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NOTE

Catalytic Activity of Mn^{3+} and Mn^{4+} Ions Dispersed in MgO for CO Oxidation

In an earlier paper (*1*) it was shown that Mn^{3+} ions dispersed in MgO are more effective than Mn^{4+} ions for the catalytic decomposition of N_2O. A parallelism was drawn between the catalytic activity and the strength of the oxygen–surface bond. The higher activity of Mn^{3+} ions for the N_2O decomposition was attributed to the presence of a weaker form of oxygen chemisorbed by Mn^{3+} ions, as compared to the oxygen held by Mn^{4+} ions. In oxidation reactions the situation will be more complex, because there is not only the reactivity of oxygen species to consider, but also the interaction of the reducing species with the surface. It was therefore of considerable interest to extend the study of the influence of the valency state of manganese ions to a simple oxidation reaction, and for this purpose the CO oxidation reaction was chosen.

The formation and dispersion of Mn^{3+} ions or of Mn^{4+} ions in MgO is achieved by addition of Li_2O in the proper ratio to the manganese oxide (*2*). The two catalysts A and B used in the present work had the following nominal compositions (atoms per 100 Mg atoms): catalyst A, Li = 6, Mn = 5; catalyst B, Li = 15, Mn = 5. The effective compositions were A: $Mn^{3+} = 5.1$, $Mn^{4+} = 0.0$, $Li^+ = 4.5$; B: $Mn^{4+} = 4.2$, $Mn^{3+} = 1.6$, $Li^+ = 9.5$; compositions being expressed in atoms per 100 Mg atoms. The Mn^{3+} and/or Mn^{4+} ions are dispersed in solid solution in both catalysts. The method of preparation, analysis and characterization (X-ray, magnetic) of the samples employed here are reported fully elsewhere (*2*). The surface areas were, respectively: A = 1.65 and B = 1.22 $m^2\ g^{-1}$.

The catalytic activity was tested with a pulse technique, adopting the following procedure. The catalysts were activated in a quartz reactor at 480°C by passing helium (flow rate $\Phi = 50$ cm^3 STP/min) for 4 hr, followed by a mixture of He–oxygen ($\Phi =$ 47 cm^3/min STP; 2.65% O_2), for 1 hr at 400°C. Finally, the temperature was adjusted to a prefixed value, chosen at random, and a pulse of CO (16.4×10^{-6} moles) was injected into the He + O_2 stream. For each temperature studied several pulses of CO (generally 6) were admitted at intervals of 15 min, and the CO and CO_2 were analyzed by a gas chromatograph.

The results, illustrated for a typical run in Fig. 1, show that the amount of CO unreacted at a given temperature is always constant for each pulse in the sequence, while the amount of CO_2 detected increases at first, and then after 3 to 4 pulses becomes constant. It is important to notice that in these last conditions (CO_2 detected constant), the stoichiometry of the reaction is fully respected as indicated in Fig. 1. Therefore the CO_2 formed, but not detected, in the first pulses must be held by the catalyst; however, it is not blocking the active sites, hence it is not chemisorbed on the oxidizing sites.

The reaction rates (molecules of CO oxidized $sec^{-1}\ cm^{-2}$) are reported in Fig. 2 as a function of the reaction temperature. The plot shows that the points pertaining to catalyst A (Mn^{3+}-rich) are always higher

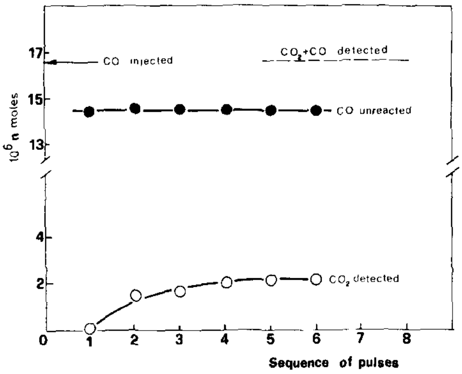

FIG. 1. Amounts of CO and of CO_2 (moles) as detected in a typical experiment, in successive pulses (sequence number in the abscissae). The level of CO_2 + CO detected is also shown, to compare with CO injected.

