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Stabilized Ruthenium Catalysts Supported on Magnesium Oxide: Formation of a Novel Surface Complex

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During the past decade, much effort has been expended in the search for catalysts capable of abating the automotive pollutants NO_x, CO and unburned hydrocarbons. It has been found that the latter two can be reduced to acceptable levels by oxidation over a Pt/Pd catalyst, and this has been developed to the point of commercialization. With regard to nitrogen oxides, however, the problem has turned out to be more difficult.

A number of substances are able to catalyze the reduction of NO_x, all of which require reducing conditions.[1] The presently contemplated dual-bed system would incorporate a NO_x-reduction catalyst, operating in a reducing atmosphere, followed by air injection to provide an oxidizing atmosphere for combustion of CO and hydrocarbon over the oxidation catalyst. A three-way catalyst which can simultaneously reduce NO_x and oxidize CO and hydrocarbons is also conceivable if careful control of the air/fuel ratio can be achieved.

It is important that the reduction of NO_x proceed to N_2 and not to NH_3, since the latter will be reoxidized to NO_x over the oxidation catalyst. To date, the only substance with sufficient catalytic activity and selectivity for the NO_x-to-N_2 conversion appears to be ruthenium *(1)*. Thus far, however, attempts to exploit these properties have been hindered by rapid ruthenium volatilization as RuO_3 and RuO_4 when ruthenium catalysts are subjected to high temperature oxidizing conditions. With production-grade carburetors, frequent excursions of the engine exhaust into the oxidizing regime cannot be avoided.

The problem of stabilizing ruthenium to oxidation without hindering its catalytic activity has received considerable attention *(2)*. This task has been pursued, quite naturally, with the aid of solid state chemical precepts. If one can, by means of compound formation, stabilize the intermediate (+3 or +4) oxidation states of ruthenium, formation of RuO_3 and RuO_4 will be suppressed. Furthermore, as these intermediate oxidation states are known to be acidic in character, a logical approach is to provide a basic oxide which can combine with, and thus stabilize, the trivalent or tetravalent oxide. In choosing a suitable basic stabilizer, one may conveniently select from the several known to form ruthenates. Shelef and Gandhi *(2)*, at Ford

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[1] The primary reductants present in automotive exhaust are CO and H_2 with small concentrations of unburned hydrocarbons. Oxygen is also present, with the carburetor setting determining the average composition (oxidizing or reducing) of the engine exhaust. The NO_x concentration in the exhaust gas is usually 0.1–0.2%, CO and H_2, 0–2% (3:1 CO/H_2) and O_2, 0–2%. The remainder of the exhaust gas is composed of 12% H_2O, 12% CO and N_2 balance.

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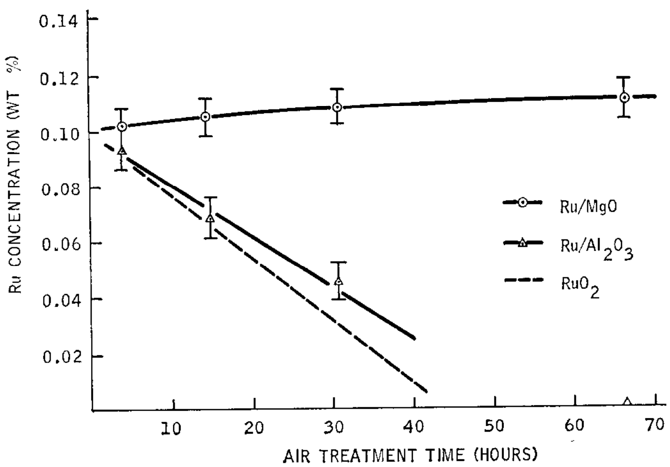

FIG. 1. Loss of ruthenium from alumina and magnesium oxide compared to loss of ruthenium from unsupported ruthenium oxide in flowing wet air (18 liters/hr) at 850°C. The rate of loss of pure RuO_2 in the figure was normalized for comparison and is the rate of loss of RuO_3 and RuO_4 determined by TGA experiments.

