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The Preparation and Characterization of the Phases Formed by the Reactions of Nickel and Lanthanum Nitrates with Magnesium Aluminate

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Samples of Ni(II) on $MgAl_2O_4$ and of Ni(II) and La(III) on $MgAl_2O_4$ were prepared and characterized by X-ray diffraction, temperature programmed reduction, and magnetic susceptibility. The results are consistent with the octahedral site preference of Ni(II) in the spinel phase. The role of lanthanum is discussed in terms of the formation of a perovskite-phase $LaAlO_3$. © 1992 Academic Press, Inc.

Introduction

Supported transition metal oxide catalysts have attracted much attention because of their wide applications as oxidation catalysts and/or as precursors to the supported transition metal and metal sulfide catalysts used in a variety of industrially important reactions (*1–4*). Understanding the interaction between dispersed metal oxide species and their supports provides insight into their catalytic behavior and elucidates the optimum conditions for the preparation of these catalysts. These preparation conditions, i.e., the precursor compound used, the pH of the precursor solution, and temperature of calcination of the precursor sample, have a profound impact on the interaction of transition metal oxides with supports (*5*).

In an earlier study (*6*), 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 diffraction analysis, temperature programmed reduction, and magnetic susceptibility measurement. The stabilization of the transition metal oxide species toward reduction was correlated with the site preference and the formal valence state of the transition metal.

In the present study, impregnation as well as codecomposition methods are used to prepare $MgAl_2O_4$ samples containing nickel(II). It has been proposed that La_2O_3 may have an important influence on the stabilization of transition metal oxides toward reduction (*7*). Therefore, the reactivity of La_2O_3 with nickel oxide as well as $MgAl_2O_4$ was studied.

Experimental

Preparation of Samples

A sample of $MgAl_2O_4$ was synthesized by dissolving the appropriate weights of magnesium and aluminum nitrates in water, adjusting the pH of the solution with $NH_3 \cdot H_2O$ to pH 10, and evaporating the solution to dryness. The product was care-

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fully decomposed at 450°C. The resulting mixed oxides were heated in air at 950°C for 24 hr. A sample of $LaAlO_3$ was synthesized by the codecomposition of lanthanum and aluminum nitrates at 1100°C in air for 24 hr. The lanthanum nitrate was prepared by dissolving La_2O_3 in 8 *M* nitric acid and drying. La_2O_3 was heated at 850°C for 24 hr to remove any carbonate before weighing.

The properties of the standard samples, bulk NiO, $NiAl_2O_4$, and $LaNiO_3$, were compared with those prepared from nickel and lanthanum nitrates reacted with $MgAl_2O_4$. Bulk NiO was prepared by the decomposition of nickel nitrate at 600°C in air. $NiAl_2O_4$ was synthesized by the codecomposition of nickel and aluminum nitrates at 1100°C in air for 24 hr. The $LaNiO_3$ was synthesized by the codecomposition of nickel and lanthanum nitrates at 1100°C in air for 96 hr. During the heating period, the sample was removed four times, cooled, and ground thoroughly in an agate mortar. The phases $MgAl_2O_4$, NiO, $LaAlO_3$, $LaNiO_3$, and $NiAl_2O_4$ were confirmed by X-ray diffraction analysis.

(*A*) *Nickel samples prepared by an impregnation method.* A nickel nitrate precursor was reacted with $MgAl_2O_4$ to give products containing 10 at% nickel as follows: $MgAl_2O_4$ was impregnated with a 0.05 *M* nickel nitrate solution, dried on a hot plate, and then heated in a drying oven at 230°C for 24 hr. A final heat treatment was carried out at 1100°C in air for 96 hr, the sample being reground four times during the process.

$MgAl_2O_4$ samples containing both nickel and lanthanum oxides were prepared by a procedure analogous to that used for the Ni(II)/$MgAl_2O_4$ sample. The nickel content was 10 at% and the lanthanum content was 20 at% (see footnote 1).

(*B*) *Nickel samples prepared by codecomposition of metal nitrates.* A sample of Ni(II)/$MgAl_2O_4$ was prepared by the codecomposition of nickel, magnesium, and aluminum nitrates to give a composition containing 10 at% nickel as follows: nickel, magnesium, and aluminum nitrates were dissolved in water; the solution was dried on a hot plate and then heated in a drying oven at 230°C; the triple salt was predecomposed at 450°C for 24 hr in order to drive off the oxides of nitrogen. A final heat treatment was carried out at 1100°C in air for 96 hr. The sample was reground four times during the process. A sample of 0.1(NiO):0.1(La_2O_3):0.233($MgAl_2O_4$) was prepared by the codecomposition of the required mixture of nickel, lanthanum, magnesium, and aluminum nitrates.

