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# The Surface of Catalytically Active Spinels

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**By substitution of the Mn and Co cations in different sites in the spinel structure of $Mn_3O_4$ and $Co_3O_4$ by other cations which are not active in the selective reduction of nitrobenzene to nitrosobenzene, the role of these sites in the catalytic reaction can be studied. By combining activity measurements with quantitative surface analysis by low-energy ion scattering, which only probes the outermost atomic layer, the catalytic performance can be related to the surface composition. The results suggest that octahedral sites are exposed almost exclusively at the surface of the spinel oxide powders and that only these sites participate in the reaction. The only two low-index planes of the spinel structure which can satisfy this condition are identified as B(111) and D(110). Although the present results pertain to $Mn_3O_4$ and $Co_3O_4$, it is believed that the absence of occupied tetrahedral sites at the surface is a more general property of spinels.** © 1994 Academic Press, Inc.

## INTRODUCTION

An important segment of the products of the chemical industry is formed by catalytic oxidation reactions. These reactions are not only of commercial interest, but also of interest from the point of view of fundamental research on catalysis.

In general, catalytic reactions on metals can be described in terms of reactions occurring in an adsorbed layer, which means that the reaction is limited only to the surface. In heterogeneous oxidation reactions, in which catalytically active oxides are used, the situation is different. In almost all cases, lattice oxygen is used by the reaction. Lattice oxygen then appears in the oxidation products, while the oxygen vacancy in the catalyst is replenished by gaseous molecular oxygen. This mechanism is known as the Mars–van Krevelen mechanism (1). Here the activity and the selectivity of the oxidation reaction depend, *inter alia*, on the metal–oxygen bond strength (the valency of the metal ion), the coordination of the metal in the lattice, the stability and properties of defects, and the morphology of the material.

In addition to selective oxidation reactions, oxides can also be used to catalyze selective reduction reactions, that is, the selective removal of oxygen atoms from organic molecules, such as nitro-compounds and carboxylic acids (deoxygenation). For these reactions, a common reducing agent ($H_2$, CO, $CH_4$) can be used or a part of a larger molecule (autoreduction). In this paper, the selective (auto-) reduction of nitrobenzene to nitrosobenzene is studied on oxides with a spinel structure.

When $MnO_2$ is used as a catalyst, it will be reduced first to $\alpha$-$Mn_3O_4$, which will then act as the catalyst in the reduction. This catalyst has been shown to be very active in the selective (auto-) reduction of nitrobenzene to nitrosobenzene (2–4). The $Mn_3O_4$ catalyst has the hausmannite structure, which is a tetragonally distorted spinel.

The structure and properties of spinels have a wide interest. Spinel ferrites are used as magnetic materials in a wide variety of applications in the electronics industry, ranging from transformer materials to recording media. Another example is the protective oxygen layer formed on some alloys to prevent corrosion. For example, on NiCr alloys, a protective spinel-structured oxide layer is formed. In catalysis, spinel structures can be found in various systems, for example, $\gamma$-$Al_2O_3$, a very common support material, supported oxide catalysts (5–7), and the catalytically active spinels discussed in this investigation.

Spinels are compounds of the general formula

$$A^{\text{tet}}(\text{II})\ B_2^{\text{oct}}(\text{III})\ O_4,$$

in which the formal valency and the cation coordination are indicated.

A principal and interesting question to ask is, which valency and which coordination are responsible for the catalytic activity and selectivity? Since the oxides of several metals are virtually inactive in the reduction of nitrobenzene (Al, Zn), it is possible to study the activity of the different sites separately by the substitution of the

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active transition element (Mn, Co) by inactive Al or Zn ions (2–4). From the present research, it has been concluded that the ions in the tetrahedrally coordinated *A*-sites, i.e., Mn(II) or Co(II), are either inactive or contribute only a little to the overall activity in the nitrobenzene reduction. Similar conclusions have been made earlier with regard to simple oxidation reactions (8–10).