Motor Co., have described the successful demonstration of reduced ruthenium volatility using BaO and La_2O_3. These are known to form the phases, $Ba^{2+}Ru^{4+}O_3$ and $La^{3+}Ru^{3+}O_3$, respectively.

As shown in this paper, stabilization of ruthenium to volatilization, however, does not intrinsically require formation of a bulk compound. Spatial factors can preclude three-dimensional lattice formation even when strong surface interaction between a basic oxide and the ruthenium oxide exists. Indeed, confining the acid–base complex to the surface will enhance the efficiency of the system, since only ruthenium at the surface can participate catalytically.

It is known that the perovskite structure (ABO_3) is stable only with A cations whose octahedral radii exceed 0.9 Å (*3*). While Ca^{2+}, Sr^{2+}, and Ba^{2+} fulfill this requirement, the octahedral radius of Mg^{2+} is only 0.72 Å (*4*). This suggests the possibility that the small radius of the Mg^{2+} cation, rather than insufficient basicity on the part of MgO, may be responsible for the instability of $MgRuO_3$. This, however, would not affect the stability of a *surface* Mg–Ru–O complex, due to the relaxation of bonding requirements that characterizes a surface structure as compared to a bulk structure. It may also be mentioned that the MgO surface has been found to exhibit strongly basic properties with respect to the acidic adsorbates SO_2 (*5*) and NO (*6*).

Figure 1 shows the results of experiments comparing the abilities of Al_2O_3 and MgO to retard the volatilization of ruthenium in flowing air at 850°C. The two catalysts were prepared in the usual manner by aqueous impregnation with $RuCl_3$ followed by drying and calcination. The rate of loss of Ru/Al_2O_3 is seen to differ little from that of RuO_2 itself, indicating a lack of interaction on the part of the Al_2O_3 surface. In the case of MgO, however, a strong stabilizing action is clearly evident. One may infer that the reactivity of MgO with RuO_2, although prevented by spatial factors from engendering a three-dimensional lattice, gives rise to a two-dimensional complex, which may be analogically termed a surface–ruthenate.

Further studies of the Ru/MgO system, at a number of temperatures, are represented in Fig. 2. It can be seen that the stability of the MgO–RuO_2 surface complex is not sufficient to withstand excessive

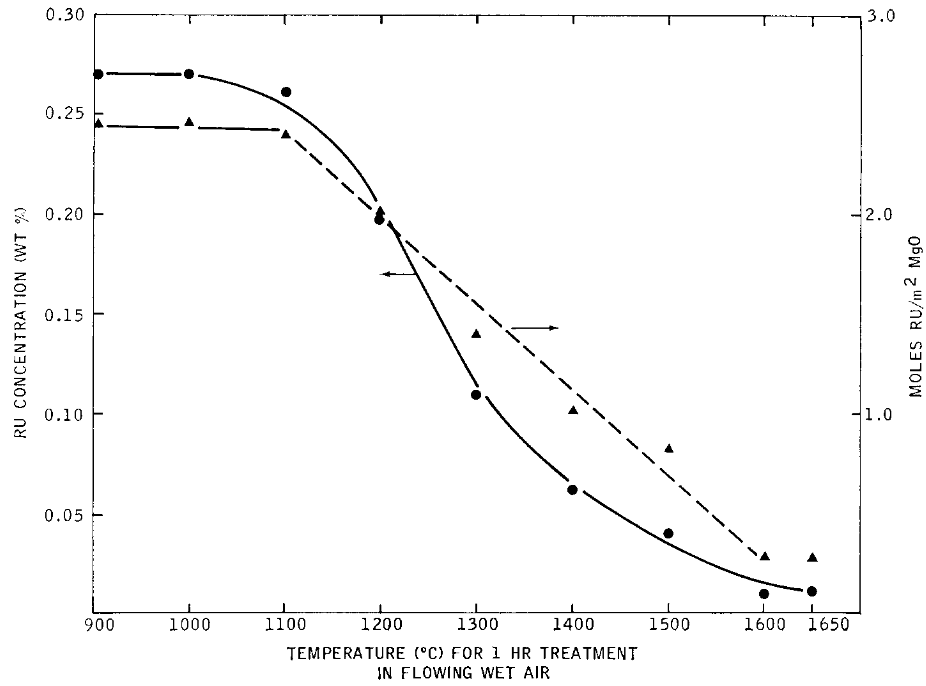

FIG. 2. Ruthenium loss from magnesium oxide as a function of temperature (in flowing wet air 18 liters/hr).

