Reduction of NO by H_2 and CO on $PdO–MoO_3/\gamma\text{-}Al_2O_3$ of low molybdena loading

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The activity and selectivity in the catalytic reduction of NO by a mixture of CO and H_2 of three $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts are compared in the presence of varying amounts of oxygen at reaction temperatures from 100 to 550°C. The catalysts were prepared by different methods and contain about 2% Mo and 2% Pd. Results are compared with those for $PdO/\gamma\text{-}Al_2O_3$, $PdO–MoO_3/\gamma\text{-}Al_2O_3$ containing 2% Pd and 20% Mo, and a commercial Pt–Rh catalyst. The $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts are more active for the selective reduction of NO to N_2 and N_2O than $PdO/\gamma\text{-}Al_2O_3$ under slightly oxidizing conditions at temperatures from 300 to 550°C. At these reaction conditions, the fresh $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts are comparable with a commercial Pt–Rh catalyst. The improved activity of $PdO–MoO_3/\gamma\text{-}Al_2O_3$ relative to $PdO/\gamma\text{-}Al_2O_3$ is believed to be due to the interaction between Pd and Mo. The effect of O_2 on the activity and selectivity of these catalysts is different in the reduction of NO by H_2, by CO, and by a mixture of H_2 and CO. The results using the mixture of reductants cannot be inferred from the results with the single reductants.

Keywords: NO reduction catalysis; NO reduction by H_2 and CO

1. Introduction

A fresh $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalyst containing 2% Pd and 20% Mo has under laboratory conditions an activity and selectivity for reducing NO to N_2 [1,2] approaching that of a commercial Rh containing catalyst [3–8]. The significant reducing species in the exhaust are CO and H_2, the source of H_2 being the water–

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gas shift reaction [4,9–11]. The Rh has two main advantages compared to other catalytic components: it is able to reduce NO selectively to N_2 without significant NH_3 production in the presence of H_2, and it selectively reduces NO in the presence of a small excess of oxygen. Since Rh is a scarce and expensive element, it is desirable to substitute it with less expensive materials [5–8]. To suppress the emission of molybdenum oxide which occurs at high temperatures in the presence of steam it is necessary to reduce the Mo content from the high values previously tried [1,2,12]. This is because the amount lost can be expected to be proportional to the amount in the catalyst and, also, because low loadings of molybdena on alumina strongly interact with the support and are stabilized thereby. Early results indicated [1] that the selectivity to N_2 of $PdO–MoO_3/\gamma\text{-}Al_2O_3$ decreases to the unsuitable level of a Pd catalyst when the Mo content is $<5\%$. It is conjectured that good selectivity requires close proximity of the Mo and Pd which is difficult to achieve at low Mo loadings.

Three different methods for the preparation of $PdO–MoO_3/\gamma\text{-}Al_2O_3$ were examined for the purpose of achieving close proximity of the Mo and Pd at relatively low loadings of Mo [12]. Results of temperature programmed reduction (TPR) and X-ray powder diffraction (XRD) measurements suggested that two of the methods achieved intimate interaction between the Pd and Mo in $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts containing 2% Pd and 2% Mo. The catalytic activity and selectivity of these catalysts has been tested for the reduction of NO by CO [13]. Three of the catalysts were found to be more active than $PdO/\gamma\text{-}Al_2O_3$ at slightly oxidizing conditions and at temperatures from 300 to 500°C. These three catalysts were also compared for the reduction of NO by H_2 [14]. In the absence of oxygen, the selective conversion of NO to N_2 and N_2O was found to be higher on $PdO–MoO_3/\gamma\text{-}Al_2O_3$ than on $PdO/\gamma\text{-}Al_2O_3$ at temperature 500°C. In the presence of oxygen, one of the $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts was more active in the selective reduction of NO by H_2 than $PdO/\gamma\text{-}Al_2O_3$.

In this report, the catalytic activities and selectivities of the above three catalysts are compared with each other for the reduction of NO by a mixture of H_2 and CO in the presence of different amounts of O_2. Also, comparison is made with the activities and selectivities of $PdO/\gamma\text{-}Al_2O_3$, of $PdO–MoO_3/\gamma\text{-}Al_2O_3$ containing 2% Pd and 20% Mo, and of a commercial Pt–Rh catalyst.

