The influence of an intermediate MoO_3 layer on the solid state reaction of cobalt oxide with γ-Al_2O_3

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In view of the importance for Co_xO_y–MoO_3/γ-Al_2O_3 hydrodesulphurization (HDS) catalysts, the reactivity of cobalt oxide layers towards cobalt aluminate formation was investigated on both MoO_3-covered and bare γ-Al_2O_3 substrates. $Co_3O_4/MoO_3/\gamma$-Al_2O_3 and Co_3O_4/γ-Al_2O_3 systems were prepared by vapour-deposition of MoO_3 (12×10^{15} Mo atoms/cm^2) and Co (400×10^{15} Co atoms/cm^2) layers onto a γ-Al_2O_3 substrate, followed by oxidation of the Co layer to Co_3O_4. After annealing at 800°C for 40 h, the interfacial reaction to cobalt aluminate was assessed using Rutherford backscattering spectrometry. The presence of molybdenum oxide appeared to enhance cobalt aluminate formation. The Mo atoms, which spread out over the entire cobalt-containing layer, presumably caused a high defect density, which explains the observed higher reaction rate. The amount of MoO_3 was much too low to stabilize all cobalt atoms by cobalt molybdate formation.

Keywords: Rutherford backscattering spectrometry (RBS); HDS catalyst; solid state reaction; cobalt aluminate; MoO_3; Co_3O_4; γ-Al_2O_3

1. Introduction

Solid state reaction between the active component and the support is an important cause of catalyst deactivation. It is often encountered with alumina-supported transition metal (oxide) catalysts, e.g., NiO may react with Al_2O_3 to $NiAl_2O_4$.

In previous studies [1–3] we investigated the interfacial reaction of transition metal oxide layers (e.g., NiO, Co_3O_4, CuO) with α- and γ-Al_2O_3 substrates to metal aluminate spinel compounds. We showed that γ-Al_2O_3 is more reactive towards aluminate formation than α-Al_2O_3, and that $CuAl_2O_4$ and $CoAl_2O_4$ are formed more readily than $NiAl_2O_4$.

The reaction of cobalt oxide with γ-Al_2O_3 to $CoAl_2O_4$ is relevant for the hydrodesulphurization (HDS) catalyst. This catalyst, Co_xO_y–MoO_3/γ-Al_2O_3 in its oxidic form, has to be treated very carefully to prevent the cobalt ions from entering the γ-Al_2O_3 lattice [4]. From literature [4–8] it appears that under oxidizing conditions molybdenum is present as Mo^{6+} in HDS catalysts, while cobalt valency switches (Co^{3+}/Co^{2+}) may occur readily. Several mixed Co-Al-O and Co-Mo-O species have been identified [5,6]; therefore the relative amounts of Co^{2+} and Co^{3+} do not only depend on temperature and oxygen partial pressure, but also on the extent of the interaction of cobalt ions with alumina or molybdenum oxide. In absence of such interactions, Co_3O_4 is the stable cobalt oxide in 0.2 atm O_2 below 896°C [9].

It has been reported that one of the roles of MoO_3 in HDS catalysts is to inhibit the diffusion of cobalt atoms into the support [5,6]. However, HDS catalysts usually contain a large number of Mo atoms, compared to the Co loading (Co/Mo < 1). The question arises what will happen with Co/Mo $\gg$ 1. Will a thin intermediate MoO_3 layer still be able to slow down the reaction of a relatively thick cobalt oxide overlayer with a γ-Al_2O_3 substrate? This note deals with this question.

2. Experimental

2.1. Sample preparation

Slices of γ-Al_2O_3 were produced by pressing γ-Al_2O_3 powder (Al 4172, Engelhard, De Meern, The Netherlands) for 3 min at 590 MPa. These slices (Ø13 mm) were calcined at 500°C in flowing 80% N_2/20% O_2 for 3 h. The BET surface area (207 m^2/g) and the pore volume (0.40 m^3/g) of these slices were considerably lower than those of the starting γ-Al_2O_3 powder (251 m^2/g and 0.99 m^3/g, respectively).

A relatively thin MoO_3 layer (12×10^{15} Mo atoms/cm^2) was vacuum vapour-deposited from an alumina crucible onto a γ-Al_2O_3 slice. During deposition a part (about 40%) of the sample was shielded from the source; therefore only 60% of the γ-Al_2O_3 substrate was covered by the MoO_3 layer. Subsequently, a much thicker Co layer (400×10^{15} Co atoms/cm^2; i.e. 44 nm Co) was deposited onto the entire sample from another alumina crucible.

The cobalt film was oxidized to Co_3O_4 (layer thickness 88 nm) by annealing at 500°C for 12 h in a flow of 80% N_2/20% O_2. The sample was subsequently kept at

800°C for 40 h in 80% N_2/20% O_2. This temperature was chosen to achieve sufficiently large diffusion distances in an acceptable period of time.

2.2. Analysis

RBS analysis was performed with 2.87 MeV $^4He^+$ ions. The incident beam was parallel to the surface normal, and the detector was positioned at a scattering angle of 170°. The beam spot size was about 1 × 1 mm.