The fact that tetrahedral sites are not active could originate from stronger metal–oxygen bonds due to the lower valency and coordination number. Another possible explanation is that the tetrahedral sites are not accessible to the reactants. Therefore, the *surface* structure of spinels has to be considered in more detail. The unit cell of a "normal" spinel consists of 32 cubic-close-packed oxygen anions. In this unit cell, 8 of the 64 tetrahedral interstices are filled with divalent metal cations, and 16 of the 32 octahedral interstices are filled with trivalent metal cations. In the literature, usually only the low-index planes are taken into consideration when discussing the surfaces of spinels (10–12). Following the suggestion by Knözinger and Ratnasamy (11) and using their notation, one can distinguish six different low-index surface planes, which are shown in Fig. 1. From the figure, it follows that the *A*(111), *C*(110), *E*(100), and *F*(100) planes have both tetrahedral and octahedral sites on the surface, while *B*(111) and *D*(110) only expose octahedrally coordinated cations. Thus, it is possible, in principle, to construct a spinel surface where the tetrahedral sites are not exposed.

Theoretical predictions for the $Co_3O_4$ spinels have been made already by Ziółkowski and Barbaux (10). According to their calculations, the *A*(111) or *D*(110) planes (using the notation as described above (11)) are preferred in the surface, but these predictions do not form a final conclusion. Experimentally, an attempt to elucidate the surface structure has been made by Shelef and co-workers (8, 13) using low-energy ion scattering (LEIS), also termed ion scattering spectroscopy (ISS). They support the idea that the tetrahedrally coordinated cations are not accessible, but they stress the preliminary nature of their results due to the rather low sensitivity in their experiment.

Various studies on spinels using XPS have been reported (14–16). Allen *et al.* (14) concluded from XPS studies that the surface composition of a number of mixed transition-metal oxide spinels reflects the bulk stoichiometry. However, as also pointed out by Vepřek *et al.* (15), who performed both LEIS and XPS on $CuMn_2O_4$, one should keep in mind that the information depth of XPS amounts to several atomic layers of the solid. This is in contrast to LEIS, where it is limited to the topmost atomic layer.

Beaufils and Barbaux have concluded from surface neutron differential diffraction (SDD) studies that the surfaces of the ideal normal spinels $MgAl_2O_4$ (17) and $Co_3O_4$ (18) consist of a mixture of the (111) and (110) planes. Furthermore, because the calculated distances matched only the octahedral $Co^{3+}$ atoms, the exposed faces are, according to the authors, limited to the *D*(110) and *B*(111) planes, which contain only octahedrally coordinated cations. For the distorted spinel structure of $\gamma$-$Al_2O_3$ (17), it is suggested that 80% of the exposed faces have the (110) direction. However, Angevaare *et al.* (3) found an indication (by CO adsorption and IR spectroscopy) that both the divalent and trivalent sites interact with CO.

Obviously, new experiments are required to solve the problem. These have been performed with LEIS because of its extreme sensitivity to the topmost atomic layer. The surface concentrations obtained by LEIS will be discussed below in relation to the most relevant catalytic data of the spinel surface. However, when spinel catalysts are studied, some complications can arise due to the redistribution of the cations among the octahedral and tetrahedral sublattice. Spinels can exhibit so-called "inversion," or alternatively, "oxidative transfer" (4, 19). Then the cations, which in the ideal case of a normal spinel are only in one sublattice (tetrahedral or octahedral), can migrate to the other sites. Therefore, in addition to the normal spinels, which show no inversion, some other spinels were synthesized and included in this study. Another reason for doing so was that these spinels with "inversion" are especially important in catalysis.

## EXPERIMENTAL

### *Catalyst Preparation*

The simple spinels were synthesized from hydroxides, obtained at room temperature by precipitation of the corresponding metal nitrates with ammonia at pH = 9. Then the hydroxides were decomposed in air at 400 K. $CoAl_2O_4$ was calcined in air at 1273 K for 20 h. $MnAl_2O_4$ was calcined in air at 873 K for 20 h after the decomposition of the nitrates, followed by a heat treatment in a flow of 5% $H_2/N_2$ at 1273 K for 48 h to form the required structure. The $Zn_{1-x}Mn_xAl_2O_4$ catalysts were prepared by the same coprecipitation, but then subsequently calcined at 1173 K for 20 h and at 1423 K for 20 h.

