Effects of mixed and ionic conduction in ZrO_2 and ThO_2 as CO oxidation catalysts

G. W. BERKSTRESSER,* R. J. BROOK,† J. M. WHELAN
Chemical Engineering and Materials Science Departments, University of Southern California, Los Angeles, California, USA

A comparison is made of the heterogeneous catalytic activities of ZrO_2, $Zr_{0.91}Ca_{0.09}O_{1.91}$ and $Th_{0.85}La_{0.15}O_{1.925}$ for the oxidation of CO by O_2. A correlation is evident with the magnitudes of the simultaneous bulk ionic and electronic conductivities. This is in accord with a postulated model for reaction at separate reactant absorption sites in which oxygen ions and electronic charge are transported in and on the surface of the oxide catalyst.

1. Introduction
The relative catalytic activities of ZrO_2, $Zr_{0.91}Ca_{0.09}O_{1.91}$ and $Th_{0.85}La_{0.15}O_{1.925}$ for the oxidation of CO with O_2 are reported. From these observations an attempt is made to assess the relative importance of simultaneous oxygen ionic and electronic conductivities in these formulations to the relative catalytic activities.

The thoria sample doped with 15 mol % lanthania is a mixed conductor over the temperature range of interest and the range of partial pressures of O_2 used in the reaction kinetic experiments. Its electronic transference number is estimated to be about 0.1 by extrapolation of data by Wimmer *et al* [1]. The first zirconia sample contained 9 mol % calcia and is essentially an ionic conductor whose ionic conductivity is assumed to approximate that of the thoria sample. A second unintentionally doped or "pure" zirconia sample is a mixed conductor under these conditions, but with an electronic conductivity markedly less than the thoria sample and an ionic conductivity substantially less than those of the doped thoria and zirconia samples [2].

It was postulated that mixed conduction would enhance the CO-O_2 reaction rates by facilitating the transfer of an adsorbed oxygen atom to within a "reaction radius" of an adsorbed CO molecule. This transfer could occur by mixed conduction involving the diffusion of oxygen ions and electronic charge on the surface

and in the sub-surface and interior regions of the solid oxide catalyst. A pair of reactions occurring at the separated adsorbed atoms of oxygen and CO sites may be written as:

(a) $O(ads) + V_O^{\cdot\cdot} = O_O^x + 2h^{\cdot}$
(b) $CO(ads) + O_O^x + 2h^{\cdot} = CO_2(ads) + V_O^{\cdot\cdot}$.
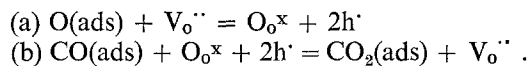
The net surface reaction, the sum of (a) and (b), requires the transfer of oxygen ions, O_O^x (or oxygen ion vacancies, $V_O^{\cdot\cdot}$), and electronic change such as holes, $h^{\cdot}$. It is reasonable to assume local hole-electron equilibrium so that the reactions may be equally well written with electrons as the reacting electronic species. If the rate limiting step is the above transport process, the reaction rate, r, is proposed to be proportional to the following quantity:

$$r \propto \sum_{\substack{\text{all CO-O} \\ \text{nearest pairs}}} \sum_{\substack{\text{all} \\ \text{paths}}} \int_{\text{O site}}^{\substack{\text{nearest} \\ \text{CO site}}} \sigma t_i t_e \, dx \; .$$

In this expression, σ represents the total electrical conductivity, t_i and t_e represents the transference numbers for oxygen ions and electronic charge, respectively. This relationship is adapted from Wagner's treatment of the tarnishing reaction of metals involving a similar transport process between parallel surfaces [3]. Although the relationship between surface, sub-surface and bulk conductivities and transference numbers is not known, compositional changes which modify

*Present address: Bell Laboratories, Murray Hill, New Jersey 07974
†Present address: Atomic Energy Research Establishment, Harwell, England

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the bulk σ, t_i, and t_e would be expected to change these properties in the near surface region in an analogous manner.

From the preceding model, one would expect $Th_{0.85}La_{0.15}O_{1.925}$ to be a superior oxidation catalyst relative to the "undoped" zirconia, which in turn would be a better catalyst than the $Zr_{0.91}Ca_{0.09}O_{1.91}$ sample. For these comparisons it is assumed that intrinsic ZrO_2 and ThO_2 are essentially identical as CO oxidation catalysts [4].

2. Experimental

The pure and calcia-doped zirconia samples were purchased from the Zirconium Corporation of America. Thoria doped with 15%m lanthania was prepared from the nitrates by repeated firing and grinding. These samples had approximately equal specific surface areas as determined by microscopic comparison. The zirconia samples had specific surface areas of 3 m^2 g^{-1} as determined by the BET method using an apparatus similar to that of Benson and Garten [5]. The thoria sample size was too small for direct surface area measurement in our apparatus.

