Oxygen Transfer Between Rhodium and an Oxygen-ion Conducting Support

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In industrial applications, it is a common practice to disperse metal catalysts over high surface area supports in order to obtain large surface area per unit mass of the catalytic metal. The ease with which a high dispersion can be achieved, stability against sintering, and cost are factors that usually enter into the selection of the support material. In some contexts, the supports modify the properties of the metal used as the catalyst and this introduces an additional consideration in the choice of support material. Strong metal-support interactions are known to exist and this has been the subject of many studies. For example, when titania is used as support for platinum, the catalyst exhibits a very high activity for methanation reaction as compared to platinum-on-alumina or -silica catalysts (Vannice et al., 1983).

Supported-metal catalysts are widely used for oxidation reactions. When inert materials such as alumina or silica are used as supports, the oxidation reactions proceed only on the surface of the metal crystallites. On the other hand, if one employs oxides exhibiting appreciable oxygen-ion mobilities at reaction temperatures [in particular, oxygen-ion conducting solid electrolytes such as yttria-stabilized zirconia, (YSZ)] as supports, an additional pathway for the oxidation reactions is made possible. This pathway involves oxygen transfer between the catalyst crystallites and the support at the three-phase interface between the crystallites, the support, and the gas phase. If the rates of these interfacial oxygen transfer reactions are comparable to the rate of the heterogeneous oxidation reaction occurring on the metal catalyst, then the metal catalyst dispersed over an oxygen-ion conducting support would exhibit an appreciably larger activity toward the oxidation reaction than the same metal catalyst dispersed over an inert support.

In a recent study (Metcalfe and Sundaresen, 1988), we reported that the CO oxidation activity of platinum dispersed over an oxygen-ion conducting support such as YSZ was much higher than that obtained when platinum was dispersed over alumina. It was argued that this enhancement in the activity was indeed due to oxygen transfer between the metal catalyst and the oxygen-ion conducting support occurring in the vicinity of the three-phase interface between the platinum, the support, and the gas phase. Electrochemical data to support this argument were also presented.

In this note, we present additional examples of relevance to automobile exhaust conversion in which a superior performance is achieved when a rhodium catalyst is dispersed over yttria-stabilized zirconia instead of alumina.

Experimental Procedure and Results

Highly dispersed rhodium catalyst was prepared on γ-alumina and YSZ supports. The supports were first dried and calcined at 773 K for 2 h and then weighed. They were then impregnated with an aqueous solution of rhodium (III) chloride. The metal loading was 0.02 wt. % in both cases. The catalyst samples were ground to approximately 100 μm dia. Ten milligrams of the catalysts were diluted in 10 g of low surface area, 100 μm alumina particles. The catalyst samples were held in place in stainless steel tubes using plugs of glass wool, which were not catalytically active. Kinetic experiments were carried out under isothermal conditions in a differential reactor mode. The reaction products and feed gases were analyzed by gas chromatography as described elsewhere (Metcalfe, 1987; Metcalfe and Sundaresan, 1988).

Figure 1 shows the rates of CO oxidation over Rh/YSZ and Rh/Al_2O_3 catalysts at 573 K. The Rh/YSZ catalyst exhibited a higher rate of CO_2 production than Rh/Al_2O_3.

In automobile exhaust conversion catalysts, the primary reason for adding rhodium is to achieve the reduction of nitric oxide to nitrogen efficiently. We studied the CO—NO reaction, instead of the CO—NO—O_2 reaction, for reasons of simplicity and also because of the evidence that the overall kinetic behavior of Rh/Al_2O_3 in CO—NO—O_2 mixtures is dominated by features characteristic of the CO—NO reaction (Oh et al., 1986a,b). A comparison of the rate of CO_2 production over the Rh/YSZ and Rh/Al_2O_3 catalysts is illustrated in Figure 2 for an inlet feed with 0.6% NO and between 2 and 10% CO (the balance being helium). The reaction temperature was 673 K.

