

The Active Sites of Manganese- and Cobalt-Containing Catalysts in the Selective Gas Phase Reduction of Nitrobenzene

A. Maltha,* H. F. Kist,* B. Brunet,* J. Ziolkowski,† H. Onishi,‡ Y. Iwasawa,‡ and V. Ponc*¹

*Gorlaeus Laboratories, Leiden University, P. O. Box 9502, 2300 RA Leiden, The Netherlands; †Institute of Catalysis and Surface Chemistry, Polish Academy of Sciences, ul. Niezapominajek, 30-239 Krakow, Poland; and ‡Department of Chemistry, The University of Tokyo, School of Science, Hongo, Bunkyo-ku, Tokyo 113, Japan

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The active sites of the spinels Mn_3O_4 and Co_3O_4 in the selective reduction of nitrobenzene to nitrosobenzene have been investigated, by total and partial substitution of Mn^{n+} (Co^{n+}) ions in tetrahedral position and/or Mn^{n+} (Co^{n+}) ions in octahedral position by redox-inactive ions. Investigation of the catalytic activities of the totally substituted manganese spinel $ZnMn_2O_4$ and that of the totally substituted cobalt spinels $CoAl_2O_4$ and $ZnCo_2O_4$ showed that the manganese and cobalt ions in octahedral position were responsible for the activity of the reaction. $MnAl_2O_4$, however, also showed some activity for the selective reduction of nitrobenzene, which should be due to surface enrichment and/or oxidative transfer of manganese from tetrahedral sites to octahedral sites. XRD results of the partially substituted spinels $Mn_xZn_{1-x}Al_2O_4$ showed that there was a linear correlation between the manganese concentration expressed by x and the lattice constant. Moreover, each sample showed segregation of Al_2O_3 ; again there was a linear correlation between x in a certain series of $Mn_xZn_{1-x}Al_2O_4$ and the amount of free Al_2O_3 . This points to an oxidative transfer of manganese from tetrahedral sites to octahedral sites. XPS showed that the concentration of manganese in the surface layers corresponded roughly to the value x , but the concentration of zinc in the surface layers was much smaller than expected. The catalytic activities of the $Mn_xZn_{1-x}Al_2O_4$ series of catalysts are larger than would be expected from the results on $ZnMn_2O_4$ and $ZnCo_2O_4$. © 1994 Academic Press, Inc.

INTRODUCTION

The selective reduction of nitrobenzene to nitrosobenzene is interesting in the first place because of its practical aspects. Nitrosobenzene is an intermediate of various organic syntheses leading, for example, to widely used antioxidants. Reduction can be performed batchwise as a stoichiometric reaction. An alternative is the continuous gas phase reduction. The disposal of the chemical waste produced by the stoichiometric reaction is so expensive that the modern, waste-lean technology of the gas phase reduction is winning (1, 2).

¹ To whom correspondence should be addressed.

The selective reduction of nitrobenzene to nitrosobenzene is also a very attractive object of fundamental studies. It is known that, for example, Mn_3O_4 is a good catalyst of this reaction (3). The oxide Mn_3O_4 has a spinel structure with Mn^{2+} ions in tetrahedral positions and Mn^{3+} ions in octahedral positions. The obvious question to be addressed is: which of these sites participates in the reaction?

Similar problems were met and studied in selective oxidation reactions (4). To attack the problem, one can replace Mn^{2+} (e.g., by Zn^{2+}) or Mn^{3+} (e.g., by Al^{3+}) with an inactive ion, determine the specific catalytic activity, and compare these values with those obtained with the Mn^{2+} (Mn^{3+}) $_2O_4$ spinels. Analogous experiments can be performed with cobalt spinels.

The conclusions obtained with the just-mentioned materials can be further confirmed by a study in which Mn^{2+} is only partially introduced in $ZnAl_2O_4$. The Mn^{2+} ions occupy the Zn^{2+} sites, i.e., the tetrahedral positions, but a part of Mn can always appear in the octahedral positions. The fraction of manganese in octahedral position can be determined by X-ray diffraction. This opens the possibility to vary the concentration of manganese in octahedral position and monitor the catalytic consequences of these variations.

When working with solid solutions (metal alloys or mixed oxides), one has to worry about the surface composition of the solids, because this composition can be different from the composition in the bulk of the catalyst. In this paper, an attempt has been made to obtain some information about the surface layer composition by standard XPS techniques.

