The Active Sites in the Selective Reduction of Nitrobenzene by Cobalt Aluminum Oxide Catalysts

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A series of mixed cobalt aluminum oxides with spinel structure has been prepared in such a way that the concentration of cobalt ions in the surface increases gradually. The crystal structure does not change with the changing amounts of Co and Al. The catalytic activity of the cobalt aluminum oxides was tested in the selective reduction of nitrobenzene to nitrosobenzene. The rate of nitrosobenzene formation increases almost linearly with increasing Co concentration in the surface. This behavior is in agreement with the Mars–van Krevelen mechanism, which requires for its operation cations with variable valencies in the catalyst surface. © 1996 Academic Press, Inc.

INTRODUCTION

Various spinel type oxides such as Mn_3O_4 and Co_3O_4 catalyze the one-step selective reduction of nitrobenzene to nitrosobenzene. Application of this reaction can be found in the synthesis of various industrial products from nitrosobenzene, including antioxidants, insecticides, and photo-lacquers. The reaction proceeds most probably according to the Mars–van Krevelen mechanism (1, 2), which implies a continuous exchange of oxygen between gas phase molecules and the oxidic lattice of the catalyst. A condition for the operation of the Mars–van Krevelen mechanism is that the catalyst contains metal ions with variable valencies, notably transition metal ions, able to cope with the varying degree of surface oxidation. A so-called normal 2:3 spinel is denoted as $(A^{2+})[B^{3+}]_2O_4$, where curved and square brackets denote tetrahedrally and octahedrally coordinated cations, respectively. An inverse 2:3 spinel is designated as $(B^{3+})[A^{2+}B^{3+}]O_4$. Many spinels have an intermediate structure which can be described as $(A_{1-\alpha}B_\alpha)[B_{2-\alpha}A_\alpha]O_4$, where α is the degree of inversion and varies between 0 for a normal spinel and 1 for a completely inverse spinel. The role of the coordination of cations in the selective reduction of nitrobenzene to nitrosobenzene has already been studied with mixed Co and mixed Mn oxides (1, 4). It has been shown, by a selective

substitution of Mn or Co ions, in octahedral and tetrahedral sites by Al^{3+} and Zn^{2+}, respectively, that the catalytic activity of these oxides is determined only by the octahedral site cations. It has been shown by low energy ion scattering (LEIS) measurements that this can be explained by the fact that only these octahedral cations are exposed at the surface of the spinels (5). A more detailed study of the role of the octahedral site cations, by preparing a series of mixed Mn spinels, showed that the quantification of this role is very difficult (4). It was established that upon preparation of the $Mn^{2+}Al_2^{3+}O_4$ spinel, a part of the Mn^{2+} ions is oxidized and transferred to the octahedral sites. Al^{3+} is simultaneously separated out of the manganese aluminum oxide phase to form a second phase: Al_2O_3. In this way the same number of manganese and aluminum ions can bind more oxygen than in the case of a single spinel phase. This behavior has been called *oxidative transfer* (4). A similar phenomenon has also been observed with $CrFe_2O_4$ spinels (6). The presence of Al_2O_3 in the manganese aluminum oxide samples has been shown by Maltha *et al.* using X-ray diffraction (XRD) (4). Oxidative transfer in manganese aluminates is also accompanied by the creation of cation vacancies and an increase in the average valency of manganese. This makes a model study of the relation between structure and composition of the spinel and the catalytic activity more difficult.

Therefore, a study was desirable with a system which does not suffer from the complications due to oxidative transfer. Preliminary experiments indicated that cobalt aluminum oxide is favorable candidate for such a study (1, 4). A series of $(Co^{2+})[Al_{2-x}^{3+}Co_x^{3+}]O_4$ spinels was prepared, with x varying from 0 in $CoAl_2O_4$ to 2 in Co_3O_4. Recently a similar series has been prepared by Murthy and Swamy (7) and tested in the catalytic dehydrogenation and dehydration of 2-propanol. They found a correlation between the amount of cobalt in the surface, detected by X-ray photoelectron spectroscopy, and the catalytic activity.

