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Preparation and Characterization of Phases Formed by the Reaction of Nickel(II) and Cobalt(II) Precursors with MgO, $MgAl_2O_4$, and γ-Al_2O_3

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Ni(II) and Co(II) precursors were reacted with MgO, $MgAl_2O_4$, and γ-Al_2O_3. The reaction products were characterized by X-ray analysis, temperature programmed reduction, and magnetic susceptibility. The different stabilizations toward reduction were correlated with the site preference and formal valence state of the transition metal ions. © 1992 Academic Press, Inc.

Introduction

In an earlier study (*1*), various cobalt oxide precursors were reacted with γ-Al_2O_3. Their properties were characterized by X-ray analysis, temperature-programmed reduction, and measurement of magnetic susceptibility. It was shown that both the precursor used and the pH of the solution had a profound impact on the interaction of cobalt with γ-Al_2O_3.

Support interactions can influence the stabilization of a transition metal oxide toward reduction to the metal and have been the subject of many investigations (*2–8*). M. Schwartz *et al.* (*9*) have reported that MgO greatly stabilized NiO toward reduction. However, when NiO was dispersed on carbon, no stabilization was observed. M. Montes (*10*) studied the influence of metal–support interaction, reducibility, and catalytic activity of Ni/SiO_2. However, there has been little systematic study of the influence of different nontransition metal oxides on the stabilization of nickel(II) and cobalt(II) toward reduction. It was the purpose of the present study to investigate the interactions of nickel(II) and cobalt(II) with the oxides MgO, $MgAl_2O_4$, and γ-Al_2O_3 and to relate these interactions with their observed stability toward reduction.

Experimental

Preparation of Samples

The oxides used in this study were MgO, $MgAl_2O_4$, and γ-Al_2O_3. MgO was prepared by the decomposition of magnesium nitrate at 950°C for 24 hr. $MgAl_2O_4$ was synthesized by dissolving appropriate weights of magnesium and aluminum nitrates in water, adjusting the pH of the solution with NH_4OH to pH 10, and evaporating the solution to dryness. The product was carefully decomposed at 450°C. The resulting mixed oxides were heated in air at 950°C for 24 hr. The γ-Al_2O_3 was prepared by heating boehmite at 500°C in air for 24 hr. Boehmite (γ-AlOOH)

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was prepared hydrothermally according to the procedure of A. B. Kiss (*11*).

Samples of bulk NiO, $NiAl_2O_4$, CoO, Co_3O_4, and $CoAl_2O_4$ were prepared, and their properties compared with those of samples prepared from the Ni(II) and Co(II) precursors reacted with MgO, $MgAl_2O_4$, and γ-Al_2O_3. Bulk NiO was prepared by the decomposition of nickel acetate at 600°C in air for 24 hr. $NiAl_2O_4$ was synthesized by the codecomposition of nickel and aluminum nitrates at 1100°C in air for 24 hr. CoO, Co_3O_4, and $CoAl_2O_4$ were prepared as previously described (*1*). The phases MgO, γ-Al_2O_3, $MgAl_2O_4$, NiO, and $NiAl_2O_4$ were confirmed by X-ray diffraction analyses.

The molecular weights of $Al(NO_3)_3 \cdot 9H_2O$, $Ni(OAc)_2 \cdot 4H_2O$, $Mg(OAc)_2 \cdot 4H_2O$, and $Ni(NO_3)_2 \cdot 6H_2O$ were determined by thermogravimetric analysis and found to be 366, 262, 204, and 298, respectively. These values were compared to the calculated values 375, 249, 214, and 291, and suitable corrections were made in order to adjust the proper stoichiometry of the catalyst.

A nickel acetate precursor was reacted with γ-Al_2O_3 and $MgAl_2O_4$ to give products containing, respectively, 14.0 and 10.45 weight% with respect to NiO. (Weight% NiO = 100 × weight NiO/(weight NiO + weight γ-Al_2O_3 or $MgAl_2O_4$)). γ-Al_2O_3 and $MgAl_2O_4$ were impregnated with a 0.049-*M* nickel acetate solution at pH 2.7, dried on a hot plate, and then heated in a drying oven at 230°C for 24 hr. The final heat treatment was carried out at 950°C in air for 24 hr. Samples of $Ni_xMg_{1-x}O$ were formed by the codecomposition of nickel and magnesium acetates in air at 950°C for 24 hr.

Reaction products of cobalt acetate with γ-Al_2O_3 and $MgAl_2O_4$ were synthesized by procedures analogous to those used for the nickel samples. Members of the series $Co_xMg_{1-x}O$ were obtained by heating CoO and MgO in sealed evacuated silica tubes at 950°C. The samples were reground under nitrogen twice during the process.

Characterization of Samples

X-ray powder diffraction analyses of the samples were obtained using a Philips diffractometer and monochromatic high intensity Cu$K\alpha_1$ radiation ($\lambda = 1.5405$ Å). The diffraction patterns were taken in the range of $12° < 2\theta < 72°$ with a scan rate of 1° 2θ/min and a chart speed of 30 in/hr.