METHODS

Preparation of the Catalysts

Oxides of the nominal composition Mn_3O_4 , $ZnMn_2O_4$, $Zn_{0.5}Mn_{2.5}O_4$, Co_3O_4 , $ZnCo_2O_4$, and $CoAl_2O_4$ were pre-

pared from hydroxides, obtained by precipitation of the corresponding metal nitrates with NH_4OH at pH 9. The hydroxides were decomposed in air at 400 K. Moreover CoAl_2O_4 calcined in air for 20 h at 1273 K.

Mn_2AlO_4 (actually $\text{Mn}^{2+}(\text{Mn}^{3+}\text{Al}^{3+})\text{O}_4$) was prepared from manganese(II) nitrate and aluminum nitrate. The mixture was dehydrated at 400 K for 20 h and calcined at 1473 K for 120 h. The XRD patterns agreed with the literature data. However, no literature XRD data were available for $\text{Zn}_{0.5}\text{Mn}_{2.5}\text{O}_4$. Therefore, this compound was characterized by means of a redox titration.

The $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ catalysts were synthesized in three different ways since it was not known in advance which procedure leads to the best-defined samples.

1. A stoichiometric mixture of the corresponding metal nitrates was calcined at 1173 K for 20 hr and then at 1423 K for 20 hr (series I). The same procedure was repeated, with a slightly different calcination program: calcination at 873 K for 20 hr then at 1323 K for 20 hr, and finally at 1473 K for 20 hr (series I*).

2. The metal hydroxides, made from the corresponding metal nitrates at pH 9, were calcined at 1173 K for 20 hr (series II). This preparation was carried out in order to compare $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ series prepared by different methods. A different surface area was expected to be found with these catalysts. Because the preparation took place at a lower temperature than the preparation mentioned above, larger surface areas were expected. Searching the optimal conditions was thought to be necessary also because of the following reasons. At high temperatures the equilibration is better, but the surface areas of the resulting oxides are smaller and there is a danger that part of Zn evaporates out of the surface. At low temperatures, the kinetic of approaching equilibrium is slower, but the surface areas are larger, the measured rates are therefore higher, and the overall composition is better defined.

3. Since it appeared that the XRD pattern showed extra Al_2O_3 , a mixture of metal nitrates, with stoichiometric amounts of manganese and zinc, but with less aluminum nitrate than the stoichiometric amount, was calcined at 873 K for 20 hr, then at 1323 K for 20 hr and then at 1423 K for 20 hr (series III).

MnAl_2O_4 is a compound that is a little bit more difficult to prepare in air. The sample used here is prepared from the corresponding metal nitrates, which were first calcined in air at 873 K for 20 h and subsequently reduced and equilibrated in a flow of 5% H_2/N_2 at 1273 K for 48 hr. The presence of a reducing gas helps to keep manganese in the valency of 2 and promotes the formation of the required compound. It is more difficult to achieve an exact reproducibility with this mixed oxide than with others.

Catalyst Characterisation

All catalysts used were analysed by X-ray powder diffraction (XRD). Diffractograms were recorded with steps of 0.05° , each step taking 5 sec. Lattice constants were calculated from all available XRD peak positions.

The concentration of the free Al_2O_3 , which appeared in most of the XRD patterns of the $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ spinels, was determined by adding a known concentration of pure Al_2O_3 to some of the $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ spinels.

Element analysis was executed by Mikroanalytisches Labor Pascher, Remagen, Germany. They used the following method: for the analysis of Mn, Zn, and Al, the sample was fused with a mixture of sodium carbonate and sodium tetraborate and solved in a HNO_3/HCl mixture. The detection of the metals was carried out by inductively coupled argon plasma emission spectroscopy. For the determination of oxygen, the sample was melted with a Ce/Ni alloy in a graphite capsule at 2000–3000°C under vacuum. Oxygen is converted into CO and detected by IR spectroscopy.

Surface area measurements were performed on a Quantasorb apparatus from Quantachrome. The simplest one-point method was used.

Thermogravimetric experiments and differential thermal analysis (TG and DTA) were done on a Setaram thermobalance. A flow of 5% H_2/Ar with a flow rate of 50 ml/min was used. The temperature was increased from 300 to 1000 K with 5 K/min. The surface composition was analyzed by X-ray photoelectron spectroscopy (XPS). Samples were pressed to pellets and dried for 2 hr at 400 K (*ex situ*) before they were brought into the apparatus. The peaks used for analysis were integrated and deconvoluted using an XPS fitting program.

The integral peak intensities were corrected for differences in cross sections, using the values calculated by Scofield (5) and for differences in the escape depth and spectrometer sensitivity for electrons of different energies (see the procedure in (6)).