The conditions for the preparation of the spinels were chosen to minimize the oxidative transfer. The samples were characterized using XRD, Transmission electron microscopy (TEM) and LEIS and were tested in the selective

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reduction of nitrobenzene to nitrosobenzene. Additionally, several samples were analyzed using neutron diffraction and atomic absorption spectroscopy (AAS).

EXPERIMENTAL

Preparation of the Catalysts

A series of different $(Co^{2+})[Al_{2-x}^{3+}Co_x^{3+}]O_4$ catalysts was prepared, with $0 \leq x \leq 2$. For each sample a stoichiometric mixture of cobalt and aluminum nitrates and citric acid was dissolved in water and heated at 90°C at 15 mbar for 24 h. The resulting purple solid (cobalt aluminum citrate) was ground and heated in a flow of oxygen in a programmable oven while the temperature was increasing by 25°C/h to 550°C, to accomplish a slow decomposition of the citrate mixture. At 550°C the gas flow was stopped; and sample was kept at that temperature for 24 h and then allowed to cool to room temperature in about 4 h within the furnace. The obtained spinel was annealed at 800°C during 24 h in air (8) and quenched at room temperature by rapid extraction from the furnace. The decomposition of the citrate during the formation of the spinel consumes oxygen, but the experience with Mn-spinels indicates that, in spite of this, oxidative transfer is minimized when citrates are used (4). The Co_3O_4 sample prepared from cobalt citrate will be denoted as Co_3O_4 (C). Additionally, a Co_3O_4 sample was prepared from $Co(OH)_2$, obtained by leading gaseous NH_3 at -30°C through a solution of cobalt nitrate in ethanol, according to Refs. (9, 10). Also this spinel was annealed at 800°C during 24 h and afterward quenched at room temperature. This sample will be denoted as Co_3O_4 (E). The latter method was not used to prepare other samples than Co_3O_4, since oxidative transfer is expected (4) during the decomposition of the hydroxides. However, this problem does not apply to Co_3O_4.

The chemicals used were p.a. grade $Co_2(NO_3)_2 \cdot 6H_2O$, p.a. grade $Al_3(NO_3)_3 \cdot 9H_2O$ and p.a. grade citric acid, all from Merck, Germany. Gaseous NH_3 was obtained by heating a 13 mol liter^{-1} ammonia solution (JT Baker Chemicals BV, Netherlands). The ethanol used was p.a. grade, also from JT Baker Chemicals BV.

Characterization of the Catalysts

The specific surface area of the samples was determined using nitrogen adsorption (BET method). The particle size and morphology of the spinel particles were studied by TEM.

X-ray diffractograms of the powdered oxides were recorded between $2\theta = 10°$ and $2\theta = 90°$, with intervals of 0.05°. The slit widths were 0.5° both at the source and at the detector. The instrument was a Philips PW1050 diffractometer, using Cu$K\alpha$ radiation. The X-ray diffraction data were processed with the Rietveld refinement program GSAS (11) to determine the lattice constants and the concentrations of cobalt and aluminum in the octahedral and tetrahedral sites of the oxide (12, 13).

Neutron diffraction was carried out at the Petten High-Flux Reactor (Netherlands Energy Research Foundation, ECN). The diffraction pattern was taken between $2\theta = 5°$ and $2\theta = 155°$, with a step size of $2\theta = 0.1°$. Although it is more accurate than XRD, this technique was applied only to $(Co)[CoAl]O_4$, since a single measurement requires 20 g of a sample. Since in Co_2AlO_4 half of the octahedral sites are filled by Co and half by Al, $(Co)[CoAl]O_4$ is considered a good representative of the catalyst series. Neutron diffraction data were also processed with the Rietveld refinement program GSAS.

Determination of Na, Co, and Al by AAS was carried out with a Perkin Elmer 3030 instrument.

LEIS Measurements

The LEIS measurements were performed with the LEIS apparatus "NODUS." It basic design and a review of the applications of LEIS to oxides can be found in Ref. (14). The measurements were performed under ultrahigh vacuum conditions. For the analysis ^{4}He ions are directed perpendicularly onto the surface and detected after scattering over 142°. By the use of a light ion (He$^+$) and a low ion flux, and by measuring only the energy interval of interest, the damage to the surface by the ion beam was minimized. Time-dependent measurements showed that the influence of the beam on the measured data can be neglected. To compensate for the surface charge the surface was flooded from all sides by low-energy electrons. Prior to analysis the catalysts were pressed to pellets and calcined in 40 mbar oxygen at 200°C to remove water and hydrocarbons which might hinder the quantification. Since the spinels have been calcined in air at 800°C, we may reasonably assume that this pretreatment does not cause any further oxidation of the samples. For the LEIS intensities of the various elements, peak areas after linear background subtraction are taken.