2. Experimental

2.1. PREPARATION OF CATALYSTS

Details of the catalyst preparation and experimental methods have been previously described [14]. A brief summary is presented here for convenience. The catalysts were made by the incipient wetness technique. The $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts were prepared by having the Pd solution adsorbed by $MoO_3/\gamma\text{-}Al_2O_3$.

Catalysts containing only Pd, only Mo, and both of these elements are identified by the symbols of the elements. The numerical suffix gives the concentration of elements. The (–) or (+) sign shows that the Pd was deposited using an anionic solution of $H_2[PdCl_2(OH)_2]$ or a cationic solution of $[Pd(NH_3)_4]Cl_2$, respectively. The (CO) suffix indicates that $Mo(CO)_6$ was used for depositing the molybdena. In all other cases, Mo was deposited from a solution of $(NH_4)_2MoO_4$. The catalysts of this paper are identified as samples 2Pd(–), 2Pd(–)20Mo, 2Pd(–)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)2Mo(CO) and correspond to samples P2, MP1, MP5, MP6, and MP9, respectively, in a previous paper [14]. The commercial (Engelhard Corp.) honeycomb-shaped monolith catalyst contained 0.03% Rh and 0.16% Pt and is identified as sample 0.16Pt0.03Rh. It should be noted that the concentration of metals is up to ten times higher in the γ-Al_2O_3 washcoat part of the catalyst [6–8]. The monolith was ground and the 80–100 mesh fraction was used for catalytic measurements.

2.2. ACTIVITY MEASUREMENTS AND ANALYSIS

Catalytic experiments were done with equal contact times for the catalysts using 0.46 cm^3 of samples. The samples were placed in a fused quartz reactor (10 mm i.d.) of the flow-through type, preheated in a flow of He (27.2 ℓ/h) for 1 h and then in a flow of H_2 (95 ml/h) + NO (27 ml/h) + He (27.2 ℓ/h) for 2 h at 550°C. To avoid a systematic error, the sequential reaction temperatures were chosen randomly. For catalytic measurements, a flow of 27 ml/h NO, 95 ml/h H_2, and 270 ml/h CO was mixed with He (27.2 ℓ/h) to achieve a total pressure of 1 × 105 Pa (1 atm). The ratio of the gases and the space velocity (SV = 60 000 h^{-1}) were chosen to approximate the conditions in an automotive exhaust [3–8] but cannot completely simulate them. To check the effect of oxygen, 60 to 300 ml/h O_2 was also added to the gas stream. Details of the experimental system are described elsewhere [2,12–17].

The NO and NO_x content in the gas stream at the reactor outlet was continuously analyzed using a Thermo Electron model 10A chemiluminescent NO–NO_x gas analyser, and it was compared with the NO content at the reactor inlet to calculate the conversion of NO. The NH_3 content was determined by its oxidation to NO. This surplus NO was also measured using the chemiluminescent NO–NO_x gas analyser.

Since no analysis for N_2 or N_2O was made, the selectivity, S, for N_2 and N_2O is calculated from the difference of all NO reacted and NO reduced into NH_3 as reported earlier [2,11]:

$$S\ (\%) = \frac{100([NO_{\mathrm{inlet}}] - [NO_{\mathrm{outlet}}] - [NH_{3\mathrm{outlet}}])}{[NO_{\mathrm{inlet}}] - [NO_{\mathrm{outlet}}]}.$$

The activity and selectivity of the catalysts are studied as a function of the redox ratio, *R*, of the reacting gas mixture. *R* is the stoichiometric ratio of oxidizing and reducing components in the gas mixture and is given by the following formula. The coefficients are determined by the number of electrons transferred.

$$R=\frac{2[\mathrm{NO}]+4[\mathrm{O_2}]}{2[\mathrm{CO}]+2[\mathrm{H_2}]}=\frac{[\mathrm{NO}]+2[\mathrm{O_2}]}{[\mathrm{CO}]+[\mathrm{H_2}]}.$$

Thus, $R = 1$ corresponds to a stoichiometric mixture, while $R > 1$ represents an oxidizing mixture. Except for oxygen, the ratio of the reactant gases is fixed at $CO : H_2 : NO = 1 : 0.35 : 0.1$. $R = 1$ when 1 mol CO, 0.35 mol H_2, 0.1 mol NO, and 0.625 mol O_2 are present. *R* is varied by varying the relative amount of oxygen.