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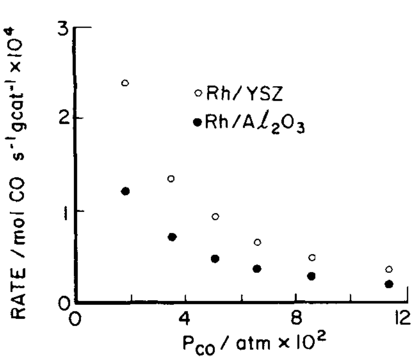

Figure 1. Rates of CO oxidation over Rh/YSZ and Rh/Al_2O_3 at 573 K.
O_2 partial pressure, 0.015 atm
Rhodium loading in each catalyst, 0.02 wt. %

The effect of water vapor (at 0.025 atm) on the performance of the rhodium catalysts is illustrated in Figure 3. The CO oxidation was carried out 573 K with partial pressures of 0.03 and 0.015 atm for CO and O_2, respectively. The water depressed the rate of CO oxidation over Rh/YSZ slightly while leaving the rate over Rh/Al_2O_3 unaltered. The addition of water vapor enhanced the rate of CO—NO reaction over both Rh/YSZ and Rh/Al_2O_3. The CO—NO reaction was carried out at 673 K with partial pressure of 0.03 and 0.006 atm for CO and NO, respectively. The effects of water vapor shown in Figure 3 were found to be fully reversible.

Discussion

We were not successful in obtaining reliable measurements of the quality of dispersion of the rhodium over the two supports. This was due to the very low levels of catalyst loading used in our study. Admittedly, a part of the difference in the reactivities observed for the Rh/YSZ and Rh/Al_2O_3 catalysts would be due to the difference in the levels of dispersion. But, we believe that the difference in dispersion levels alone cannot explain the observed difference in the reactivity levels. This is because the dispersion levels obtained by the impregnation procedure at such low metal loading levels used in our study are usually very high, approaching 100% (Akubuiro and Verykios, 1985). Thus a factor of two difference in reactivity levels is rather unlikely to be entirely due to differences in the dispersion levels. Furthermore, it is hardly reasonable to suspect dispersion effects while trying to explain the activity difference shown in Figure 2. This difference in activities between Rh/Al_2O_3 and Rh/YSZ is certainly not due to reactions on the supports alone. Kinetic experiments conducted using only supports revealed that neither support had any measurable activity toward either reaction at the temperatures indicated in Figures 1 and 2.

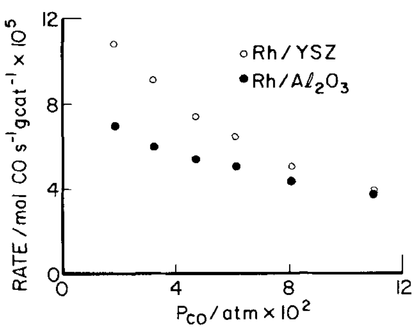

Figure 2. Rates of CO—NO reaction over Rh/YSZ and Rh/Al_2O_3 at 673 K.
NO partial pressure, 0.006 atm
Rhodium loading in each catalyst, 0.02 wt. %

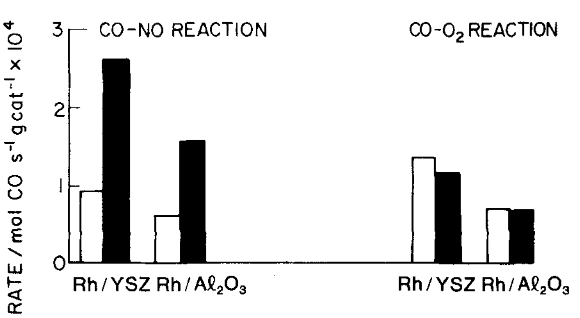

Figure 3. Effect of water vapor on rates of CO—NO and CO—O_2 reaction over Rh/YSZ and Rh/Al_2O_3.
Shaded: wet reaction conditions
Unshaded: dry reaction conditions