### *Catalyst Characterization*

The catalytic activity measurements were carried out in an open flow system with a fixed bed reactor. The reaction conditions were as follows: the reaction temperature was 573 K at 1 bar, the carrier gas was He, containing nitrobenzene at a partial pressure of 70 Pa, and the flow rate was 25 ml/min. The reaction was monitored using a gas chromatograph. For further details, see Ref. (4).

The surface compositions of the catalysts were studied using low-energy ion scattering (LEIS). The most charac-

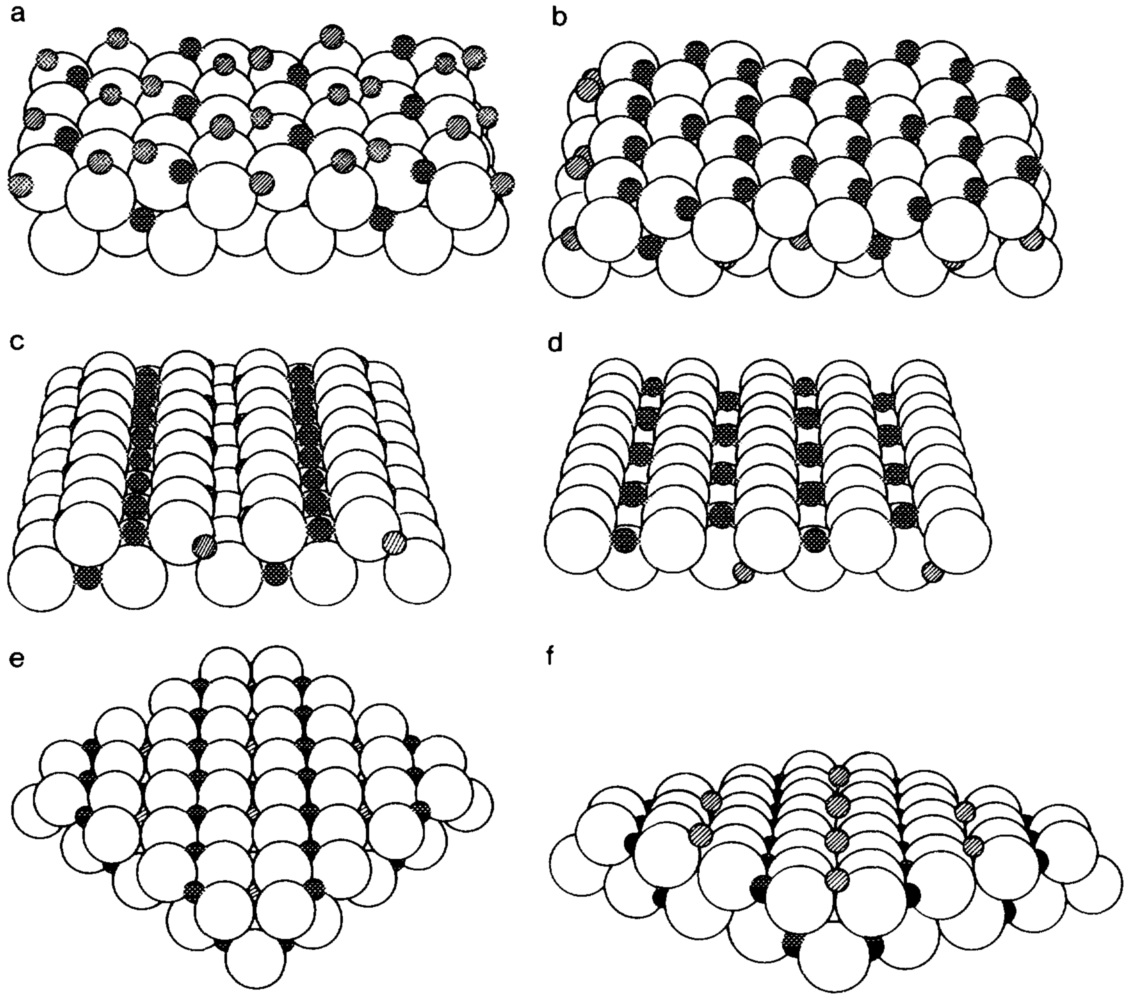

FIG. 1. The low-index planes of a normal spinel structure: (a) (111)*A*, (b) (111)*B*, (c) (110)*C*, (d) (110)*D*, (e) (100)*E*, (f) (100)*F* (notation according to Ref. (11)). The open spheres represent the oxygen anions, the solid spheres the octahedrally coordinated cations, and the crosshatched spheres the tetrahedrally coordinated cations in the normal spinel structure.

