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NOTE

Catalytic Oxidation of Ammonia to Nitric Oxide over La_2MO_4 (M = Co, Ni, Cu) Oxides[1]

Mixed oxides adopting the K_2NiF_4 structure with alternating ABO_3 perovskite and AO rock salt layers (1) form an interesting class of compounds, as their structure and oxygen stoichiometry can be tuned to investigate structure–property relations in catalysis (2, 3). In the present work we have studied the catalytic oxidation of ammonia to nitric oxide over La_2MO_4 (M = Co, Ni, and Cu) oxides synthesized by a previously described combustion method (4). Catalytic oxidation of ammonia over oxides is important in two ways: (i) ammonia serves as a better probe molecule than carbon monoxide in oxidation, as it gives distinct product selectivity based on the type of the surface oxide species; and (ii) ammonia leaves no surface-contaminating product.

The catalyst oxides La_2CoO_4 and La_2NiO_4 were prepared by the combustion of redox mixtures containing corresponding metal nitrates as oxidizer and triazole as fuel. La_2CuO_4 was prepared from a mixture of metal nitrates and tetraformaltrisazine (TFTA). The details of the combustion technique are described elsewhere (4). Phase purity and structure of the fresh and used oxide catalysts were examined by powder X-ray diffraction employing a JEOL-8PDX X-ray diffractometer and cell parameters determined by a least-squares refinement method. Particle size distributions were analyzed by sedimentation technique employing a Model SKC 2000 micrometer photosizer. Surface area measurements were carried out by nitrogen absorption (BET method). Catalytic activity of the oxides toward ammonia oxidation was studied by a temperature programmed surface reaction (TPSR) method employing home-built equipment (5). The catalyst (100 mg) was loaded into an 8-mm silica tube which served as a continuous flow reactor, evacuated to 10^{-5} mbar, and heated to 600°C at a rate of 15°C/min. Flow rates of NH_3 and O_2 each were maintained at about 15–20 μmol/s in the catalytic oxidation, whereas in the stoichiometric reaction only ammonia was used at the same flow rate and the product gases were mass analyzed on-line (5).

Figure 1 shows the X-ray diffraction patterns of the fresh and used catalyst oxides. La_2CuO_4 and La_2CoO_4 crystallized in an orthorhombic K_2NiF_4 structure whereas La_2NiO_4 adopted a tetragonal modification. The cell parameters, surface area, and particle sizes for the fresh and used oxide catalysts are summarized in Table 1.

The temperature programmed desorption (TPD) experiments on all three oxides showed no significant oxygen emanation below 600°C. Also, the anaerobic oxidation of ammonia carried over all three oxides did not show any significant reaction below 500°C, confirming the absence of any labile oxygen species in the oxides. Carrying out the reaction at higher temperatures resulted in the reduction of the parent phase to basic oxides. Figure 2 shows the typical TPSR profile for the catalytic oxidation of ammonia over La_2CoO_4. Similar profiles were obtained in other cases as well. In all three cases nitric oxide and water were the exclusive products. The onset temperatures for NO formation over the La_2MO_4 oxides were about 275, 350, and 420°C for M = Co, Ni, and Cu, respectively.

Assuming NO desorption from the surface to follow first-order kinetics without readsorption, the activation energies for NO formation were estimated by fitting the nitric oxide profile to the expression

$$C = C_0 \cdot \exp[(k \cdot \tau) \cdot \exp(-E_a/RT)]$$

by a nonlinear regression method, where C_0 is the initial concentration of NO (with a nonzero value), k is the frequency factor, and τ is the space time. The product $k \cdot \tau$ was varied as a single constant during the regression cycles. The experimental and fitted profiles for the NO formation for all the three catalyst oxides are shown in Fig. 3. The activation energies for NO formation were estimated to be 25.8, 28.7, and 35.9 kcal/mol, respectively, for M = Co, Ni, and Cu.