Catalytic Data: Measurements and Evaluation

Catalytic measurements were carried out in an open flow system with a fixed bed reactor. Products were analysed with a GC. The reaction conditions were the following: the standard temperature of the reaction was 573 K, the carrier gas was helium, the pressure of nitrobenzene was 70 Pa (total pressure was 1 bar), and the flow rate was 25 ml/min. Reaction was performed as "autoreduction," which means that fragments of the phenyl ring serve as the reductant of the catalyst. Analysis was performed on line by a GC, using an automatically driven sampling valve. For other details, see (3).

RESULTS

Characterisation of the Catalysts: XRD and Element Analysis

Element analysis was done for the samples $\text{Mn}_{0.5}\text{Zn}_{0.5}\text{Al}_2\text{O}_4$ and $\text{Mn}_{0.7}\text{Zn}_{0.3}\text{Al}_2\text{O}_4$. According to this analysis, the real formulae should be $\text{Mn}_{0.45}\text{Zn}_{0.49}\text{Al}_{1.91}\text{O}_4$ and $\text{Mn}_{0.67}\text{Zn}_{0.30}\text{Al}_2\text{O}_4$. This corresponds quite well with the concentrations used for synthesis.

The XRD results are presented below.

a. Spinel with the nominally total substitution of manganese in tetrahedral and/or octahedral positions. For the purpose of comparison, analogous cobalt catalysts were also prepared and tested. X-ray powder diffraction confirmed that, indeed, Mn_3O_4 , ZnMn_2O_4 , ZnAl_2O_4 , Mn_2AlO_4 , Co_3O_4 , ZnCo_2O_4 , and CoAl_2O_4 have been formed. The diffractogram of a spinel prepared as nominally being $\text{Zn}_{0.5}\text{Mn}_{0.5}\text{O}_4$ is almost identical to that of Mn_3O_4 . An elemental analysis, performed by a titration, shows that the real composition is $\text{Zn}_{0.2}\text{Mn}_{2.8}\text{O}_4$. With all these catalysts, there is no difference observed in the XRD pattern between the fresh and the "spent" (after reaction with nitrobenzene) catalysts.

b. Spinel with a partial substitution of manganese in tetrahedral position by zinc, the $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ catalysts.

Lattice Constant Variations

All oxides of the type $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ (with $x = 0$ to 1) show the same XRD pattern, only the position of the peaks shifts, as expected, to lower diffraction angles with increasing manganese content x . It has been assumed that the oxides have a cubic spinel structure, characterised by a single lattice constant, a . According to the literature data, a is 0.8088 nm for ZnAl_2O_4 and 0.8258 nm for MnAl_2O_4 (7).

Figure 1 shows the lattice constant a as a function of the manganese content in the spinels for the powders of series I and I* (maximum equilibration temperatures are 1423 and 1473 K, respectively). The lattice constants of series I and I* have been placed in one figure, because in most cases there were no differences in lattice constants for a certain x . The MnAl_2O_4 catalyst appeared to be more difficult to reproduce.

A straight line of similar quality is also obtained with the catalysts of series III (maximum equilibration temperature is 1423 K). However, series II shows a larger spreading of the points (maximum equilibration temperature is only 1173 K). This is an indication that the equilibration temperature of 1173 K was probably not high enough. There are several more indications that the equilibration temperature of 1173 K is insufficient. The XRD patterns of the $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ catalysts of series I show rather

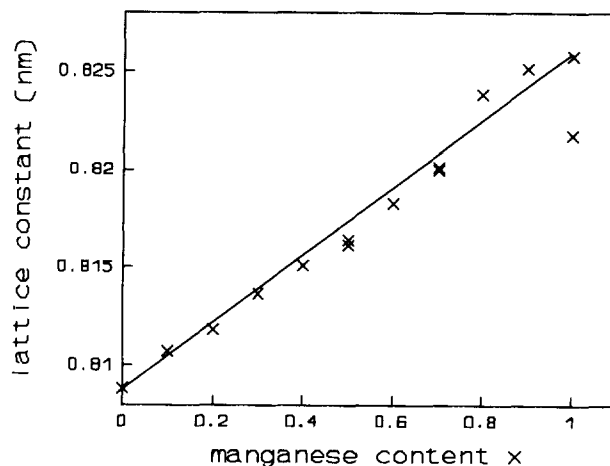


FIG. 1. Lattice constants as a function of the nominal manganese content x of $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ (series I, equilibrated at 1423 K, and series I*, equilibrated at 1473 K). Two series of $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ were synthesised from nitrates (series I, equilibrated at 1423 K, and series I*, equilibrated at 1473 K). The points of both series fall on the same line, indicating that a small change in preparation does not change the lattice constant of $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ with a certain x .

sharp diffraction peaks, but spinels prepared from hydroxides at a lower equilibration temperature show broad peaks with a low signal/noise ratio. The difference between the samples of series I and II manifests itself also by the differences in the total surface area. The surface areas of oxides of series I and III (equilibration temperature of 1423 K) vary between 0.3 and 3 m^2/g , but the surface areas of oxides of series II (maximum equilibration temperature is 1173 K) are about 15 m^2/g . Tables 1 and 2 show the lattice constants and the surface areas of series I (and I*) and II, respectively.