Characterization of Samples

X-ray powder diffraction analyses of the samples were obtained using a Philips diffractometer and monochromatic high intensity $CuK\alpha_1$ radiation ($\lambda = 1.5405$ Å). The diffraction patterns were taken over 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 both 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

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$$10\ \text{at\% Ni(II)} = \frac{1\ \text{g-at Ni(II)}}{1\ \text{g-at Ni(II)} + 2\ \text{g-at La(III)} + 7/3\ \text{g-at Mg(II)} + 14/3\ \text{g-at Al(III)}}$$

and

$7/3$ mole $MgAl_2O_4 \equiv 7/3$ g-at Mg(II) + 14/3 g-at Al(III).

TABLE I

PHASES FORMED BY THE REACTIONS OF NICKEL AND LANTHANUM NITRATES WITH $MgAl_2O_4$

Samples	Temperature of decomposition (°C)	Phases
Bulk NiO	600	Rock salt
Bulk MgO	950	Rock salt
Bulk $NiAl_2O_4$	1100	Spinel
Bulk $LaAlO_3$	1100	Perovskite
Bulk $LaNiO_3$	1100	Perovskite
Ni(II)/$MgAl_2O_4$ (impregnation)	1100	Rock salt + spinel
Ni(II)/$MgAl_2O_4$ (codecomposition)	1100	Rock salt + spinel
Ni(II) + La(III)/$MgAl_2O_4$ (impregnation)	1100	Perovskite + spinel + rock salt
Ni(II) + La(III)/$MgAl_2O_4$ (codecomposition)	1100	Perovskite + spinel + rock salt

Cahn system 113 thermal balance. All samples (approximately 50 mg) were preheated in air at 400°C for 4 hr in order to remove most of the residual water before reduction. The samples were cooled down to room temperature and 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. In order to correct for all of the residual water, a standard sample of $MgAl_2O_4$ was heated in air from 400°C up to 950°C, and its weight loss was used to correct the initial sample weights.

Results and Discussion

A bulk $NiAl_2O_4$ standard sample was prepared by the codecomposition of nickel and aluminum nitrates at 1100°C in air for 24 hr. X-ray diffraction analysis of the product confirmed the presence of single phase $NiAl_2O_4$ (spinel, Table I). The product was studied by temperature programmed reduction under an atmosphere of Ar/H_2 (85/15) from room temperature up to 950°C, and maintained in a reducing atmosphere at 950°C for a total of 4 hr in order to ensure constant weight. For the standard $NiAl_2O_4$ sample, it can be seen from Table II that reduction commenced at 720°C; at 950°C the observed weight loss corresponds to 97% of the calculated value for the reducible nickel present. X-ray analysis of the reduction products formed from bulk $NiAl_2O_4$ indicated the presence of metallic nickel and α-Al_2O_3. The X-ray diffraction peaks of the reduced nickel appeared sharp, which indicated that the nickel tended to agglomerate and crystallize. These results are consistent with those obtained from the temperature programmed reduction studies.

X-ray analysis of the products formed by the impregnation of $MgAl_2O_4$ with a nickel nitrate solution which was then decomposed at 1100°C in air for 96 hrs indicated the formation of both spinel and rock salt phases (Table I). It can be seen from Table II that the reduction temperature of this sample was 720°C, which is identical to the value for Ni(II) in bulk $NiAl_2O_4$, and magnetic susceptibility measurements confirmed the octahedral coordination of nickel(II) (Table III). This result suggests that the nickel substitutes for aluminum on the octahedral sites of the spinel. As a consequence, an equivalent amount of aluminum displaces magnesium from tetrahedral sites. This is consistent with the formation of MgO (rock salt) as a second phase. In addition, it can be seen from Table II that the reduction of this