Magnetic susceptibility was measured with a Faraday balance at a field strength of 10.4 kOe from liquid nitrogen to room temperature. Honda–Owens (field dependency) measurements (susceptibility vs $1/H$) were also made at room temperature and liquid nitrogen temperature, and all magnetic susceptibility data were corrected for core diamagnetism.

Temperature programmed reduction (TPR) measurements were taken using a Cahn system 113 thermal balance. All samples (approximately 50 mg) were preheated in air at 400°C for 4 hr to remove most of the residual water before reduction. However, to correct for all of the residual water, samples of the oxides MgO, $MgAl_2O_4$, and γ-Al_2O_3 were heated in dry air to 950°C, and their weight losses were used to correct the initial sample weights. The samples were cooled down to room temperature and were then heated at 60°C/hr from room temperature to 950°C in a purified Ar/H_2 (85/15) atmosphere; the rate of gas flow was 60 ml/min. The samples were maintained at 950°C for 4 hr in order to ensure constant weight.

Results and Discussion

MgO, NiO, and CoO crystallize with the rock salt structure (Table I). Hence, both NiO and CoO can form solid state solutions with MgO. The samples of $Ni_xMg_{1-x}O$ were prepared by double decomposition of the appropriate acetates in air at 950°C for 24 hr. The formation of a solid solution was confirmed by X-ray analysis.

Temperature programmed reductions of

TABLE I

PHASES FORMED BY THE REACTION OF Ni(II) AND Co(II) PRECURSORS WITH VARIOUS OXIDES

Supports	Temperature of decomposition (°C)	Phases
Bulk NiO	600	Rock salt
$Ni_xMg_{1-x}O$	950	Rock salt
$Ni(II)/MgAl_2O_4$	950	Rock salt + spinel
$Ni(II)/\gamma\text{-}Al_2O_3$	950	Spinel
Bulk CoO	1100	Rock salt
$Co_xMg_{1-x}O$	950	Rock salt
$Co(II)/MgAl_2O_4$	950	Rock salt + spinel
$Co(II)/\gamma\text{-}Al_2O_3$	950	Spinel

TABLE III

TEMPERATURE PROGRAMMED REDUCTION DATA FOR $Co_xMg_{1-x}O$ SAMPLES AT 950°C

Samples	Weight loss (%)	Reduction percentage Co(II) → Co(0)
$Co_{0.1}Mg_{0.9}O$	0.56	15.3
$Co_{0.2}Mg_{0.8}O$	1.60	23.6
$Co_{0.5}Mg_{0.5}O$	4.28	30.9
$Co_{0.8}Mg_{0.2}O$	15.32	81.4
$Co_{0.9}Mg_{0.1}O$	19.86	98.5
$Co_{0.95}Mg_{0.05}O$	20.57	99.1
CoO	21.35	100

the $Ni_xMg_{1-x}O$ samples were carried out under an atmosphere of Ar/H_2 (85/15) from room temperature to 950°C. It can be seen from Table II that there was no apparent reduction of $Ni_{0.1}Mg_{0.9}O$. Although pure NiO was completely reduced at 950°C, the members of the solid solution were not reduced completely at 950°C. The cobalt samples, on the other hand, reduced more readily. From Table III, it can be seen that the cobalt in $Co_{0.1}Mg_{0.9}O$ was approximately 15% reduced at 950°C. This reduced stability of the cobalt samples is consistent with the greater stabilization of Ni(II) $3d^8$ on an octahedral site.

Bulk NiO and CoO show antiferromagnetic behavior. Magnetic susceptibility measurements of $Ni_{0.1}Mg_{0.9}O$ and $Co_{0.1}Mg_{0.9}O$ indicated that Co(II) and Ni(II) show paramagnetic behavior. The observed moments of 2.8 BM and 5.5 BM for Ni(II) and Co(II), respectively (Table IV), are consistent with octahedral coordination of these ions.

TABLE II

TEMPERATURE PROGRAMMED REDUCTION DATA FOR $Ni_xMg_{1-x}O$ SAMPLES AT 950°C

Samples	Weight loss (%)	Reduction percentage Ni(II) → Ni(0)
$Ni_{0.1}Mg_{0.9}O$	0	0
$Ni_{0.2}Mg_{0.8}O$	0.63	9.3
$Ni_{0.5}Mg_{0.5}O$	2.68	19.3
$Ni_{0.8}Mg_{0.2}O$	13.96[a]	73.9
$Ni_{0.9}Mg_{0.1}O$	19.09[b]	94.5
$Ni_{0.95}Mg_{0.05}O$	20.20	97.0
NiO	21.41[c]	100

[a] Reduction begins at 430°C.
[b] Reduction begins at 340°C.
[c] Reduction begins at 230°C