The Presence of Free Al_2O_3 in Annealed Samples

It was seen that even after a prolonged annealing, the samples contain free alumina. The amount of free alumina (in mol% Al_2O_3) increases with the manganese content x , as can be seen in Fig. 2 and Tables 1 and 2. However, the amount of free Al_2O_3 is not the same for series I and I*, indicating that the amount of free Al_2O_3 strongly depends on the details of the preparation method. However, within the same series the results are mutually very consistent and reproducible.

Since it could be expected that the occupation of the octahedral sites by manganese also increases with x , and manganese placed in the octahedral sites actually displaces aluminum out of these sites, we suspected that the amount of free alumina would supply additional information on the spinel formation. The detailed analysis of this phenomenon has been therefore performed and results are presented in a separate paper (8). Here we mention only briefly the main result of that analysis, in Fig. 3.

TABLE 1

Lattice Constants, Content of Free Al_2O_3 , and Surface Area of $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ Prepared from Nitrates (Series I and I*)

x	a (nm)		mol% Al_2O_3	S_{BET} (m^2/g)
	Fresh	Spent		
0_{lit}	0.80883	0.80883	0	—
0.1 ^a	0.81069(4)	0.81071(7)	6	4.6
0.2	0.81200(10)	0.81162(2)	<4	3.1
0.3	0.81398(7)	0.81331(3)	5	0.7
0.4	0.81498(2)	0.81517(8)	8	0.4
0.5	0.81641(7)	0.81640(10)	12	2.7
0.5 ^a	0.81619(5)	0.81610(10)	17	1.0
0.6	0.81840(10)	0.81822(4)	10	0.7
0.7	0.82046(5)	0.81980(20)	12	0.7
0.7 ^a	0.81981(8)	0.82010(10)	22	1.5
0.8		0.82385(5)	14	2.4
0.9 ^a	0.82490(20)	0.82540(20)	32	1.7
1.0	0.82182(8)	0.82170(10)	15	5.7
1_{lit}	0.82580	0.82580	—	—

^a These catalysts were made at slightly different temperatures (series I*) than the unmarked catalysts (series I).

Series II samples show higher amounts of free alumina than samples of series I and the values show also a worse correlation with x than that in Fig. 2. Therefore, we conclude that the amount of free alumina is also dictated by the annealing procedure and the kinetics of the approach to the equilibration. Also the availability of oxygen in the space where the synthesis occurs is obviously important (8).

Aluminum ions, which obviously cannot all occupy the octahedral position at equilibrium, can appear either as free alumina or as Al^{3+} in tetrahedral positions. To discern

TABLE 2

Lattice Constants, Content of Free Al_2O_3 , and Surface Area of $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ Prepared from Hydroxides (Series II)

x	a (nm)		mol% Al_2O_3	S_{BET} (m^2/g)
	Fresh	Spent		
0_{lit}	0.80883	0.80883	0	—
0.1	0.80890(10)	0.80890(40)	0	29
0.5	0.81450(10)	0.81490(20)	14	13
0.7	0.81480(10)	0.81560(10)	22	19
1_{lit}	0.82580	0.82580	—	—

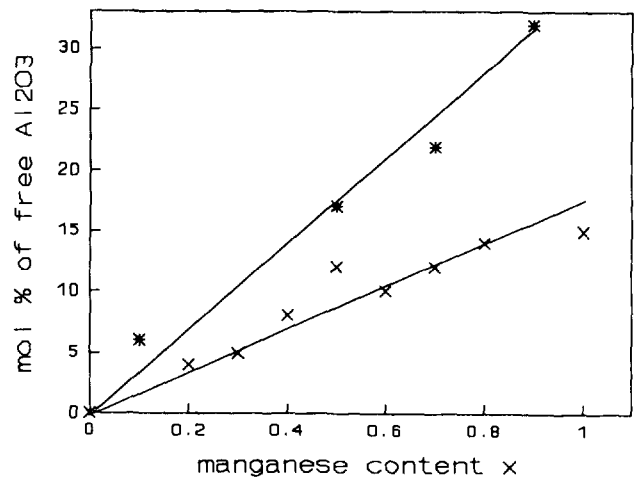


FIG. 2. The amount of free Al_2O_3 (mol%) as a function of the manganese concentration x in $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$. Two series of $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$ were synthesised from nitrates (series I, equilibrated at 1423 K and series I*, equilibrated at 1473 K). The amount of free Al_2O_3 increases with the manganese content x , but is different for series I (lower line) and series I* (upper line).