teristic feature of LEIS is the fact that the peaks in the spectra result from scattering by the topmost atomic layer of the solid only. There is also a smooth background as a result of ions that have suffered many collisions at greater depth. In catalytic investigations, the selective sensitivity for the outermost atomic layer is essential because when the analysis depth is two or more layers, as in XPS experiments, no exact information can be obtained for the catalytically active top layer and both tetrahedral and octahedral sites will be detected at the same time. Recent investigations have proven the value of LEIS even for the study of rough insulating surfaces, which catalysts mostly are. Reviews of LEIS in catalysis research (and its latest developments) can be found in Refs. (20, 21).

The experiments were performed with the LEIS apparatus NODUS, of which the basic design has been described elsewhere (22). In this setup it is possible to compensate for surface charging by flooding the surface with thermal electrons from all sides. The base pressure of the ultrahigh vacuum (UHV) system is $1 \times 10^{-9}$ mbar, which increases during operation to $1 \times 10^{-8}$ mbar. This increase is due to the inert gas of the ion beam, and does not affect the measurements.

The samples used for the LEIS experiments consisted of powders pressed into pellets. For the LEIS analysis, a $^4$He ion beam of 3 keV was used. The reason for the choice of this relatively high energy, as compared to the energies used by others (20, 21), is to reduce the shielding of the catalytically interesting elements by adsorbed hydrogen on the surface; the shadowing effect is much smaller at these energies compared to the 500–1000 eV range. Furthermore, from earlier results it was found that the influence of roughness on the LEIS results is not as important an effect as was previously reported in the literature (23). To retard destruction, a light ion ($^4$He) is used and the ion flux on the sample is kept as low as

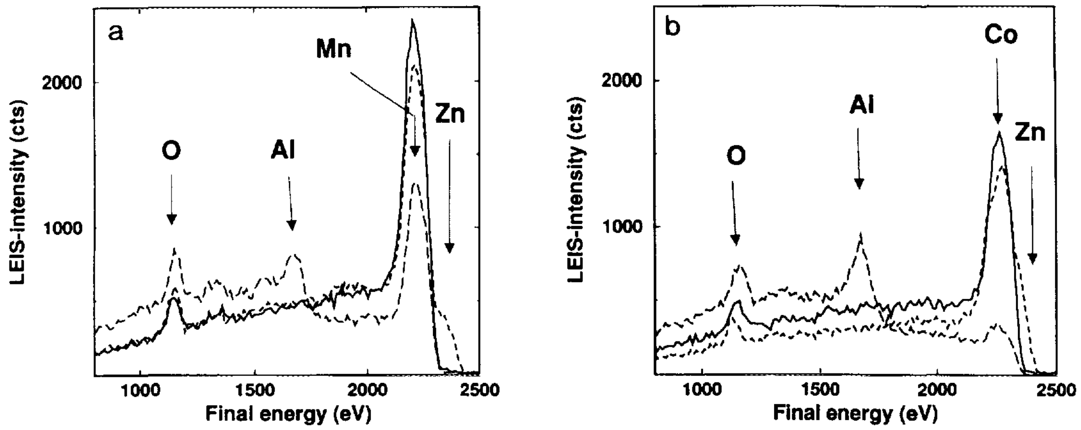

FIG. 2. LEIS spectra from simple spines (3 keV, $He^+$). (a) Mn spinels: (———) $Mn_3O_4$, (—–—) $MnAl_2O_4$, (-------) $ZnMn_2O_4$; (b) Co spinels: (———) $Co_3O_4$, (—–—) $CoAl_2O_4$, (-------) $ZnCo_2O_4$.

possible (less than $10^{13}$ ions/cm$^2$ s), while only the interval of interest is measured. Time-dependent measurements show that the influence of damage by the ion beam on the present data can be neglected. Provided that the scattering conditions are kept constant during the experiments, LEIS signals of the different powder catalysts, having specific surface areas ranging from 0.7 to 30 m$^2$/g, can be compared in an absolute sense.