than those of catalyst B (Mn^{4+}-rich) in the temperature range studied (200 to 350°C). Hence the Mn^{3+} ions in solid solution in MgO have a higher efficiency in the catalytic oxidation of CO than Mn^{4+} ions. For example, at 214°C a 5% conversion was detected on A while less than 0.2% of CO_2 was formed on B. At 360°C the two types of catalyst have substantially the same activity, thus indicating that the activation energy of catalyst B is larger. Arrhenius plots of curves shown in Fig. 2 give very good straight lines when a first order rate constant is assumed. The apparent activation energies E_a are, respectively, 10.7 kcal/mole on A and 16.1 kcal/mole on B. While it is obvious that the absolute values of E_a are scarcely significant because of the choice of the kinetic order, it is significant that the relative order of E_a values is the same as the one obtained for N_2O decomposition (*1*) for these same catalysts: Mn^{3+}-rich catalysts, 17.0 kcal/mole; Mn^{4+}-rich 26.6 kcal/mole.

The present results seem to indicate that, as already found for the case of N_2O decomposition, the higher E_a value on Mn^{4+} containing catalysts reflects a higher oxygen–surface bond strength (*3–5*). This conclusion would be in agreement with the hypothesis of Klier (*6*) and with the extensive work of Boreskov (*7*, *8*). In particular the whole body of studies by Boreskov and co-workers shows that the predictive value of the efficiency of an oxidation catalyst based on oxygen–surface bond strength rests upon the idea that the oxygen–metal ion bond strength is the most important factor, although not the only factor, for the oxidation reaction. This situation, however, is not necessarily encountered for all oxidation reactions.

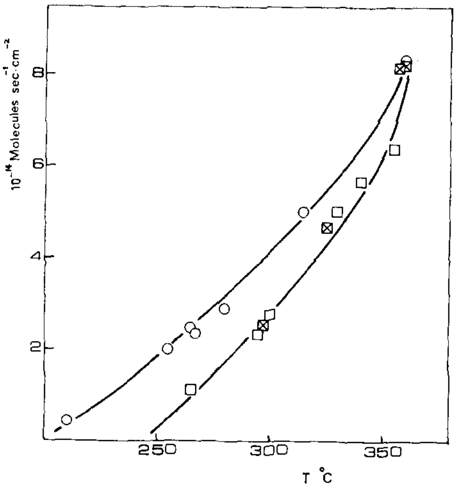

FIG. 2. CO oxidation rate (molecules sec^{-1} cm^{-2}) on sample A (Mn^{3+}-rich) (○); and on sample B (Mn^{4+}-rich)(□) (☒) two different portions of same batch.

The constancy of activity, in spite of CO_2 retention, proves that CO_2 produced on active sites migrates on the surface towards different adsorption sites. In order to throw some light on the CO_2-retention sites, the direct adsorption of molecular CO_2 was studied on A and B catalysts, in a conventional static system (total volume, 199 cm^3; CO_2 pressure, ~0.7 Torr, *P*-reading by McLeod). The chemisorption was considered complete when three successive readings, at 20 min intervals, did not differ by more than 0.008 Torr. The fresh specimen was given a vacuum treatment at 480°C for 4 hr; successive adsorptions were preceded by a 30 min vacuum treatment at 480°C, except when a measurement of more loosely bound CO_2 was taken. In such a case, a 30 min evacuation at the adsorption temperature was used, and the amount successively chemisorbed at the same temperature gave a measure of the CO_2 which could be easily desorbed (hereafter called "reversible CO_2" as distinct from the "total CO_2"; the difference between the two is "irreversible CO_2").

The amount of reversible CO_2 (Fig. 3) does not differ for the two catalysts, whereas the amount of irreversible CO_2 is substantially higher in the case of the Mn^{4+}-rich sample. Pure MgO was found to chemisorb about 20 times less CO_2 than A or B. This finding gives a clue to the nature of the sites responsible for irreversible CO_2 adsorption. Both A and B contain lithium ions and segregated lithium oxide which can form stable carbonate. Furthermore, the amount of "free Li_2O" (*1*, *2*) present in catalyst A was 4.7×10^{-5} g atom m^{-2}, while in B it was 7.4×10^{-5} g atom m^{-2}. These free lithia amounts can account for the amount of CO_2 retained (1 to 2×10^{-5} mole m^{-2}), especially considering that the lack of detection of Li_2O by X-rays indicates good dispersion of Li_2O, and hence a high reactivity. It may be noted that the ratio (CO_2 irreversibly chemisorbed by B)/(CO_2 irreversibly chemisorbed by A) is 1.4 to 1.8, which is in good agreement with the Li_2O content ratio between B and A (1.7).