between these two possibilities is of great importance. Fortunately, the NMR-MAS analysis can help here. It is known from the research on zeolites that free aluminum ions, with Al^{3+} in octahedral position, and framework aluminum ions, with Al^{3+} in tetrahedral position, differ in their NMR spectra. It appeared that the spinels studied here do not contain Al^{3+} in the tetrahedral positions at all. In the strict sense, the spinels are thus not inverted, although manganese is divided over tetrahedral and octa-

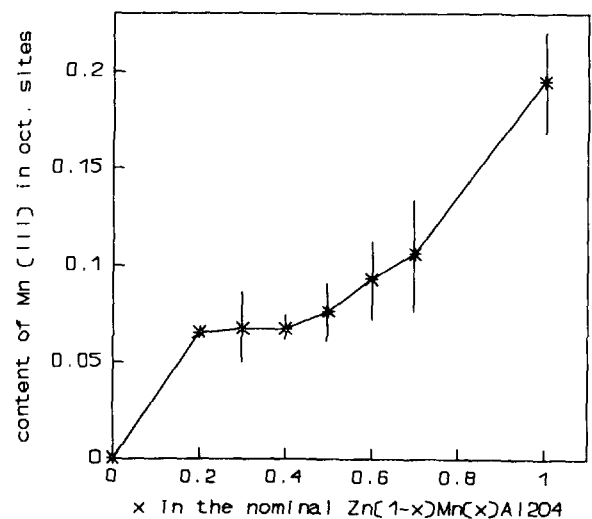


FIG. 3. The extent of the oxidative manganese transfer as a function of the manganese content x in the spinel $\text{Mn}_x\text{Zn}_{1-x}\text{Al}_2\text{O}_4$, the errors of estimation are indicated (from Ref. (8)).

TABLE 3
Reduction Temperature of Different Catalysts, Measured by TGA

Catalyst, nominal composition	T_{red} (K)
Mn_3O_4	740
$ZnMn_2O_4$	780
$Zn_{0.2}Mn_{2.8}O_4$	723
$Mn_{0.2}Zn_{0.8}Al_2O_4$	>1073
$Mn_{0.5}Zn_{0.5}Al_2O_4$	>1073
$MnAl_2O_4$	>1073
Mn_2AlO_4	>1073

hedral positions. Rather, we observe, with substituted spinels, an oxidative transfer of $Mn^{2+}(T_h)$ to $Mn^{3+}(O_h)$ positions, accompanied by a partial oxidation of Mn^{2+} in the tetrahedral positions (8).

Analysis of the distribution of manganese over the octahedral and tetrahedral positions is performed elsewhere (8). Here we present only the ultimate results, the extent of the oxidative manganese transfer as a function of the manganese content x in the spinel $Mn_xZn_{1-x}Al_2O_4$. Only the $MnAl_2O_4$ catalyst in Fig. 3 is not the same sample described in this article.

Reducibility of Various Spinel

The most relevant information obtained by thermogravimetric analysis (TGA) has been summarised in Table 3; the "reduction temperature" is that value where the derivative of the temperature-weight graph is most negative.

The reducibility of $ZnMn_2O_4$ is marginally higher than the reducibility of Mn_3O_4 and $Zn_{0.2}Mn_{2.8}O_4$. The spinels, which contain aluminum, like Mn_2AlO_4 and the oxides of the series of $Mn_xZn_{1-x}Al_2O_4$, are not reduced below the temperature of 1073 K, the maximum temperature that could be achieved with the instrument available. However, by differential thermal analysis it can be seen with all catalysts studied that there is an endothermic peak at 553 K. Moreover, there is a small loss in weight (0.05%) seen at that temperature with the catalyst $Mn_{0.5}Zn_{0.5}Al_2O_4$. According to this weight loss, only a small amount of Mn^{3+} would have been reduced to Mn^{2+} .