Catalytic Activity Measurements

The catalytic activity measurements were carried out in an open continuous flow system with a fixed bed reactor. Products were analyzed with a Chrompack 438A gas chromatograph (GC) equipped with a Tenax column and an FID detector. The reaction temperature was 300°C, the carrier gas was helium, the partial pressure of nitrobenzene was 0.7 mbar and the flow rate was 25 ml/min. The reaction was followed in its autoredox mode (2–4), which means that part of the nitrobenzene is oxidized by lattice oxygen to products like CO, CO_2, and methanol. This limits the fraction of nitrobenzene that is available for reduction to nitrosobenzene. The same approach was also used in an

earlier study (2) where the various possible side products of nitrosobenzene are discussed in more detail.

During the steady state of the reaction the main product is nitrosobenzene. Small amounts of benzene, sometimes aniline, and smaller molecules are detected by GC.

RESULTS

X-Ray and Neutron Diffraction

The X-ray diffractograms show that all samples consist of a single spinel phase. The lattice constants of the oxides were also determined with our samples (with an accuracy of 0.00035 nm) from their X-ray diffractograms. In agreement with Végard's law, there is a linear relationship between the lattice constant and the cobalt concentration (Co_x) in $(Co)[Al_{2-x}Co_x]O_4$ (Fig. 1).

The Rietveld refinement program used permits the determination of the amounts of cobalt and aluminum in the octahedral and the tetrahedral sites separately. However, the relatively small difference between the scattering factors of Co and Al limits the accuracy of the fractions determined. Within the experimental error, no aluminum was found in the tetrahedral sites with any of the samples. It can therefore be concluded that there is probably no oxidative transfer or inversion. In the literature, the reported inversion parameter α of $CoAl_2O_4$ varies from 0.11 to 0.31 (7, 13, 15–19). It has been shown that high calcination temperatures give rise to a higher degree of inversion (13, 15, 18). The relatively low maximum temperature of our preparation method (800°C) could explain the absence of inversion found here.

The results of neutron diffraction confirm that $(Co)[CoAl]O_4$ consists of a single spinel phase. The peak intensity analysis shows that less than 1% of Al ions are found in tetrahedral sites. The fractions of Co and Al in the
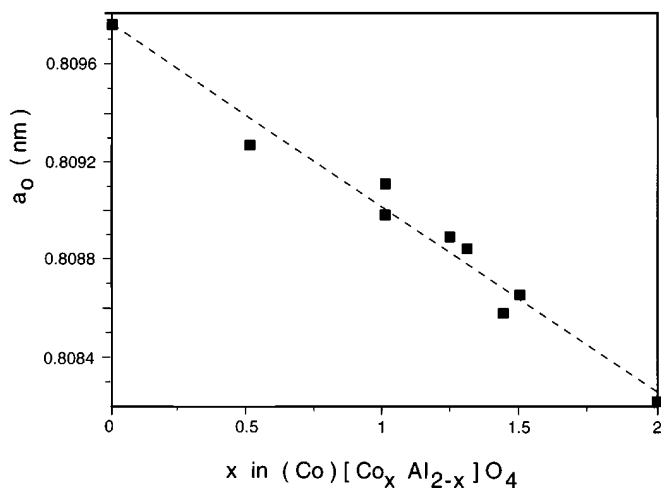
TABLE 1

Composition of the Octahedral Sites in $(Co^{2+})[Al^{3+}_{2-x}Co^{3+}_x]O_4$ as Expected from the Reaction Mixture, the Amount x of Cobalt Ions in Octahedral Sites and the Specific Surface Area Determined by the BET Method