## RESULTS

This study is divided into two parts. First, various simple spinels are discussed. Second, a series of mixed $Zn_{1-x}Mn_xAl_2O_4$ spinels is discussed, where $x$ ranges from zero to one. XRD showed, as discussed in more detail by Maltha *et al.* (4), that all catalysts studied indeed had the spinel structure. Some oxidative transfer was observed for manganese. This will be discussed in more detail elsewhere (19).

Some typical LEIS spectra of the simple spinels are shown in Figs. 2a and 2b. The different elements can be clearly distinguished when no Zn is present. For the Zn-containing spinels, this is unfortunately not the case. Therefore, the individual peak areas which represent the surface-sensitive information are extracted using a deconvolution of the peaks after background subtraction. The peak shape and the background curve are based on the semiempirical model suggested by Nelson (24) and Young *et al.* (25). The method will be described in more detail elsewhere (26). Due to the overlap of the Mn–Zn and Co–Zn signals and the fact that the Zn signal in the spinel is rather small, the error in the Zn signal is rather large (up to 50%). An example of a fitted spectrum of a simple spinel ($MnAl_2O_4$) is shown in Fig. 3. The spectrum shows

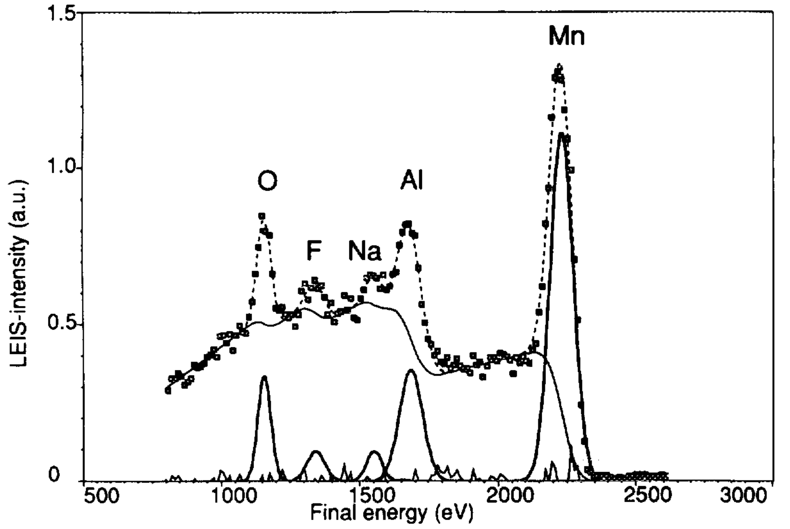

FIG. 3. Example of fitted spectra ($MnAl_2O_4$). The measured data (□), background curve (———), extracted peaks, total fitted curve (background and peaks added) (—–—), and the difference between fit and data are shown.

TABLE 1

Results of the Activity Measurements in the Selective Reduction of Nitrobenzene to Nitrosobenzene ($\phi$NO) and of LEIS Experiments[a]

| Compound | LEIS signals ($10^4$ cts) | | | | | Yield of $\Phi$NO ($10^{-10}$ mol $m^{-2}$ $s^{-1}$) |
|---|---|---|---|---|---|---|
| | O | Al | Mn | Co | Zn | |
| (1) $\gamma$-$Al_2O_3$ | 2.1 | 3.9 | | | | <0.1 |
| (2) $\mathrm{Mn}\mathit{Mn}_2\mathrm{O}_4$ ($\alpha$-$Mn_3O_4$) | 1.4 | | 24.6 | | | 5.5 |
| (3) $\mathrm{Mn}\mathit{Al}_2\mathrm{O}_4$ | 3.2 | 3.3 | 12.4 | | | 2.3 |
| (4) $\mathrm{Zn}\mathit{Mn}_2\mathrm{O}_4$ | 2.0 | | 23.9 | | 1.1 | 5.3 |
| (5) $\mathrm{Co}\mathit{Co}_2\mathrm{O}_4$ ($Co_3O_4$) | 1.4 | | | 14.8 | | 1.6 |
| (6) $\mathrm{Co}\mathit{Al}_2\mathrm{O}_4$ | 2.2 | 4.3 | | 1.9 | | <0.1 |
| (7) $\mathrm{Zn}\mathit{Co}_2\mathrm{O}_4$ | 2.0 | | | 14.1 | 3.0 | 1.5 |
| (8) $\mathrm{Zn}\mathit{Al}_2\mathrm{O}_4$ | 2.0 | 4.2 | | | <0.1 | <0.1 |
| (9) 20% MnO/ZnO | 1.3 | | 5.8 | | 9.8 | — |
| (10) ZnO | 1.7 | | | | 15.8 | <0.1 |