Composition of the Surface Layers

By using the standard XPS apparatus as available to us, analysis can be performed with Mg $K\alpha$ radiation under such conditions that the kinetic energy of escaping electrons is 594 eV ($Mn2p_{1/2}$), 1200 eV ($Mn3p$), 717 eV ($O1s$), 1226 eV ($O2s$), 1226 eV ($O2s$), 225 eV ($Zn2p_{3/2}$), 1108 eV ($Zn3s$), and 1129 eV ($Al2s$), respectively. The lowest value of these values corresponds to the mean free path of

electrons $\lambda = 1.4$ nm (about 5 monolayers), the highest value to $\lambda = 3.4$ nm (about 13 monolayers (9)).

Due to this, the $Mn2p_{1/2}/O1s$ ratios are reflecting the composition of a thinner surface layer than the $Mn3p/O2s$ and $Zn3s/O2s$ ratios.

The corrected ratios (see Methods) have been multiplied by a factor of 4 for a better comparison of the ratios obtained by XPS and the various stoichiometric formulae of the spinels shown in the first column of Table 4.

Determination of the ratios of concentrations in the surface layers by using the theoretical correction factors cannot be considered as very exact and, therefore, the absolute values must be discussed with caution. However, the various trends in changes accompanying the variations in the nominal composition are more reliable. The values in Table 4 confirm the expected general tendency of the composition of the surface layers in Zn, Mn, and Al, in Mn_3O_4 , $ZnMn_2O_4$, and in the $Mn_xZn_{1-x}Al_2O_4$ spinels: the higher the x , the higher the Mn/O signal ratio and the lower the Zn/O signal ratio. Moreover, the $Zn2p_{3/2}/O1s$ ratios (thinner surface layers) are much lower than would be expected from the stoichiometry, which indicates that the outermost surface layers are depleted in zinc. However, there is a considerable spread of values and the indicated increase is not exactly linear.

At the moment, we have no good explanation of the low Mn/O signal ratio observed with $MnAl_2O_4$ (0.62 instead of 1). Perhaps Al_2O_3 is decorating the surface of the spinel. The surface content of manganese, characterised by the XPS signal ratio $Mn2p_{1/2}/O1s$, is plotted in Fig. 4 as a function of the manganese content x according to the concentration used in the precursors of spinel synthesis.

Catalytic Activity in the Nitrobenzene Formation

The activity in the reduction of nitrobenzene to nitrosobenzene under standard conditions is expressed as the

TABLE 4

The Corrected Mn/O, Zn/O, and Al/O Ratios of Different Catalysts of the Series I of $Mn_xZn_{1-x}Al_2O_4$, Determined by XPS

Catalyst	$Mn2p_{1/2}/O1s$	$Mn3p/O2s$	$Zn2p_{3/2}/O1s$	$Al2s/O1s$
Mn_3O_4	2.73	2.77		
$ZnMn_2O_4$	2.00		0.44	
$Mn_{0.3}Zn_{0.7}Al_2O_4$	0.40		0.13	1.96
$Mn_{0.4}Zn_{0.6}Al_2O_4$	0.36	0.59	0.13	1.69
$Mn_{0.5}Zn_{0.5}Al_2O_4$	0.40	0.55	0.09	1.84
$Mn_{0.6}Zn_{0.4}Al_2O_4$	0.44	0.40	0.09	1.61
$Mn_{0.7}Zn_{0.3}Al_2O_4$	0.73	0.79	0.09	1.65
$Mn_{0.8}Zn_{0.2}Al_2O_4$	0.80	0.91	0.07	1.69
$MnAl_2O_4$	0.62			1.80

Note. All ratios have been also multiplied by "4," as explained in the text.

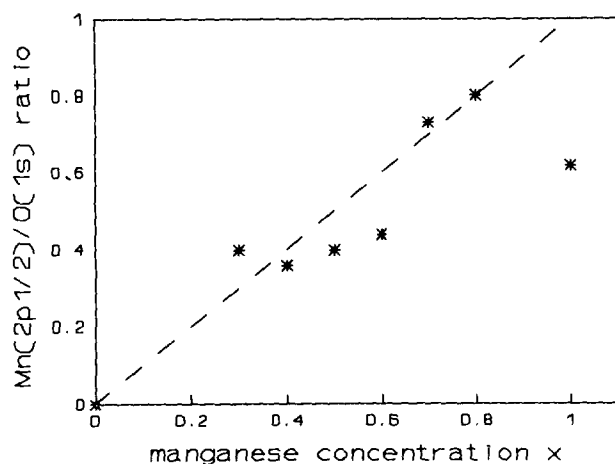


FIG. 4. The $Mn(2p_{1/2})/O(1s)$ signal ratio of series I as a function of x , calculated from the used amounts of precursors.

rate of nitrosobenzene formation in 10^{-10} mol/m² sec.