3. Results and discussion

3.1. CATALYTIC ACTIVITY FOR THE REDUCTION OF NO

In the absence of oxygen ($R = 0.1$), more than 99% NO conversion was measured on all catalysts at temperatures over 200°C. The high conversion of NO persists in the presence of oxygen up to $R = 1.2$. Fig. 1 shows NO conversion at $R = 1.2$. At higher *R* values, a sharper drop of activity occurs, very similar to that reported for 2Pd(–)20Mo [2].

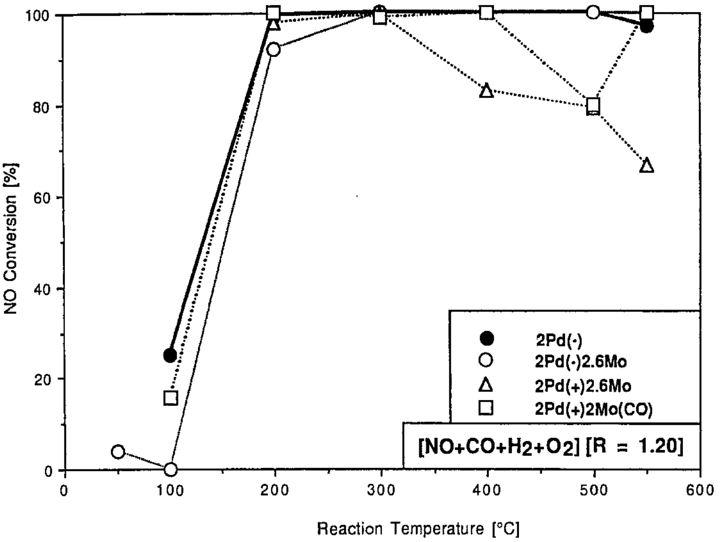

Fig. 1. Comparison of the activity of different catalysts at $R = 1.2$ redox ratio. Concentration of reactants: 0.1% NO + 1% CO + 0.3% H_2 in He; total pressure = 1.0×105 Pa; SV ≈ 60 000 h^{-1}.

Using only H_2 (instead of the mixture of CO and H_2) for the reduction of NO, a strong decrease in conversion was observed at temperatures above 200°C in the presence of oxygen even at $R = 1.0$ on samples 2Pd(−)20Mo, 2Pd(−)2.6Mo, and 2Pd(+)2.6Mo. The activity of 2Pd(−) and 2Pd(+)2Mo(CO) was found to be less sensitive to the presence of oxygen for this reaction [14]. Using only CO (instead of the mixture of CO and H_2) for the reduction of NO, only the activity of 2Pd(−) decreased significantly (~ 50% NO conversion) at 300 and 400°C at R values near to 1.2 [14]. In contrast, higher than 90% NO conversions were measured at the same reaction conditions on all four of these $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts [14]. However, only on samples 2Pd(−)20Mo and 2Pd(+)2Mo(CO) were the conversions higher than 70% at $R > 1.2$ at 500 and 550°C for the reaction of NO with CO [13].

The following results indicate that there is an interaction between the Pd and Mo in samples 2Pd(−)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)2Mo(CO), but it has no advantage for the overall activity in the reduction of NO by *an oxygen-free mixture* of CO and H_2 compared to the monometallic catalyst 2Pd(−). Further, when NO is reduced by a mixture of CO and H_2 at 500 and 550°C in the presence of O_2, the conversion is *much higher* on all catalysts studied than found for either the reduction of NO by CO alone or the reduction of NO by H_2 alone.

3.2. SELECTIVITY FOR N_2 AND N_2O

The ability to reduce NO to N_2 and N_2O instead of to NH_3 in the presence of H_2 is an important requirement for automotive catalysts [2,4]. Fig. 2 shows that the