[a] The italic characters indicate octahedral site preference.

a small contamination by F and Na. In most of the other studied spinels, however, no contamination was found.

### *Simple Spinel Surfaces*

A whole series of different spinels has been investigated in which the Co and Mn cations in the different sites were substituted: (a) by Zn in the tetrahedral interstices and (b) by Al in octahedral interstices. The reactivity obtained in the selective reduction of nitrobenzene to nitrosobenzene together with the LEIS-signals, which represent the surface composition, are summarized in Table 1.

From the table, it can be seen that in the Zn-containing spinels, only very little Zn can be detected by LEIS. This confirms the LEIS results of Shelef *et al.* (13), cited in the Introduction. The LEIS signals and, therefore, the surface concentration of the catalytically active Mn are the same for $\alpha$-$Mn_3O_4$ and $ZnMn_2O_4$. A similar effect can be noticed when $Co_3O_4$ and $ZnCo_2O_4$ are compared. This not only holds for the surface composition but also for the catalytic activity (see Table 1). Replacing the cations in the tetrahedral sites by Zn, which is not active in the reaction, has no effect on the performance of the catalyst. The fact that no Zn is detected by LEIS on the surface of the spinels cannot be attributed to a lack of sensitivity for Zn. For ZnO, and for a 20 wt% MnO/ZnO mixture, Zn is easily detected. However, for the $ZnAl_2O_4$ spinel, no Zn is detected on the surface, just as in the other simple oxide spinels.

If the octahedral sites are occupied by Al ($CoAl_2O_4$, $MnAl_2O_4$), the Co and Mn LEIS signal and the catalytic activity decrease. For the $CoAl_2O_4$, only a very small amount of Co is detected and the catalytic activity is also found to decrease dramatically. The analogous decrease in the Mn spinel is not so pronounced. About half of the Mn content is still found on the surface, while the activity, compared to $\alpha$-$Mn_3O_4$, is also about half. This difference between the Co and Mn compounds can be attributed to the oxidative transfer of Mn from tetrahedral to octahedral sites (4). This transfer is much stronger in the Mn-containing spinels than in the Co-containing ones.

The fact that no Zn is detected on the surface of the spinels supports the idea that practically no tetrahedral sites are exposed on the surface. It is also striking that the activity correlates neatly with the surface composition, as measured by LEIS. Thus, all the Mn or Co detected by LEIS is also active in the catalytic reaction. As pointed out in the Introduction, this is in good agreement with earlier results. It seems correct to conclude that the surface of spinel oxide powders contains mainly octahedral sites. This fact limits the possible exposed faces to $B(111)$ or $D(110)$, as shown in Fig. 1.

### *$Zn_{1-x}Mn_xAl_2O_4$ Spinels*

In the second part of the investigation, a series of $Zn_{1-x}Mn_xAl_2O_4$ spinels was studied. The results of the activity measurements, as a function of the Mn content, are shown