X-ray analysis of the product (14.0 wt% NiO) formed by the reaction of nickel acetate with $\gamma\text{-}Al_2O_3$ indicated that only a spinel phase is formed. The TPR results showed that this sample was almost completely reduced at 950°C. The degree of reduction was similar to that observed for bulk $NiAl_2O_4$. Furthermore, the observed magnetic moment was 3.3 BM, which is almost identical to the value for Ni(II) in bulk $NiAl_2O_4$ (3.2

TABLE IV

MAGNETIC SUSCEPTIBILITY DATA FOR NICKEL(II) AND COBALT(II) REACTION PRODUCTS WITH MgO, $MgAl_2O_4$, AND $\gamma\text{-}Al_2O_3$

Samples	μ(BM)/mol Ni(Co)	θ(K)
NiO	4.6[a]	−1961
$NiAl_2O_4$	3.2	−39
CoO	5.2	−309
$CoAl_2O_4$	4.2	−94
$Ni_{0.1}Mg_{0.9}O$	2.8	−27
$Ni(II)/MgAl_2O_4$	2.8	−62
$Ni(II)/\gamma\text{-}Al_2O_3$	3.3	−9.5
$Co_{0.1}Mg_{0.9}O$	5.5	−65
$Co(II)/MgAl_2O_4$	4.1	−36
$Co(II)/\gamma\text{-}Al_2O_3$	4.2	−45

[a] The apparent value differs from the spin-only value of 2.8 because the measurement could not be made at a temperature sufficiently greater than the Néel temperature.

TABLE V

TEMPERATURE PROGRAMMED REDUCTION DATA FOR NICKEL(II) AND COBALT(II) REACTION PRODUCTS WITH $MgAl_2O_4$ AND γ-Al_2O_3 AT 950°C

Samples	Weight loss (%)	Reduction percentage
Ni(II)/$MgAl_2O_4$ (10.45 wt%, NiO)	2.14[a]	96
Ni(II)/γ-Al_2O_3 (14.0 wt%, NiO)	2.87	96
$NiAl_2O_4$	8.76	97
Co(II)/$MgAl_2O_4$ (10.32 wt%, CoO)	2.21	100
Co(II)/γ-Al_2O_3 (13.93 wt%, CoO)	2.72	91
$CoAl_2O_4$	8.37	93

Note. wt% defined as 100 × wt(*Mo*)/[wt(*Mo*) + wt(oxide)], *Mo* = NiO, CoO.

[a] Reduction begins at 450°C.

BM). These results imply that the reacted nickel behaves similarly to what is observed in bulk $NiAl_2O_4$.

The product formed by the reaction of cobalt acetate with γ-Al_2O_3 was described previously (*1*). X-ray diffraction analysis, temperature programmed reduction, and magnetic susceptibility measurements (Tables I, IV, V) indicated that all of the Co(II) occupies tetrahedral sites of the spinel structure.

X-ray analysis of the products (10.45 wt% NiO) formed by the reaction of nickel acetate with $MgAl_2O_4$ indicated the formation of both rock salt and spinel phases. Magnetic susceptibility measurements (Table IV) confirmed the octahedral coordination of Ni(II). The value of the Weiss constant of −62 K for this sample, compared to −1961 K for bulk NiO and −39 K for bulk $NiAl_2O_4$, suggests that the nickel is present on the octahedral sites of the spinel. Consequently, an equivalent amount of aluminum displaces magnesium from tetrahedral sites. This is consistent with the formation of MgO (rock salt) as a second phase. From Table V, it can be seen that the reduction of this sample was nearly complete at 950°C. This is in agreement with the degree of reduction of bulk $NiAl_2O_4$. X-ray analysis of the reduction products indicated the formation of metallic nickel and magnesium aluminate spinel. Thus when nickel is removed from the spinel structure, Mg(II) ions reoccupy the tetrahedral sites of the spinel, and the aluminum(III) ions that had been displaced to tetrahedral sites move back to octahedral sites.

X-ray diffraction analysis of the products formed by the reaction of cobalt acetate with $MgAl_2O_4$ indicated the presence of two phases, i.e., both rock salt and spinel structures. Magnetic susceptibility measurements indicated that the Co(II) was located on tetrahedral sites (Table IV), which is similar to the behavior of Co(II) on γ-Al_2O_3. Hence, Co(II) is present primarily in the spinel structure, and the rock salt must be almost pure MgO. X-ray analysis of the reduction products from this sample, which was reduced at a maximum temperature of 950°C in an atmosphere of Ar/H_2 (85/15), showed the presence of metallic cubic cobalt and spinel phase. In this reduction, all of the Co(II) was reduced to cobalt metal (Table V). There was no evidence for the existence of a rock salt phase. These results indicate that after the cobalt ions were reduced, the Mg(II) ions reoccupied the tetrahedral sites.

Conclusions

There is a marked difference in the stabilization of Ni(II) and Co(II) toward reduction when reacted with MgO, $MgAl_2O_4$, and γ-Al_2O_3. These differences can be attributed to the octahedral site preference of Ni(II) versus the tetrahedral site preference of Co(II).

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