The data for fully substituted spinels are presented in Fig. 5. Surface areas of catalysts used are in Table 5. It can be seen that Mn_3O_4 , $ZnMn_2O_4$, and $Zn_{0.2}Mn_{2.8}O_4$ have almost the same activity. The same holds for Co_3O_4 and $ZnCo_2O_4$. $ZnAl_2O_4$ does not show any activity for the reduction of nitrobenzene. $CoAl_2O_4$ has a very low activity. However, $MnAl_2O_4$ shows a lower but still considerable reaction rate. The value shown for Mn_2AlO_4 ($Mn^{2+}(Mn^{3+}, Al^{3+})O_4$) lies between the values of $MnAl_2O_4$

TABLE 5
The Rate of Reaction and Surface Area of Mn_3O_4 , Mn-Substituted Catalysts, Co_3O_4 , and Co-Substituted Catalysts

Catalyst	Rate of reaction (10^{-10} mol/m ² s)	S_{BET} (m ² /g)
Mn_3O_4	5.5	20.0
$ZnMn_2O_4$	5.3	22.8
$Zn_{0.2}Mn_{2.8}O_4$	6.2	17.1
$MnAl_2O_4$	2.3	5.2
$ZnAl_2O_4$	0	73.3
Co_3O_4	1.6	9.6
$ZnCo_2O_4$	1.5	11.1
$CoAl_2O_4$	0.03	15.1
Mn_2AlO_4	3.9	0.4

and Mn_3O_4 . However, due to a small surface area, this value is much less accurate than the other values in Table 5.

Figure 6 shows the catalytic data of the partially substituted $Mn_xZn_{1-x}Al_2O_4$ spinels of series I. The rate of nitrosobenzene formation has been corrected for the amount of free alumina (surface area and activity corrections). It is assumed that the Al_2O_3 particles were divided through the catalyst in a uniform way. The left side shows the values for x from 0 to 1, and the right side also includes $ZnMn_2O_4$ (formally $x = 2$) and Mn_3O_4 (formally $x = 3$).

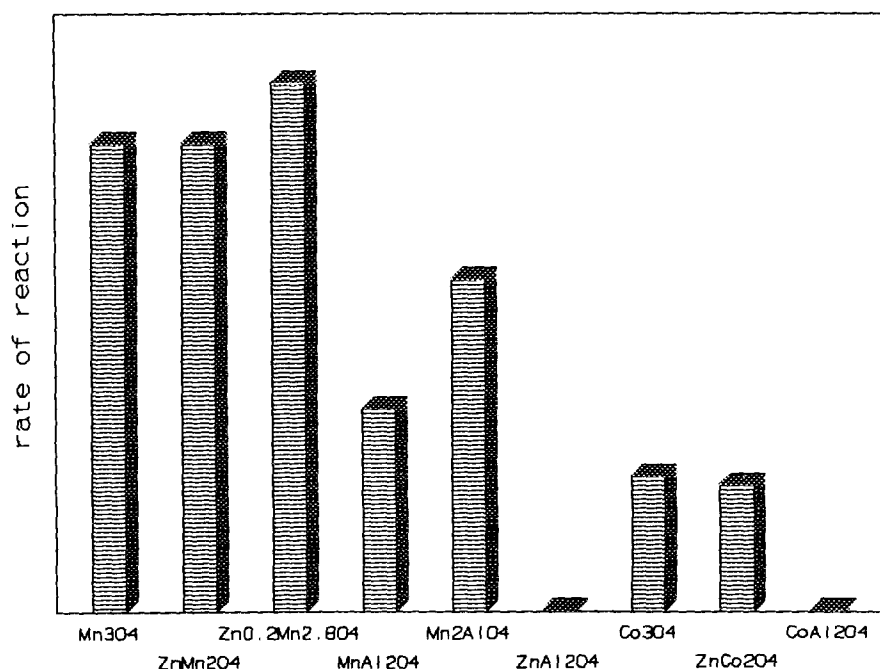


FIG. 5. The rate of nitrosobenzene formation as a function of different manganese and cobalt oxide catalysts.