temperature. The data from Fig. 2 can be compared on a surface-area-independent basis which is also plotted in Fig. 2. There is an approximately linear decrease in the amount of ruthenium retained per unit surface area of MgO between 1100 and 1600°C. Therefore, the ruthenium lost at temperatures ≥1200°C must be due to factors other than a decreasing number of bonding sites per gram of MgO.

TABLE 1

Ruthenium Loss from Magnesium Oxide as a Function of Temperature and Ruthenium Concentration

Catalyst sample (wt% Ru)	Temp (°C) of treatment in flowing wet air for 16 hr	Ruthenium analysis of catalyst (wt%)[a]	Ruthenium volatilized
0.20	600	0.20	0
0.20	700	0.20	0
0.20	800	0.20	0
0.20	900	0.18	0.02
0.50	850	0.48	0.02
0.60	600	0.60	0
0.60	700	0.58	0.02
0.60	800	0.53	0.07
0.60	900	0.54	0.06
1.00	600	1.00	0
1.00	700	1.00	0
1.00	800	0.94	0.06
1.00	900	0.77	0.23

[a] The precision of the above ruthenium analyses obtained by X-ray fluorescence is ±2% for all samples.

Table 1 represents the results of experiments in which Ru/MgO catalysts with Ru loadings of 0.2–1% were subjected to flowing air at temperatures of 600–900°C, in which range the surface area of the MgO support is not decreased from its starting value of 10.5 m^2/g. The most dilute catalyst was not affected by this treatment, indicating that the capacity of this MgO surface to stabilize ruthenium, expressed in wt% Ru, exceeds 0.2%. For 0.6% Ru/MgO, a definite loss occurs at 800°C, and this loss does not increase up to 900°C. This suggests loss of ruthenium, (which was completed at 800°C), in excess of the stabilization capacity of MgO, and indicates a value of about 0.54% Ru for the stabilization capacity. The 1.0% Ru/MgO catalyst loses 0.06% Ru at 800°C and about fourfold this amount at 900°C, indicating the lack of sufficient time for complete removal of excess ruthenium.

The stabilization capacity of 0.54 wt% Ru on MgO of 10.5 m^2/g can be used to calculate the MgO surface area required to stabilize a single RuO_x group. The calculated value is 0.31 nm^2 (31A^2), which can be empirically compared to the estimated spherical diameter of the RuO_2 molecule, 0.25 nm^2, using covalent radii and assuming a linear O–Ru–O geometry. Therefore, the MgO stabilization capacity appears to correspond to a surface which is completely occupied by a surface complex of MgO and RuO_x. Since there are about 10 oxide ions (but only 3 stabilized RuO_x groups)/nm^2 of MgO surface, the capacity of MgO appears to be limited by the steric requirement of the surface–ruthenate complex. The surface complex may be an ordered two-dimensional array of octahedrally coordinated ruthenium cations with magnesium cations occupying tetrahedral and/or octahedral sites. The high stability of the Mg–Ru–O surface complex, leading to complete occupancy of the MgO surface at 900°C, is remarkable in view of the lack of any stable bulk compound in the Mg–Ru–O system.

It is seen from Fig. 2 that the stability of the Mg–Ru–O surface complex is not sufficient to withstand temperatures above 1200°C (*7*). Attempts to develop a practical catalyst system incorporating MgO as the ruthenium-stabilizing component were successful in engine dynomometer studies, but failed in vehicle tests (*8*). This was apparently due to short bursts of extreme temperature under oxidizing conditions which characterize the latter.

In order to take advantage of the marked stability of Ru on MgO catalysts for NO_x reduction in automobiles, a system would have to be developed which would not allow the surface temperature of the catalyst to exceed 900°C. Reduction of the stable Mg–Ru–O surface complex is not a limitation as rapid regeneration to well-dispersed ruthenium occurs at temperatures of 300°C.

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