Sample No.	Spinel	x in $(Co)[Al_{2-x}Co_x]O_4$	Surface area (m²/g)
1	$CoAl_2O_4$	0.0	33.1
2	$Co_{1.5}Al_{1.5}O_4$	0.5	15.9
3	Co_2AlO_4	1.0	5.9
4	Co_2AlO_4[a]	1.0	2.4
5	$Co_{2.24}Al_{0.76}O_4$	1.24	2.3
6	$Co_{2.3}Al_{0.7}O_4$	1.3	2.8
7	$Co_{2.44}Al_{0.56}O_4$	1.44	2.1
8	$Co_{2.5}Al_{0.5}O_4$	1.5	2.7
9	Co_3O_4 (C)	2.0	1.3
10	Co_3O_4 (E)	2.0	1.7

[a] This sample has been analyzed by neutron diffraction.

octahedral sites according to neutron diffraction are closer to the values expected from the composition of the synthesis mixture than the fractions found by fitting the XRD. Since neutron diffraction is more reliable than XRD in determining the fractions of ions in a mixed oxide, we trust this conclusion, and the amount of Co ions in octahedral sites (Co_{oct}) as expected from the synthesis mixture (the weighed amount of Co_{oct}) will be taken below as the actual value for Co_{oct}.

The results show that for the Co–Al oxides a normal spinel structure can be assumed. Furthermore, no oxidative transfer is expected in the bulk since neither XRD nor neutron diffraction detected the formation of an Al_2O_3 phase.

Nitrogen Adsorption and TEM

The specific surface area of the oxides varies from 33 m²/g with $CoAl_2O_4$ to 1.3 m²/g with Co_3O_4 (Table 1). Generally, the specific surface area decreases with increasing cobalt concentration.

The results of the surface area measurements are confirmed by TEM. The particle size increases with increasing cobalt concentration (from 30 nm for $CoAl_2O_4$ to 140 nm for Co_3O_4). There are no substantial changes in the particle morphology with varying Co content. Most particles are more or less spherical, with some of them showing developed crystal faces and looking hexagonally shaped. Both from the TEM images and from the diffraction patterns of individual particles, there is no indication for any phase other than the spinel cobalt aluminate.

LEIS Measurements

LEIS has been used to study the surface composition of the topmost atomic layer of the Co–Al spinels. In Fig. 2 the LEIS signals for Co, Al, and O of the $(Co)[Al_{2-x}Co_x]O_4$

FIG. 1. Lattice constant a_0 in nm as a function of x in $(Co^{2+})[Al^{3+}_{2-x}Co^{3+}_x]O_4$.

samples are given as a function of the total amount of Co in the spinels. The intensity of the O signal is constant, which supports the conclusion that the spinel structure remains intact when cations are exchanged. The gradual substitution of Al by Co is reflected by a decrease and an increase in their surface peak intensities, respectively.

Only the Co_3O_4 (C) sample shows in the LEIS spectrum a significant alkali contamination by Na and K/Ca on the surface, and, as will be seen below, a low catalytic activity. Several attempts were made to prepare alkali-free Co_3O_4 (C), using highly purified water, very pure starting materials, and Teflon beakers, but all attempts failed. The influence of the contaminants on the Co signal intensity is dramatic as the results obtained with the clean Co_3O_4 (E) show. We discuss this subject later in this paper.

The surface composition as measured by LEIS shows that the amount of Co at the surface increases almost linearly with increasing Co_{oct} concentration. Surprisingly, some Co was also detected by LEIS at the surface of $CoAl_2O_4$, which is virtually inactive in the selective reduction of nitrobenzene. Obviously this amount of Co is not sufficient to catalyze the selective reduction of nitrobenzene to nitrosobenzene.