The CO oxidation reaction was studied in a flow reactor using a reactant stream of 95 cm^3 min^{-1} (25°C and 1 atm) composed of 3.4%m CO, 3.2%m O_2, and the balance He. Approximately a 1 g sample of the catalyst powder is contained in the reactor. The reactor design is basically a countercurrent flow concentric tube type. The reactant gases are pre-heated in the annular section, and the catalyst powder is contained as a loose bed in the end section of the centre tube. A sketch of the reactor is presented in Fig. 1. The reaction temperature is adjusted by automatic control of a horizontal tube furnace in which the reactor is positioned.

Analysis for the extent of CO conversion to CO_2 was performed by collection for a given period of time the product CO_2 in a trap cooled with liquid nitrogen. The amount of CO_2 collected was then compared with the known
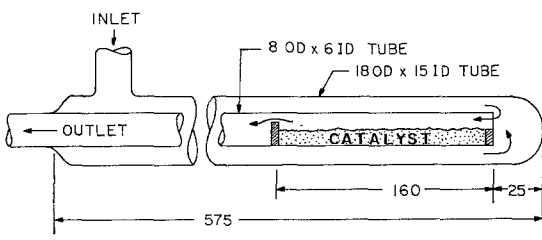

Figure 1 Quartz catalytic reactor for powder samples. Dimensions are in mm.

CO flow rate. Based upon experience with over seventy duplicate observations made during the research, about 90% of the data were within a precision range of ±5% of the observed mean value of conversion. This is within the expected limits resultant from an estimated ±2.5% accuracy in evaluation of the individual conversion level.

3. Results

The results of the catalytic oxidation of CO with O_2 over these oxides are presented in Fig. 2. Relative catalytic activity is commonly judged by comparison of the temperatures necessary to achieve some low level of conversion, e.g., about 20%.
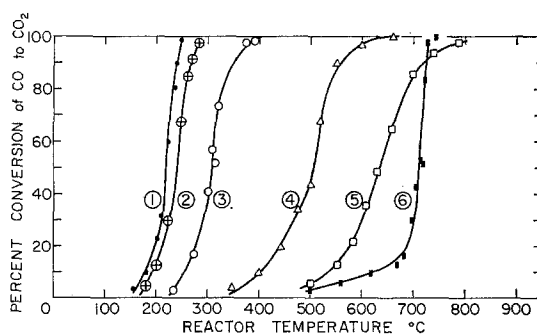

Figure 2 Heterogeneous catalytic oxidation of CO by O_2. The reactant stream (95 cc min^{-2} at 25°C, 1 atm) contained 3.4 mol % CO and 3.2 mol % O_2 in He. Conversion curves are for the following catalysts: 1. $LaCoO_3$, 1 g; 2. $LaCoO_3$, 0.5 g; 3. NiO, 1 g; 4. $Th_{0.85}La_{0.15}O_{1.925}$, 1 g; 5. ZrO_2, 1 g, and 6. $Zr_{0.91}Ca_{0.09}O_{1.91}$, 1 g.

When inspecting the data shown in Fig. 2 one notes achievement of 20% conversion of CO requires temperatures of 440, 575, and 685°C for the $Th_{0.85}La_{0.15}O_{1.925}$, ZrO_2 and $Zr_{0.91}Ca_{0.09}O_{1.91}$, respectively. This ranking of catalytic activity is as expected from the conclusions drawn in the preceding discussions of these catalysts. To allow one some perspective on the catalytic activities of these oxides, a sample of NiO annealed in air at 1000°C was examined, and these data are presented in Fig. 2. In addition, observations were made using 1 and 0.5 g charges of $LaCoO_3$ which has a high specific activity [6, 7]. The relatively small differences in temperatures necessary to achieve the 20% conversion level between these two samples illustrate the sensitivity of the present apparatus. There appears to be no difficulty introduced into judging relative catalyst activity

of the reported samples because of errors from operational variables or mass and energy transport processes occurring in the reactor.

Alternative explanations for the higher activity of the doped thoria at lower temperatures, relative to the zirconia samples, include the possibility of enhanced adsorption sites for one of the reactants involved in the rate limiting process where the reactant may be either polarized or ionized. This would be reasonable if oxygen vacancies or oxygen vacancy-acceptor pairs at, or near, the surface were associated with these adsorption sites. Concentrations of these defects would be expected to be roughly comparable in the doped ThO_2 and ZrO_2 samples. For equal surface concentrations of adsorption sites, one would expect higher occupations for a polarized or ionized adsorbent if screening by mobile electronic charge were possible, as it is for the doped thoria and least so for the doped zirconia.

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