The sample was analyzed after deposition of the MoO_3 layer, before and after oxidation of the Co layer, and after annealing at 800°C. RBS spectra were recorded both at the Mo-free and at the Mo-containing part of the sample.

3. Results and discussion

Fig. 1 shows the relevant part of one RBS spectrum of the Co_3O_4/γ-Al_2O_3 region and three RBS spectra of the $Co_3O_4/MoO_3/\gamma$-Al_2O_3 region of the specimen, after various preparation and annealing steps.

After deposition of the MoO_3 layer, a sharp peak is visible at the Mo surface energy position. This means that the Mo atoms are concentrated near the surface of the sample. After deposition and oxidation of the cobalt overlayer, both the Mo peak and the Al edge were shifted to lower energies, because the Mo and Al atoms were covered by Co_3O_4. The Mo peak also became lower and broader, due to some diffusion away from the interface during calcination. Similar RBS spectra were recorded at the Co_3O_4/γ-Al_2O_3 area (not shown), besides of course the absence of the Mo signal. The sample colour after calcination was dark greenish grey, which is the colour of Co_3O_4. This is in agreement with XRD results from our previous study [3]. Only Co_3O_4 diffraction peaks were found (apart from peaks originating from the support) in the XRD patterns of similarly prepared cobalt oxide/α-Al_2O_3 and cobalt oxide/γ-Al_2O_3 samples.

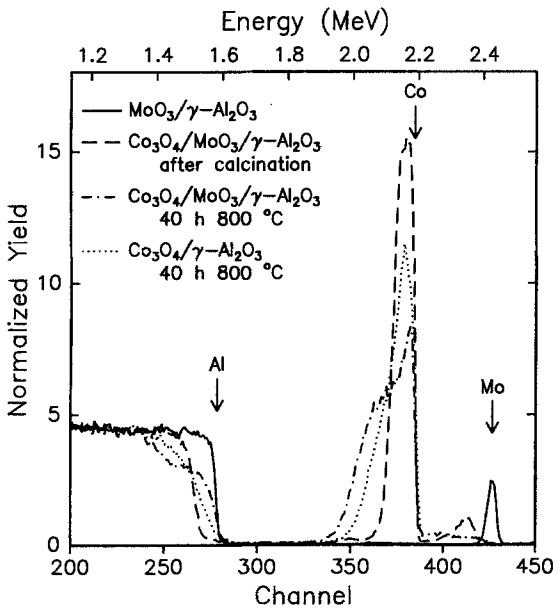

Fig. 1. RBS spectra of a $Co_3O_4/MoO_3/\gamma$-Al_2O_3 sample after various preparation and annealing steps. Calcination and annealing were carried out in flowing 80% N_2/20% O_2. The thickness of the deposited MoO_3 and Co films amounted to 12×10^{15} and 400×10^{15} metal atoms/cm^2, respectively (6 nm MoO_3; 44 nm Co).

Upon annealing at 800°C for 40 h in N_2/20% O_2, a shoulder developed at the low-energy side of the cobalt peak and the peak height decreased. At the same time, the high-energy side of the aluminium edge moved to higher energies and at lower energies the same edge retreated. These two observations, which indicate the penetration of cobalt ions into the alumina substrate and/or aluminium ions into the cobalt oxide overlayer, are clearly more pronounced in the $Co_3O_4/MoO_3/\gamma$-Al_2O_3 region of the sample than in the Co_3O_4/γ-Al_2O_3 region. This implies that the reaction between Co_3O_4 and γ-Al_2O_3 had taken place to a considerably larger extent in the $Co_3O_4/MoO_3/\gamma$-Al_2O_3 region. Simultaneously, the Mo atoms spread out over the entire cobalt-containing layer. A distinct colour difference between the Mo-free and the Mo-containing regions of the sample was observed: the former had the greenish grey colour of Co_3O_4, whereas the latter was blueish grey. This is attributed to the presence of cobalt aluminate, which has a characteristic blue colour [7], not far below the sample surface. The results shown in fig. 1 were reproduced with separately prepared Co_3O_4/γ-Al_2O_3 and $Co_3O_4/MoO_3/\gamma$-Al_2O_3 samples.

Apparently, the presence of MoO_3 had an accelerating effect on the reaction between Co_3O_4 and γ-Al_2O_3. In the first instance this might be surprising, since MoO_3 is thought to suppress the diffusion of Co atoms into the γ-Al_2O_3 lattice in HDS catalysts [5,6,8]. However, Richardson [10] reported that cobalt aluminate formation was prevented at low Co/Mo ratios (below 0.3), due to the formation of cobalt molybdate, but at higher Co/Mo ratios spinel formation occurred. In our sample the Co/Mo ratio was very high, and the amount of MoO_3 was by far not sufficient to stabilize all cobalt atoms by cobalt molybdate formation. The observation that the interfacial reaction is even accelerated by the presence of Mo atoms might be explained by assuming that the incorporation of highly charged Mo^{6+} cations, which spread out over the cobalt oxide and spinel layers, in a matrix with di- and trivalent cations causes a high defect density.

Thus in $Co_3O_4/MoO_3/\gamma$-Al_2O_3 systems with Co/Mo $\gg 1$ we found an opposite effect of MoO_3 on cobalt aluminate formation as compared to literature data for Co/Mo $\ll 1$.

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