The La_2CuO_4 system crystallizes normally in a tetragonal form at higher temperatures. This structure can easily adopt an orthorhombic structure by the cooperative rotation of the MO_6 octahedra about the [110] axis (6). Also, both $La_2CuO_{4+\delta}$ and $La_2NiO_{4+\delta}$ phases are known to give rise to biphasic mixtures due to the segregation of oxygen defects (7, 8). The solubility of oxygen in La_2NiO_4 is more comparable to that of La_2CuO_4. The excess oxygen in these oxides is located between the two adjacent LaO layers.

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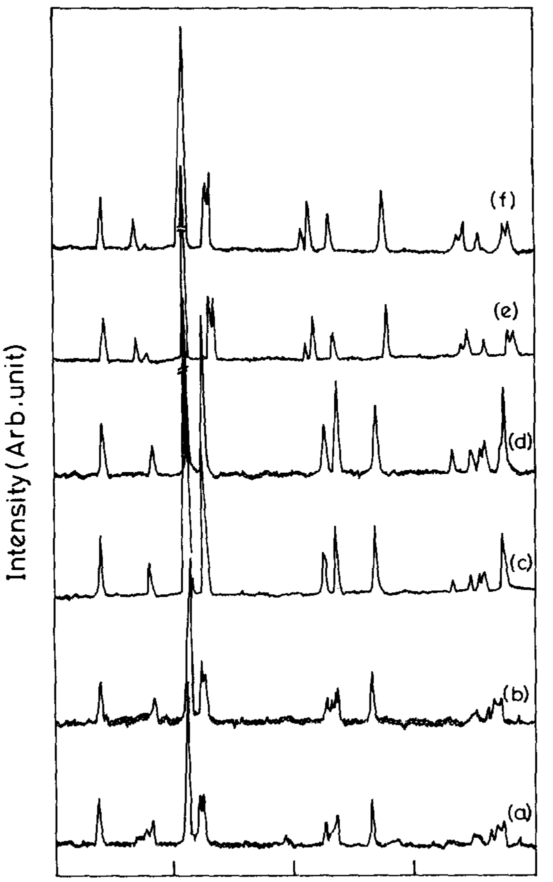

FIG. 1. X-ray diffractogram of (a) fresh La_2CoO_4, (b) used La_2CoO_4, (c) fresh La_2NiO_4, (d) used La_2NiO_4, (e) fresh La_2CuO_4, and (f) used La_2CuO_4 oxide catalysts.

TABLE 1

Cell Parameters,[a] Surface Area (*S*), and Particle Size (*d*) of the La_2MO_4 Catalyst Oxides and Spent Solids

Compound	*a* (Å)	*b* (Å)	*c* (Å)	*S* (m^2/g)	*d* (μm)
$La_2CoO_{4\pm\delta}$ (catalyst)	5.516	5.451	13.012	2.4	2.0
$La_2NiO_{4\pm\delta}$ (catalyst)	5.453	5.453	13.141	6.7	1.9
$La_2CuO_{4\pm\delta}$ (catalyst)	5.422	5.387	13.217	1.5	2.9
$La_2CoO_{4\pm\delta}$ (spent solid)	5.581	5.404	12.785		
$La_2NiO_{4\pm\delta}$ (spent)	5.468	5.468	12.949		
$La_2CuO_{4\pm\delta}$ (spent)	5.416	5.391	13.227		

[a] Accurate within ±0.004.

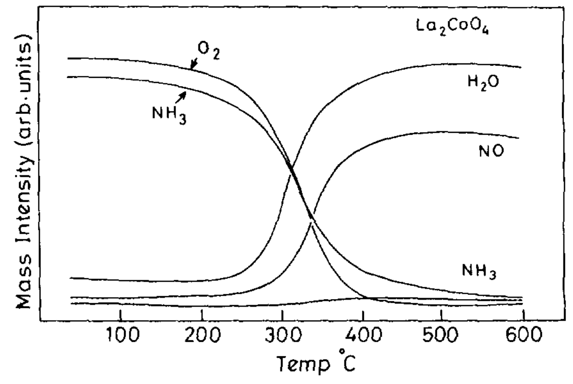

FIG. 2. TPSR profile of catalytic oxidation of ammonia over La_2CoO_4.