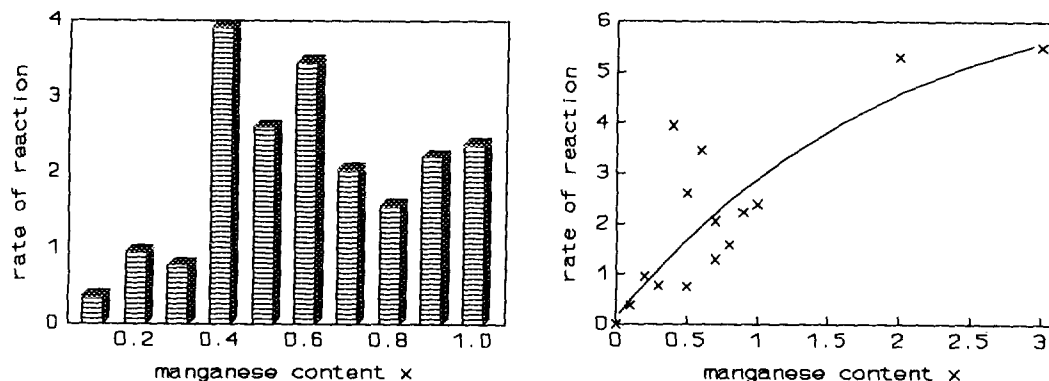


FIG. 6. The rate of nitrosobenzene formation a function of the manganese content x in $Mn_xZn_{1-x}Al_2O_4$ (series I for $x = 0$ to 1 is shown on the left side; the graph on the right side includes Mn_3O_4 (virtually $x = 3$)).

It can be seen that the activity increases when the concentration of manganese, calculated from the amounts of precursors used, increases essentially. Similar results are obtained with series II and III.

DISCUSSION

The areal catalytic activity of spinels having more or less all manganese in octahedral positions is almost the same. An analogous comparison holds for cobalt-containing spinels. However, with spinels, in which manganese or cobalt ions are nominally in tetrahedral positions, the areal activity is much lower. The spinel $CoAl_2O_4$ shows only a very small fraction of the activity of Co_3O_4 ; the residual activity of $MnAl_2O_4$ is low but measurable. The last result indicates that in $MnAl_2O_4$ some manganese ions are likely in octahedral positions. It is worthwhile to mention that the catalytic activity of spinels in the dioxygen isotopic exchange is mainly determined by the nature of the triply charged octahedrally coordinated cations in $ZnFe_2O_4$, $ZnMn_2O_4$, $ZnCr_2O_4$, and $ZnCo_2O_4$. The role of the double charged cations is less important (10). The question is how does Mn get from the tetrahedral positions into the octahedral positions? A known example is $NiAl_2O_4$, in which a mere exchange of sites between Ni and Al has been postulated (11) and documented (12). However, spinels studied in this paper are different in detail from the inverted spinels just mentioned (11, 12). The NMR analysis revealed a full absence of aluminum ions in the tetrahedral positions. Therefore, in our case it was not an "inversion" in the spinels, but rather an "oxidative transfer" of manganese, accompanied by exclusion of Al_2O_3 . A similar phenomenon was observed with $CrAl_2O_4$ spinels (13). The idea that the activity of $MnAl_2O_4$ should be ascribed to the oxidative transfer of manganese into the octahedral positions is confirmed in this paper by the results obtained with partially substi-

tuted spinels. With $Mn_xZn_{1-x}Al_2O_4$ spinels the activity increases with x as does the content of Mn^{3+} in the octahedral position (Figs. 3 and 6). The scatter of experimental data does not allow us to be beyond this qualitative statement.

It is, of course, an intriguing question why only one of the manganese cations manifests the catalytic activity. There could be two reasons:

- Mn^{2+} is not present in the crystallographic planes, which form the surface of the catalyst particles. There is some indication for this, because the XPS signals show that the surface layers are depleted in zinc, another divalent cation.
- Mn^{2+} is intrinsically not active, for example, because its metal-oxygen bond strength is too high.

To solve this problem definitively, experiments are required to be performed by a surface analytic technique sensitive to the outermost surface layer only. Such a technique is, for example, a selective chemisorption or low-energy ion scattering spectroscopy (LEIS). If the explanation of the observed IR spectra of chemisorbed CO, as presented in (14) is correct, both Mn^{2+} and Mn^{3+} should be present in the surface. Shelef *et al.* (15) made a cautious conclusion that the Mn^{2+} ions are so screened by oxygen anions that they are not easily accessible from the gas phase. However, the authors warned that their LEIS technique might not have been sensitive enough to detect Mn^{2+} in the tetrahedral positions in the surface of the spinels. Obviously, measurements by a more sensitive instrument are necessary and they have been performed (16). From the results available at the moment, it seems that effect "a" prevails.

CONCLUSION

The experimental data and their evaluation indicate that the sites active in the selective reduction of nitrobenzene

to nitrosobenzene are the manganese or cobalt ions in the octahedral positions of spinels studied.

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