TABLE 2

LEIS Signals of $Zn_{1-x}Mn_xAl_2O_4$ Spinels

| $x$ in $Zn_{1-x}Mn_xAl_2O_4$ | LEIS signals ($10^4$ cts) | | | |
|---|---|---|---|---|
| | O | Al | Mn | Zn |
| 0 | 2.0 | 4.2 | 0.0 | <0.1 |
| 0.2 | 2.3 | 2.8 | 5.5 | 0.3 |
| 0.3 | 2.5 | 3.9 | 6.4 | 0.9 |
| 0.5 | 2.4 | 3.1 | 7.8 | 0.3 |
| 0.7 | 2.3 | 2.8 | 8.8 | 0.6 |
| 1.0 | 2.3 | 3.3 | 12.4 | 0.0 |

in Fig. 4a. The corresponding LEIS results can be found in Table 2 and the LEIS signal of the catalytically active Mn is shown in Fig. 4b. One notices immediately an enrichment of Mn in the surface of the catalyst. This is also reflected by its catalytic activity. The surface concentration of Zn is very small. This is in full agreement with the previous section. Since zinc ions do not move to the octahedral sites, it is obvious that no Zn should be detected when the surface consists only of octahedral sites.

## DISCUSSION

This investigation has been performed to support and rationalize the information obtained by determining the catalytic activity in the reduction of nitrobenzene to nitrosobenzene (deoxygenation).

The spinel $Co_3O_4$ is an active catalyst for the above mentioned reaction. The activity is not decreased when Co(II) ions in the tetrahedral positions of the spinel are replaced by redox-inactive Zn(II) ions. The spinel $ZnCo_2O_4$ shows almost the same areal activity as the pure Co spinel, $Co_3O_4$. However, the activity of another fully substituted spinel $CoAl_2O_4$, is practically zero. Two possible explanations which can account for this effect will be considered.

One is that tetrahedrally coordinated Co(II) is not active when it appears on the surface. Alternatively, the surface of spinels is formed by such crystallographic planes that the Co(II) is not directly exposed to the molecules from the gas phase, which collide with the surface, or it is, at least, screened by neighboring oxygen atoms.

The surface-analytical technique LEIS, with its selectivity for the outermost atomic layer, is extremely well suited to distinguish between the two proposed explanations. It appears that in spinels $A(\mathrm{II})B(\mathrm{III})_2O_4$, hardly any $A$(II) cations are exposed to direct collisions of the probing ions. LEIS results thus confirm the claims of Beaufils and Barbaux (17, 18) and of Shelef and Yao (8, 13). Also, the theoretical predictions of Ziółkowski and Barbaux (10) seem to be confirmed.

The catalytic activity of $ZnMn_2O_4$ is almost the same as that of $Mn_3O_4$, in full analogy with the Co spinels. However, although the activity of $MnAl_2O_4$ is lower than that of $Mn_3O_4$ and $ZnMn_2O_4$, it is much higher than that of $CoAl_2O_4$. When the spinel structure is considered, only two possible explanations for this enrichment are mentioned in the literature. First, there could be an inversion of Mn(II) into octahedral positions (27, 28). An alternative explanation can be derived from the paper of Eggert and Riedel (29), which is that there is an oxidative transfer of Mn(II) in the tetrahedrally coordinated sites to Mn(III) in octahedral positions, accompanied by exclusion of $Al_2O_3$ from the spinel. A detailed theoretical analysis of spinel formation revealed that in $MnAl_2O_4$ and in the spinels of nominal composition $Zn_{1-x}Mn_xAl_2O_4$, an oxidative transfer does indeed take place, whereby most probably part of the Mn(II) in the tetrahedral sites also becomes oxidized to $Mn^{oct}$(III). Keeping in mind what has been established with fully substituted spinels, namely that mainly (or even solely) $Mn^{oct}$(III) ions are detected by LEIS in the outermost atomic layer, we can conclude, when inspecting Fig. 3, that the transfer of Mn(II) to octahedral sites made Mn visible for LEIS detection. These experiments thus self-consistently support the conclusions concerning oxidative transfer, as they have been made from the XRD measurements and theoretical calculations (Ziółkowski *et al.* (19)).

The next question is whether the extent of the presence of Mn(III) in the surface of $Zn_{1-x}Mn_xAl_2O_4$ spinels corresponds with the extent of the oxidative transfer in the bulk. When studying the two relevant curves in Fig. 4, we are inclined to conclude that the Mn surface concentration is too high to set the two values equal. The cause for this enrichment can be explained as follows.