TABLE II

TEMPERATURE PROGRAMMED REDUCTION DATA FOR THE REACTION PRODUCTS OF NICKEL AND LANTHANUM NITRATES WITH $MgAl_2O_4$

Samples		Beginning reduction temperature (°C)	Reduction percentage at 950°C for 4 hr
NiO		230–330	100
$LaNiO_3$	1st step:	205–320	
	2nd step:	340–475	100
$NiAl_2O_4$		720	97
Ni(II)/$MgAl_2O_4$ (impregnation)		720	98
Ni(II)/$MgAl_2O_4$ (codecomposition)		725	99
Ni(II) + La(III)/$MgAl_2O_4$ (impregnation)		720	98
Ni(II) + La(III)/$MgAl_2O_4$ (codecomposition)		725	98

sample was nearly complete at 950°C. X-ray analysis of the reduction products indicated the formation of metallic nickel and magnesium aluminate spinel. Although the X-ray diffraction peaks of metallic nickel are not as sharp as those obtained from the reduced sample of $NiAl_2O_4$, there is still evidence of appreciable agglomeration and crystallization of the metallic nickel. When nickel is removed from the spinel structure on reduction, the aluminum(III) ions reoccupy the octahedral sites of the spinel and the Mg(II) ions reoccupy the tetrahedral sites. Hence, the x-ray diffraction pattern of the reduced sample indicates the absence of a rock salt phase (Fig. 1).

The products formed by the codecomposition of nickel, magnesium, and aluminum nitrates at 1100°C were characterized by X-ray diffraction analysis, temperature programmed reduction, and magnetic susceptibility measurements. It can be seen from Tables I, II, and III that the reacted nickel in this sample behaves similarly to what was observed for the sample prepared by impregnation. These results imply that the reaction products are the same regardless of the method of preparation, provided that an equilibrium state is reached.

X-ray analysis of the products (which contain 10 at% nickel and 20 at% lanthanum) formed by the impregnation of $MgAl_2O_4$ with an aqueous solution of nickel and lanthanum nitrates, followed by decomposition at 1100°C in air for 96 hr, indicated the formation of perovskite, rock salt and spinel phases (Table I). The 2θ values, relative peak intensities and peak shapes of the per-

TABLE III

MAGNETIC SUSCEPTIBILITY DATA FOR THE REACTION PRODUCTS OF NICKEL AND LANTHANUM NITRATES WITH $MgAl_2O_4$

Samples	μ(BM)/mol Ni(II)	θ(K) (Weiss constant)
NiO	4.6[a]	−1961
$NiAl_2O_4$	3.2	−39
Ni(II)/$MgAl_2O_4$ (impregnation)	2.8	−39
Ni(II)/$MgAl_2O_4$ (codecomposition)	2.9	−35
Ni(II) + La(III)/$MgAl_2O_4$ (impregnation)	2.9	−170
Ni(II) + La(III)/$MgAl_2O_4$ (codecomposition)	2.8	−194

[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.

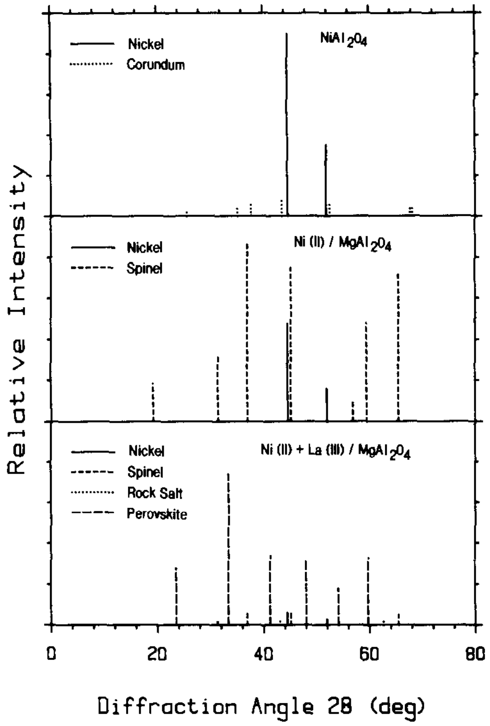

FIG. 1. Phases present after the reduction of $NiAl_2O_4$, $Ni(II)/MgAl_2O_4$, and Ni(II) + $La(III)/MgAl_2O_4$.

ovskite phase in this sample are identical to those found for pure bulk $LaAlO_3$. Therefore, the perovskite phase is essentially $LaAlO_3$ and can contain little or no nickel oxide. Magnetic susceptibility measurements confirmed that the Ni(II) ions are located on octahedral sites, which might be in the rock salt phase. However, comparison of the reduction temperature and reduction percentage of this sample with that of bulk $NiAl_2O_4$ (Table II) suggests that the Ni(II) is present only in the spinel.