The sites for CO_2 strong chemisorption having been identified, let us consider again the CO oxidation process. The relative inactivity of pure MgO alone for CO oxidation shows that Mn^{3+} ions or Mn^{4+} ions are involved. Once CO_2 is formed, neither Mn^{3+} ions nor Mn^{4+} ions are capable of retaining it strongly. It is relevant to notice that no carbonates of Mn(III) or Mn(IV) are known. Klier and Kuchynka (*9*) report that MnO_2 has a low reactivity for CO_2 adsorption, in agreement with the low basicity of MnO_2. The ions Mn^{3+} and Mn^{4+} dispersed in MgO would tend to pull electrons from neighboring O^{2-} ions, thus decreasing their basicity. The reversible CO_2 could be associated with CO_3^{2-} surface complexes, formed by CO oxidation and held in close proximity to manganese ions. Another indication that the sites responsible for the reversible adsorption of CO_2 are connected with manganese ions comes from the observation that A and B catalysts, having similar manganese contents, have roughly the same amount of reversible CO_2, hence independent of lithium oxide content. The weakly held CO_2 formed in the oxidation could then migrate on the surface to form strongly held carbonate ions linked to lithium ions. Once the sites for strong chemisorption are full (or are effectively inaccessible) the CO_2 produced is desorbed. The higher capacity for CO_2 irreversible adsorption of sample B, as well as the higher CO_2 deficit observed during catalysis on B catalysts is thereby explained.

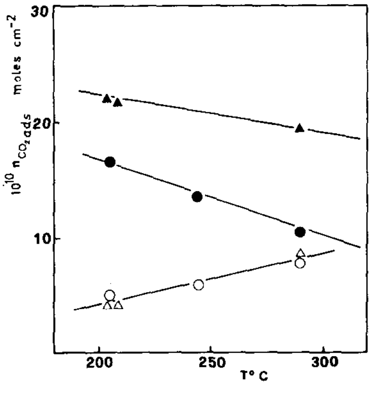

FIG. 3. "Reversible CO_2" chemisorbed on A (○) and on B (△), and "irreversible CO_2" on A (●) and on B (▲) as a function of temperature.

The dispersion of manganese ions in MgO, and the ensuing stabilization of valency states, allows us to extend the question of catalytic activity of Mn^{3+} ions and Mn^{4+} ions to the case of CO oxidation. Having shown that Mn^{3+} ions are more active, the data for CO oxidation on pure manganese oxides can be interpreted along the same lines. Brooks (*10*) reported that stoichiometric MnO_2 is less active than defective MnO_2, where the valency state 3+ is present. Bickley, Roberts and Storey (*11*) also found that the oxide initially formed on manganese films (MnO) is inactive, while further oxidation (possibly Mn_2O_3) produces an active catalyst. They also show that thermodynamically favored reactions of CO with manganese oxides can take place with Mn_2O_3 and Mn_3O_4, but not with MnO or MnO_2.

In conclusion, the solid solution approach allows one to identify more clearly than with pure oxides the pattern of activity of different valency states. It is interesting that the order of activity $Mn^{3+} > Mn^{4+}$ is the same as predicted from the N_2O decomposition study, thus pointing to the role of the metal ion–oxygen bond. The higher activity of Mn^{3+} ions now found in the CO oxidation is rather surprising at first if one compares the "turnover numbers" for the CO oxidation n_{CO} with those for N_2O decomposition n_{N_2O} where n is defined as (molecules/site) sec^{-1} assuming homogeneous distribution of manganese ions. At 265°C, on catalyst A, we have $n_{CO} = 5$; and at 260°C, on a catalyst of the same composition, $n_{N_2O} = 3 \times 10^{-3}$. The difference of three orders of magnitude indicates that the cleavage of the metal ion–oxygen bond is assisted strongly by the reducing power of CO, thus rendering the elementary step of the metal ion–oxygen cleavage much more efficient. The firmness by which oxygen is held during N_2O decomposition (*1*) can indeed be contrasted with the ease by which CO_2 formed in CO oxidation can be lost either to lithium oxide sites or to the atmosphere.

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