Atomic Absorption Spectroscopy

Analysis by AAS showed that $(Co)[Co_{1.44}Al_{0.56}]O_4$, which shows no Na on the surface according to LEIS, contained 0.005 wt% Na. The pure cobalt oxide sample Co_3O_4 (C) has a considerable amount of Na on the surface, as observed in the LEIS spectrum. However, the average amount of Na in the bulk found by AAS was less than 0.002 wt%. The small amount of Na in the bulk of Co_3O_4 (C) is remarkable, since about 30% of the Co at the surface of this
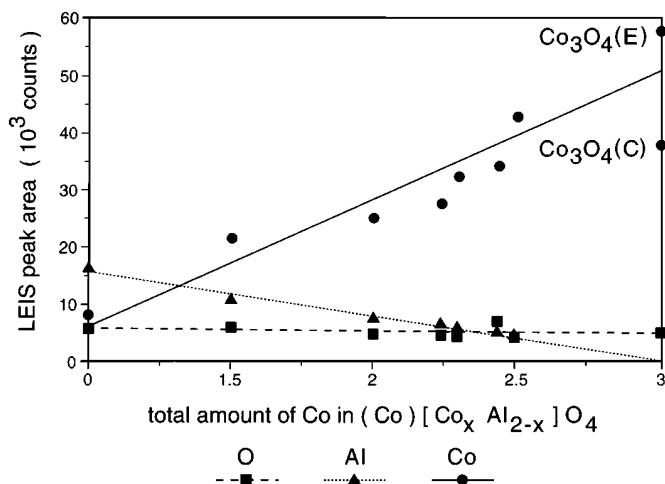

FIG. 2. LEIS intensities of Co (●), Al (▲), and O (■) as a function of the total amount of Co in the $(Co^{2+})[Al^{3+}_{2-x}Co^{3+}_x]O_4$ spinels. Lines are obtained by linear regression.
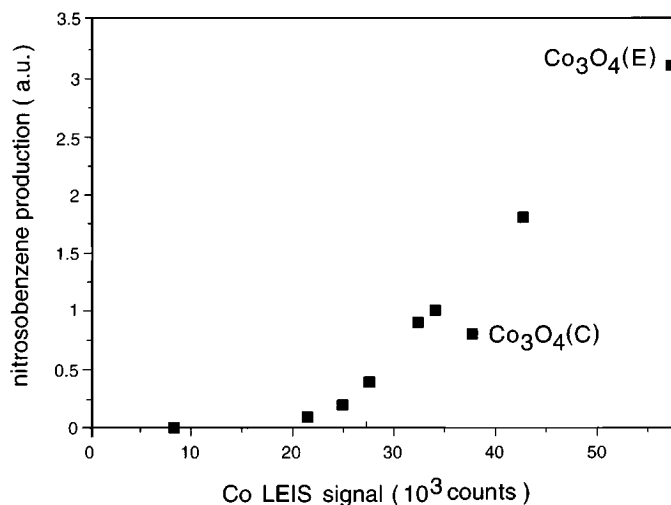

FIG. 3. Reaction rate (au $= 10^{-10}$ mol/m$^2 \cdot$ s) in the selective reduction of nitrobenzene to nitrosobenzene as a function of the amount of Co detected by LEIS at the surface of the $(Co^{2+})[Al^{3+}_{2-x}Co^{3+}_x]O_4$ samples.

sample is shielded from LEIS detection. This is concluded by comparing the Co LEIS peaks of Co_3O_4 (C) and of the clean Co_3O_4 (E). This indicates a high concentration of Na at the surface.

AAS analysis of the amounts of Co and Al in $(Co)[Co_{1.44}Al_{0.56}]O_4$ shows that the actual composition and cation distribution of the sample is identical to the composition derived from the synthesis mixture. This supports our assumption, based on the neutron diffraction results, that the amounts of Co and Al weighed out can be taken as the actual amounts of these ions in the catalysts, and the amounts of Co_{oct} can be calculated from it.

Catalytic Activity Measurements

In Fig. 3 the steady state rate of nitrosobenzene formation is plotted as a function of the amount of Co determined by LEIS at the surface of the $(Co)[Al_{2-x}Co_x]O_4$ samples. It can be seen from the plot that the catalytic activity increases with the amount of Co in octahedral sites, although it is obvious that the relationship is not linear from the origin. The results show that the surface contamination which was detected by LEIS with Co_3O_4 (C) results in a strong decrease in the catalytic activity of this sample. The Co_3O_4 (E), which was judged clean by LEIS, follows the trend set by the cobalt aluminum mixed oxides.