The stoichiometric La_2CoO_4, although it adopts an orthorhombic K_2NiF_4 structure, has cobalt, which is found to be easily oxidizable to a trivalent state, and to that extent can accommodate excess oxygen. The fact that no significant oxygen desorption or anaerobic reaction took place below 500°C over these compounds supports the view that there is no labile oxygen available from the oxide systems, at least up to 500°C. This suggests that the reaction is unlikely to follow a Mars–van Krevelen pathway.

On the other hand, the lower reaction temperature in the presence of O_2 gas in a catalytic reaction suggests that the oxide surface does provide suitable active sites for both NH_3 and O_2 to adopt a Langmuir–Hinshelwood pathway. It is instructive to note that both La_2CuO_4 and La_2NiO_4 are known to catalyze the oxidation of carbon monoxide via a Langmuir–Hinshelwood pathway (9). Such a pathway is controlled by the local site symmetry of the transition metal ions. Infrared spectroscopic investigations have revealed that the local site symmetry of the transition metal cation in La_2MO_4 (M = Co, Ni, and Cu) to be the same (10, 11). With identical local geometry of metal ions in La_2MO_4 oxides the observed catalytic activity can be explained in terms of the oxidation state and reducibility of the central metal ion. The oxidizing power of the surfaces of mixed oxides of the type La_2MO_4 has been found from the studies on the catalytic activity of solid solutions of the type $La_{2-x}Sr_xMO_4$ to be directly proportional to the concentration of M^{3+} ions, for M = Ni, Co, and Cu (3, 12, 13). On similar lines the catalytic activity of the La_2MO_4 members can be correlated to the extent of stabilization of the M ion in a trivalent state. From the structure and solubility of oxygen it follows that the concentration of M^{3+} ions in $La_2MO_{4+\delta}$ varies in the order $Co^{3+} > Ni^{3+} > Cu^{3+}$ and is directly correlated to the catalytic activity toward the oxidation of ammonia to nitric oxide. In accordance with the mechanism of Yu *et al.* (14), the ammonia molecule is suggested to be adsorbed and activated by the

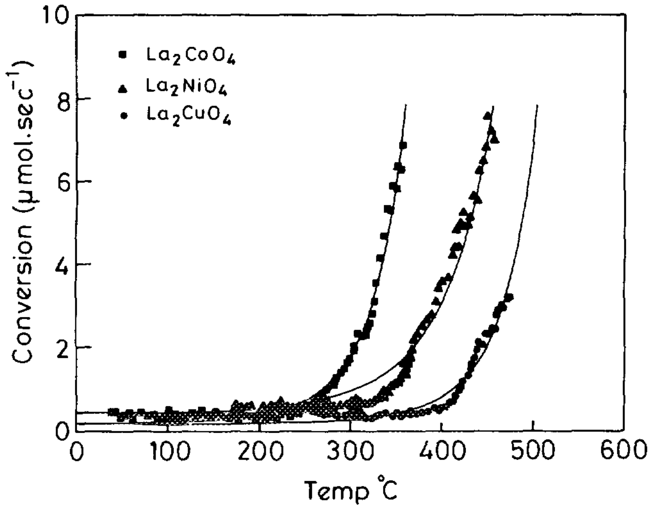

FIG. 3. Experimental and fitted profiles for the formation of nitric oxide over La_2MO_4 (M = Co, Ni, and Cu) oxides.

transition metal ion, while the oxygen vacancies serve as active sites for the adsorption of oxygen.

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