For CO oxidation, the qualitative features observed with the rhodium catalyst, Figures 1 and 3, are very similar to those observed with the platinum catalyst (Metcalfe and Sundaresan, 1987). For both Pt and Rh, higher oxidation activities were obtained with YSZ support than with Al_2O_3 support. Furthermore, for both catalysts, the water vapor had little effect if Al_2O_3 support was used, while a poisoning effect due to water vapor was observed with YSZ support. These similarities suggest that the explanation for the difference observed between the YSZ and Al_2O_3 supports is likely to be the same for both Pt and Rh.

In an earlier paper (Metcalfe and Sundaresan, 1988), we presented electrochemical measurements of oxygen transfer between Pt and YSZ under CO oxidation, and on the basis of these measurements proposed that the difference in the CO oxidation activity between Pt/YSZ and Pt/Al_2O_3 was due to the oxygen transfer between the YSZ support and the catalyst. We also described when and how this oxygen transfer would give rise to an enhancement in the CO oxidation activity. The observed poisoning effect due to water vapor was explained as resulting from the adsorption of water in the three-phase interface between the metal catalyst, YSZ, and gas phase.

We speculate here that interfacial oxygen transfer between the catalyst and YSZ is responsible for the enhancement in the rate of CO oxidation observed over Rh as well. Accordingly, in addition to the Langmuir-Hinshelwood reaction between carbon monoxide and oxygen adsorbed on rhodium (which occurs on both Rh/Al_2O_3 and Rh/YSZ), the following pathway is also believed to be available for CO oxidation on Rh/YSZ (and not Rh/Al_2O_3):

$$CO^* + O_0 \rightarrow V_0^{\bullet\bullet} + CO_2 + 2e^- + * \qquad (1)$$

Here * and CO* denote unoccupied site and carbon monoxide chemisorbed on the Rh surface, respectively; O_0 and $V_0^{\bullet\bullet}$ are oxygen and oxygen-ion vacancy in the lattice of the YSZ support, respectively. The reoxidation of the YSZ support (which must occur at the same rate as the above reaction under steady state conditions) can proceed according to

$$O^* + V_0^{\bullet\bullet} + 2e^- \rightarrow O_0 + * \qquad (2)$$

and

$$O^*_{ysz} + V_0^{\bullet\bullet} + 2e^- \rightarrow O_0 + *_{ysz} \qquad (3)$$

where O* denotes oxygen chemisorbed on Rh; $*_{ysz}$ and O^*_{ysz} denote vacant site and oxygen adsorbed on the YSZ surface, respectively. It was shown in an earlier paper (Metcalfe and Sundaresan, 1988) that under CO-rich conditions reaction 3 must indeed be more dominant than reaction 2 in order to realize the rate enhancement when YSZ is used as support. The same arguments are applicable for the present case as well.

In order to rationalize the difference in the rates of CO—NO reaction on Rh/YSZ and Rh/Al_2O_3, we propose the following pathway, which is possible with the YSZ support but not with the alumina support. The oxidation of CO adsorbed on the rhodium surface is postulated to occur in the three-phase region according to reaction 1 described above. The reoxidation of the YSZ support (which must occur at the same rate as reaction 1 under steady state conditions) can occur according to

