide vapour pressures of cobalt oxide and nickel oxides, the two intermediate cases, is only small (9.9×10^{-6} and 11×10^{-6} atm, respectively). It seems, however, that the loss rate of cobalt atoms observed in our experiments (fig. 4) was more than 10% lower than the loss rate of nickel atoms (fig. 1). This is attributed to the stabilization of the cobalt atoms by the formation of $CoAl_2O_4$. The calculations of McCarty also show that the equilibrium vapour pressures of the metal hydroxides are lowered when the metal oxides (MeO) are replaced by metal aluminates ($MeAl_2O_4$). For example, the equilibrium $Co(OH)_2$ vapour pressure of $CoAl_2O_4$ at 1227°C in 0.5 atm H_2O/0.5 atm O_2 is 1.0×10^{-6} atm (9.9×10^{-6} atm for CoO). It has been shown previously that the reaction of CoO and Al_2O_3 to $CoAl_2O_4$ proceeds at a substantially higher rate than the reaction of NiO and Al_2O_3 to $NiAl_2O_4$ [5,6]. From fig. 4 it is deduced that the cobalt atoms remaining after 70 h annealing in N_2/O_2/30% H_2O at 1000°C are present as aluminate. Since the reaction to aluminate proceeds faster with CoO/Al_2O_3 than with NiO/Al_2O_3 samples, the cobalt atoms benefit more rapidly from the stabilization against the formation of a volatile hydroxide.

In our opinion, the agreement between our findings and the calculations of McCarty leaves little doubt that the loss of transition metal atoms observed in our experiments must be attributed to the formation of volatile metal hydroxides.

These results have very important implications for the use of transition metal (oxides) as a catalyst when steam is present. Approximate materials stability guidelines indicate that when the mole fraction of metal vapour exceeds 1 ppb (at 1 atm), then vaporization-assisted sintering can occur. When the mole fraction of metal vapour exceeds 0.1–1 ppm, then loss by volatilization becomes important.

Because of its very high volatility, the use of copper oxide must be avoided in applications asking for high temperatures and steam pressures, such as high-temperature catalytic combustion. Other active materials, such as MnO_2 and, especially, PdO and Fe_2O_3 show a much better stability under such reaction conditions.

In section 3.3 it has been demonstrated that the presence of steam enhances the solid state reaction of MeO (Me = Ni, Co or Cu) with γ-Al_2O_3 very appreciably. Because a small fraction of the Me atoms penetrates rather deeply into the substrate, we assume that the grain boundaries and the internal surface of the pores of the γ-Al_2O_3 play a decisive role in this phenomenon. It is well known that the surface of γ-Al_2O_3 is hydroxylated, even after calcination at high temperatures (500–900°C) [10]. Upon annealing in steam, the degree of hydration will increase, and a mixed Me–Al-hydroxide may be formed. Formation of such compounds during preparation of NiO/γ-Al_2O_3 catalysts from aqueous solutions has been observed [3,11]. This can be explained by the assumption that the nickel and aluminium cations have a much higher mobility on a thus hydrated γ-Al_2O_3 surface than on a surface of a much lower concentration of hydroxyl groups. It has been reported that the humidity during calcination of $NiO/\gamma\text{-}Al_2O_3$ and $NiO/\eta\text{-}Al_2O_3$ catalysts at 600°C had a clearly evident effect on their structure [12]. In the samples calcined in moist air the Ni^{2+} ions were largely located in octahedrally coordinated sites at the surface of the carrier, whereas after calcination in dry air, when a large part of the hydroxyl ligands were removed, a considerable fraction of the Ni^{2+} ions appeared to have entered the tetrahedrally coordinated sites below the surface of the support.

We finally mention the effect of steam on the sintering of $\gamma\text{-}Al_2O_3$ that was demonstrated in our previous paper [6]. With 0.3 atm steam in the gas flow at 800°C the BET specific surface area decreased at a considerably higher rate than during similar annealing experiments in a dry atmosphere. This also demonstrates that the surface mobility of ions on $\gamma\text{-}Al_2O_3$ is enhanced in the presence of steam.

5. Conclusions

In the presence of 0.3 atm steam, nickel, cobalt and copper volatilize at 1000°C from Al_2O_3-supported metal oxide or metal aluminate layers. Especially copper was found to disappear very quickly in the presence of steam, even at a temperature as low as 800°C. This implies that copper (oxide) is not useful as a catalyst component in applications requiring high temperatures and steam partial pressures, such as high-temperature catalytic combustion.

Infrared spectroscopy data and an excellent agreement with thermochemical calculations support our conclusion that the volatile species are metal hydroxides.

At lower temperatures (500–800°C), when evaporation of metal hydroxides does not play an important role, the presence of steam was found to accelerate the solid state reaction of MeO (Me = Ni, Co or Cu) with $\gamma\text{-}Al_2O_3$ enormously. Presumably, this is due to a higher degree of hydration of the surface and grain boundaries of the $\gamma\text{-}Al_2O_3$ substrate of the steam-treated samples. Hydration could lead to a higher mobility of nickel and aluminium ions, which are diffusing along these grain boundaries and the internal surface of the pores of the $\gamma\text{-}Al_2O_3$ support.

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