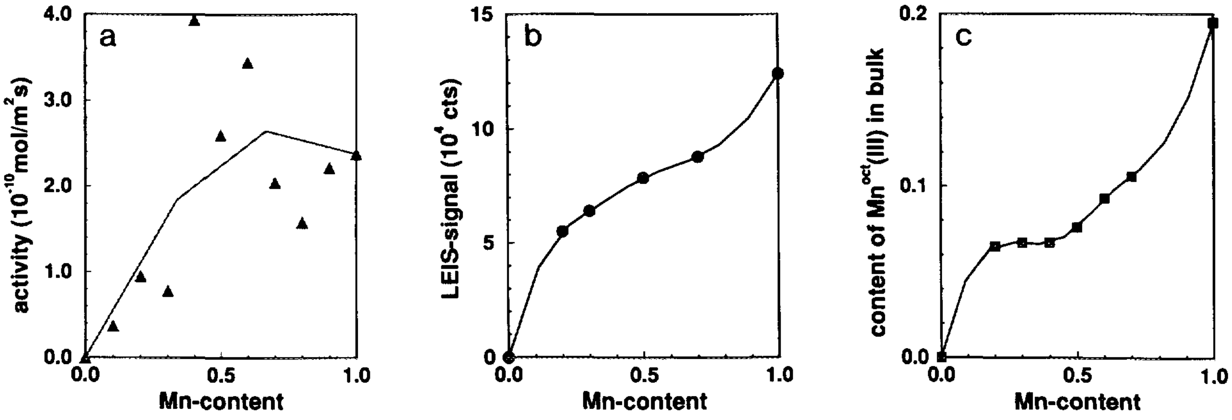

FIG. 4. Results for $Zn_{1-x}Mn_xAl_2O_4$ spinels: (a) activity in the selective reduction of nitrobenzene to nitrosobenzene (a line is drawn to guide the eye); (b) LEIS signals of Mn (see Table 2); (c) oxidative transfer of $Mn^{2+}$ to $Mn^{3+}$ into octahedral sites (19).

The oxidative transfer within the outermost atomic layer of the spinel unit cell could be higher at the surface, or there could be a depletion of Zn. This depletion could be caused by surface segregation or by evaporation of Zn during the spinel preparation. Due to either of these two effects, the surface layer could tend to form a $Mn_3O_4$-like spinel and the catalytic activity would be higher than expected on grounds of the average bulk composition.

XPS results on these mixed oxides performed by Maltha *et al.* (4) suggest a depletion of Zn in the surface region while the Mn follows the trend of the bulk composition in the $Zn_{1-x}Mn_xAl_2O_4$. However, it should be kept in mind that the mean free path for the $Mn(2p_{1/2})$ photoelectrons is about 10 atomic layers, while for the $Zn(2p_{3/2})$, it is limited to only 5 atomic layers. This indicates that the depletion of Zn and the enrichment of Mn that are observed in LEIS are indeed limited to the outermost surface region. Thermal gravimetric analysis seems to support this suggestion (4).

Although for the establishment of the spinel defect structure this is a marginal effect, the surface enrichment in Mn should have an important effect on the catalytic activity. The results presented in Fig. 4 show that this is indeed the case. Hence, the catalytic activity measurements reflect a surface enrichment in Mn, too.

It is interesting to realize the important difference in the surface composition and catalytic activity of the Co spinels on the one hand and that of the Mn spinels on the other. A comparison of entries 5, 6, and 7 in Table 1 shows that practically no Co can be detected on the surface of $CoAl_2O_4$ and the activity is in compliance with it, also very low. However, the $MnAl_2O_4$ spinel shows relatively more surface Mn and a higher activity. A similar surface enrichment of Mn compared to Co in other mixed oxides is also reported by Yang *et al.* (9).

## CONCLUSIONS

The results demonstrate the advantage of the use of the surface-analysis technique of LEIS to analyze catalytically active materials. By the use of absolute LEIS signals in the comparison of the different catalysts, the catalytic data on various spinels could be rationalized and additional support could be obtained for a model of the oxidative transfer of tetrahedral Mn(II) ions to the octahedral positions. The data for the mixed-oxide spinels indicate a strong surface enrichment in Mn. It can furthermore be concluded that the strong correlation between the different techniques suggests that no chemically induced segregation occurs in these oxides. This should be taken into account when discussing reaction models for the selective reduction.

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