$$NO^* + V_0^{\bullet\bullet} + 2e^- \rightarrow N^* + O_0 \qquad (4)$$

where N* and NO* denote nitrogen and nitric oxide adsorbed on rhodium. If the mechanism for the interfacial reactions is indeed that described by reactions 1 and 4, one can easily show, as described below, that the rate of the CO—NO reaction by the interfacial reactions should be proportional to $(\theta_{CO}\theta_{NO})^{1/2}$ where θ_{CO} and θ_{NO} denote the fractional surface coverage of CO and NO over rhodium. The rate of reaction 1 can be written as (Metcalfe and Sundaresan, 1988) $r_1 = \ell_3 k_1\,\theta_{CO} \exp\,[2(1-\beta)F\Delta\phi/RT]$ where ℓ_3 is the length of three-phase contact, k_1 is the Arrhenius rate constant, $\Delta\phi$ is the potential difference between the metal and YSZ support, β is the symmetry factor for the charge transfer reaction, F is the Faraday constant, R is the gas constant, and T is the temperature. The rate of reaction 4 can be written in an analogous fashion as $r_4 = \ell_3 k_4\,\theta_{NO} \exp\,(-2\beta F\Delta\phi/RT)$ where k_4 is an Arrhenius rate constant. At steady state, $r_1 = r_4$ and hence $\exp\,(F\Delta\phi/RT) = (k_4\,\theta_{NO}/k_1\theta_{CO})^{1/2}$. Metcalfe (1988) has verified through electrochemical measurements that for platinum deposited on YSZ, β is equal to ½, which indeed is its typical value. If we assume that the same value of β holds for rhodium deposited on YSZ as well, we have $r_1 = r_4 = \ell_s(k_1 \cdot k_4)^{1/2}(\theta_{CO}\theta_{NO})^{1/2}$.

Under the CO-rich conditions used in our study, it seems reasonable to expect the surface to be almost completely covered by CO, i.e., $\theta_{CO} \sim 1$. Furthermore, if adsorption-desorption equilibrium prevails for NO on the rhodium surface, θ_{NO} would be approximately proportional to P_{NO}/P_{CO}, the respective partial pressures of NO and CO in the gas phase. It then follows that in order for the proposed explanation to be consistent with the experimental data, the difference in the rates of the CO—NO reaction on Rh/YSZ and Rh/Al_2O_3 should vary linearly with $(P_{NO}/P_{CO})^{1/2}$ in the range of compositions studied here. This indeed was found to be the case, as shown in Figure 4, lending support to our hypothesis.

Note that both CO and NO participating in the interfacial reactions 1 and 4 are supplied by the rhodium crystallites. Thus the Rh/YSZ catalyst will outperform the Rh/Al_2O_3 catalyst only when the CO—NO reaction on the Rh surface is limited by the kinetics of the Langmuir-Hinshelwood reaction, and not the adsorption or desorption of one of the reactants. For example, if we increase the partial pressure of CO considerably so that the CO—NO reaction on Rh becomes limited by the rate of adsorption of NO, the difference in the activities of the Rh/YSZ and Rh/Al_2O_3 catalysts will disappear, Figure 2. Under excess CO conditions, what is required to enhance the rate of CO—NO reaction is another pathway for bringing NO to the catalytic sites, but neither the YSZ nor the Al_2O_3 provides such an additional pathway.

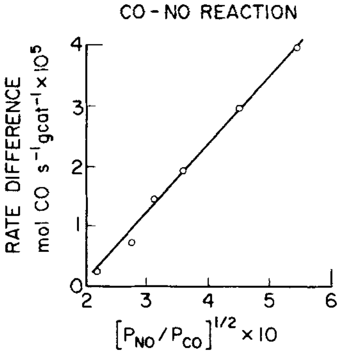

Figure 4. Difference in rates of CO—NO reaction over Rh/YSZ and Rh/Al_2O_3 vs. $(P_{NO}/P_{CO})^{1/2}$ at 673 K.
NO partial pressure, P_{NO}, 0.006 atm

In the context of CO oxidation, Pt/YSZ and Rh/YSZ outperform Pt/Al_2O_3 and Rh/Al_2O_3, respectively, even under excess CO conditions (where the reaction is limited by the rate of arrival of oxygen). This is because of the fact that the YSZ support introduces an additional pathway for bringing oxygen to the catalytic sites (Metcalfe and Sundaresan, 1988).

The presence of water vapor increased the rate of CO—NO reaction over both catalysts. We simply wish to point out that the Rh/YSZ catalyst outperforms the Rh/Al_2O_3 catalyst under both wet and dry reaction conditions.

Acknowledgment

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