DISCUSSION

Since $CoAl_2O_4$ shows no nitrosobenzene production, it is confirmed that cobalt ions in tetrahedral sites do not contribute to the selective reduction of nitrobenzene. It is proven quantitatively by Fig. 3 that the activity for nitrosobenzene production increases with the amount of

cobalt ions in octahedral sites. According to the LEIS measurements, the Co concentration at the surface of the samples is almost proportional to the concentration of Co_{oct} in the bulk of the cobalt aluminum oxides. This agrees with the fact that the surface of spinel compounds consists generally of low-index crystal planes which contain octahedral-site cations only (5, 20, 21–23). Jacobs *et al.* (5) have shown that the surface of Mn_3O_4 and Co_3O_4 consists of the planes coded as B(111) and D(110), but they suggest that these planes are found at the surface of spinel structured oxides in general. The observation in the LEIS spectrum that some Co occurs at the surface of $CoAl_2O_4$, while there are no Co ions in octahedral sites, might be explained by the occurrence at the surface of planes other than B(111) and D(110), likely at the edges and corners of the cobalt aluminate crystallites. The influence of edges and corners is expected to be more pronounced with $CoAl_2O_4$ than with the other oxides in the series, since this oxide has the smallest particle size. A nonlinear relationship (as in Fig. 3) can also be expected when more than one Co_{oct}^{3+} ion is accociated with a catalytically active site.

The fact that Co_{oct} ions are responsible for the catalytic selective reduction of nitrobenzene by Co–Al spinels is in agreement with the Mars–van Krevelen mechanism.

It was shown by LEIS and by the catalytic activity measurements that Co_3O_4 (C) deviates from the other catalysts in the series. Its surface is contaminated by Na and K and it has an unexpectedly low activity (this difference is less pronounced when, as in Fig. 3, the blocking of Co sites is accounted for). Although small amounts of alkali ions are promoters of the selective reduction of nitrobenzene over Mn_3O_4 (24), at higher concentrations they can reduce the catalytic activity of spinel oxides (25), which is obviously the case with Co_3O_4 (C). It is remarkable that no contaminants were found on the surface of the cobalt aluminum oxides prepared according to the same method as Co_3O_4 (C). Since it is known that Na can be dissolved in aluminum oxide (26), we suppose that also the aluminum-containing $(Co)[Al_{2-x}Co_x]O_4$ can dissolve alkali ions in the lattice, whereas in Co_3O_4 these ions are segregated out to the surface. The AAS analysis showed that Co_3O_4 (C) contains even less Na than $(Co)[Co_{1.44}Al_{0.56}]O_4$, yet no Na is detected by LEIS on the surface of the latter oxide. From a comparison of the Co LEIS peaks of Co_3O_4 (C) and of the clean Co_3O_4 (E), it can be concluded that about 30% of the Co at the surface of Co_3O_4 (C) is covered by alkali compounds. Assuming that sodium, in the form of a monolayer of Na_2O or NaOH, accounts for half of the blocking (potassium for the other half), and that one NaOH or $Na_{0.5}O$ unit blocks 6.36×10^{-20} m^2 of the active surface (the ionic radii of Na^+ and O^{2-} being 0.098 nm and 0.146 nm, respectively), the amount of Na needed to explain the observed shielding is 0.006 wt%. If the sodium is present in the form of microcrystals or if some sodium can disappear in the bulk,

the amount of Na needed would be larger. Thus, we must conclude that the decrease in the catalytic activity due to alkali contaminations on the surface is not fully understood. However, the detected amount of Na is sufficient to cover an appreciable fraction of the Co_3O_4 (C) surface and obviously the deactivating effect prevails at this coverage over the promoting effect.

CONCLUSIONS

A series of $(Co)[Al_{2-x}Co_x]O_4$ spinels has been prepared, characterized and tested in the selective reduction (deoxygenation) of nitrobenzene to nitrosobenzene. XRD, neutron diffraction and TEM have shown that all samples consist of a single spinel phase. No indication has been found for the occurrence of inversion or oxidative transfer. LEIS measurements confirmed that octahedrally coordinated cations are exposed at the surface of cobalt aluminate spinels.

The catalytic activity of cobalt aluminum oxide (with the spinel structure) is related to the concentration of cobalt ions at the catalyst surface. This is in agreement with the operation of the Mars–van Krevelen mechanism.

One of the samples used was contaminated at the surface by alkali ions. This resulted in high LEIS signals for Na and K, low LEIS signals for Co, and consequently a lower catalytic activity.

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