When the reaction reaches equilibrium during the calcination of the sample, 20 at% La(III) has reacted with an equivalent amount of Al(III) to form $LaAlO_3$. The source of the aluminum(III) for the formation of the perovskite $LaAlO_3$ is from the spinel $MgAl_2O_4$. Hence, there should be a decrease in the amount of the spinel phase, and this is in agreement with a comparison of the X-ray diffraction data shown in Fig. 2 for the $Ni(II)/MgAl_2O_4$ and Ni(II) + $La(III)/MgAl_2O_4$ systems. In addition, there is a substitution of the 10 at% nickel on the octahedral sites of the spinel $MgAl_2O_4$, which displaces an equivalent amount of aluminum(III) onto the tetrahedral sites. This results in the removal of 10 at% of Mg(II) from the tetrahedral sites to the rock salt phase MgO in addition to that removed by the formation of $LaAlO_3$. X-ray results, TPR data, and magnetic susceptibility measurements support this mechanism. If magnesium aluminate is impregnated with a solution containing 10 at% Ni(II) and 20 at% La(III) nitrates, then

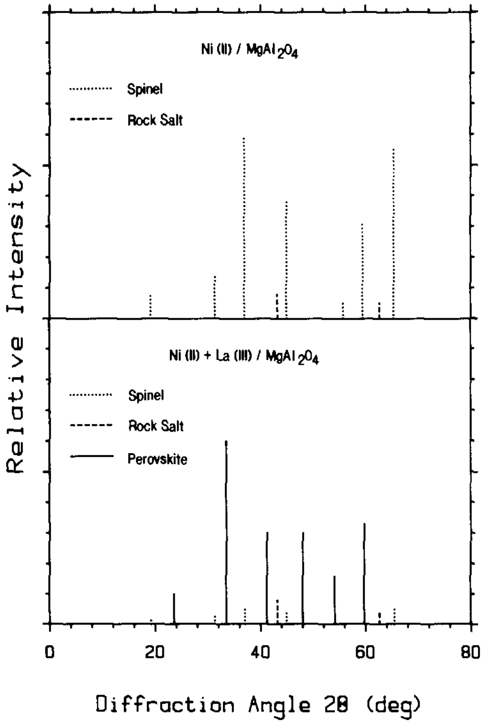

FIG. 2. Comparison of the decomposition products before reduction for $Ni(II)/MgAl_2O_4$ and Ni(II) + $La(III)/MgAl_2O_4$.

for each mole of NiO and La_2O_3 there are 7/3 mole of $MgAl_2O_4$.[1]

The formation of both the perovskite $LaAlO_3$ and rock salt MgO phases reduced the total spinel phase content to 4/3 mole, and the final composition of the spinel can be represented as $Mg_{0.25}Al_{0.75}[Al_{1.25}Ni_{0.75}]O_4$. This is consistent with the marked decrease in the magnitude of the spinel peaks in the X-ray diffraction data (Fig. 2) compared to the Ni(II)/$MgAl_2O_4$ system.

Acknowledgments

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References

1. H. Knözinger, *in* "Proceedings, 9th International Congress on Catalysis, Calgary, 1988" (M. J. Phillips and M. Ternan, Eds.), Vol. 5, p. 20, Chem. Inst. of Canada, Ottawa (1988).
2. G. Meunier, B. Mocaer, S. Kasztelan, L. R. Le Coustumer, J. Grimblot and J. P. Bonnelle, *Appl. Catal.* **21,** 329 (1986).
3. S. S. Chan, I. E. Wachs, L. L. Murrell, and N. C. Dispenziere, Jr., *J. Catal.* **92,** 1 (1985).
4. L. V. Burggraf, D. E. Leyden, R. L. Chin, and D. M. Hercules, *J. Catal.* **78,** 360 (1982).
5. C-S. Bai, S. Soled, K. Dwight, and A. Wold, *J. Solid State Chem.* **91,** 148 (1991).
6. C-S. Bai, S. Soled, R. Kershaw, K. Dwight, and A. Wold, *J. Solid State Chem.* **96,** 376 (1992).
7. Y-C. Zhang, R. Kershaw, K. Dwight, and A. Wold, *J. Solid State Chem.* **72,** 131, (1988).