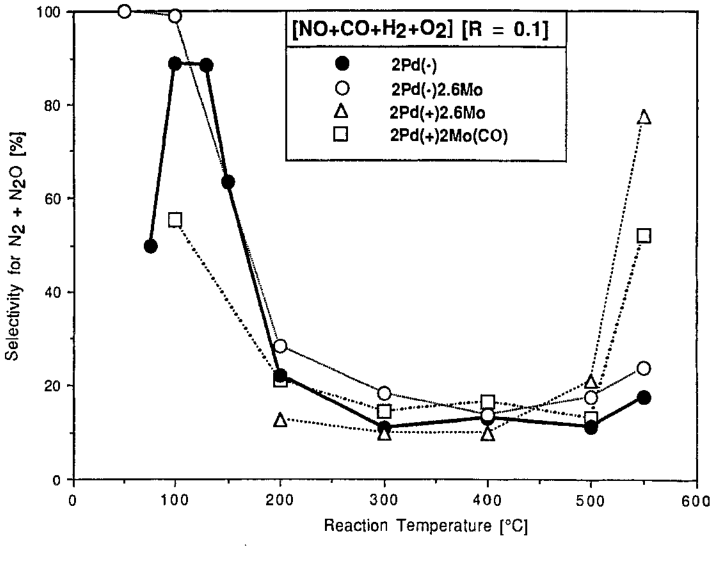

Fig. 2. Comparison of the selectivity of different catalysts in the absence of oxygen. Reaction parameters are the same as in fig. 1.

temperature dependence of selectivities on some catalysts for the reduction of NO by CO and H_2 in the absence of O_2. At temperatures <500°C, selectivity changes are opposite to those observed for the activities. At 550°C, the selectivities of 2Pd(+)2.6Mo and 2Pd(+)2Mo(CO) increase while the selectivities of the other two catalysts do not. The shapes of the curves in fig. 2 resemble those observed for the selectivity of these catalysts in the reaction of NO with H_2 [14]. The temperature dependence of selectivities of 2Pd(+)2.6Mo and 2Pd(+)2Mo(CO) are similar to that of 2Pd(−)20Mo [2]. The difference between the selectivities of 2Pd(−) and those of the PdO–MoO$_3$/γ-Al$_2$O$_3$ samples is tentatively ascribed to the interaction of Pd and Mo [2,13,14].

In the presence of O_2, the selectivity of all samples varies depending on the relative amount of oxygen added. Fig. 3 shows the selectivities of sample 2Pd(−)2.6Mo as a function of the redox ratio. The behavior is typical for all the other PdO–MoO$_3$/γ-Al$_2$O$_3$ catalysts studied. Fig. 3 clearly indicates that the selectivity gradually increases in the presence of oxygen. At $R < 1.2$, the increase of the selectivity is particularly strong at temperatures of 400 and 500°C. The best selectivities over the full temperature range are observed at $1.2 < R < 1.3$. At $R > 1.3$, selectivities at low temperatures (300°C) are high. However, at temperatures from 400 to 550°C, the selectivities at $R > 1.3$ are significantly lower than the selectivities at $1.1 < R < 1.2$.

These results indicate that the formation of NH_3 is inhibited in the presence of O_2. Similar observation was made for the reduction of NO by H_2 [14]. The switch of selectivity at $R \approx 1.2$ at high and low temperatures (fig. 3) is probably associated

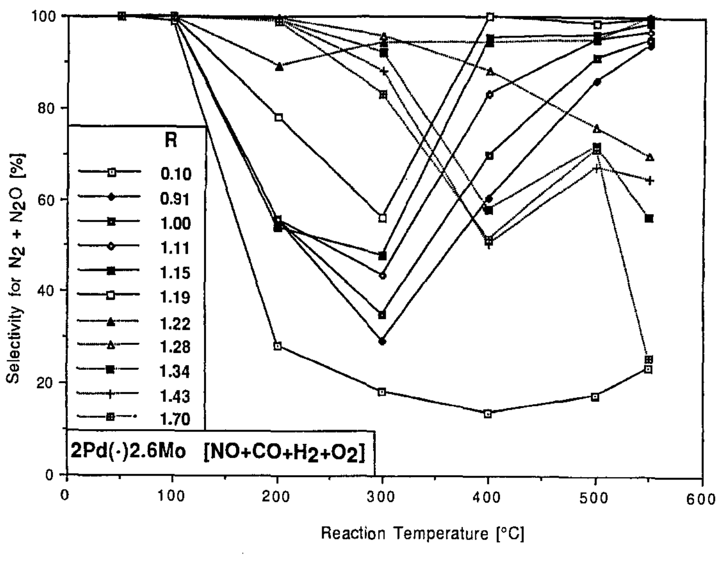

Fig. 3. Selectivity versus reaction temperature at different redox ratios (R) over the 2Pd(−)2.6Mo sample. Reaction parameters are the same as in fig. 1.

with the decline in activity at $R \approx 1.2$ (fig. 1). Since oxygen has a smaller effect on the reactivity of CO compared to that of H_2 [2,13,14] and maximum activity is observed at $R \approx 1.2$ at temperatures from 300 to 400°C in the reaction of NO with CO [13], it appears that CO does contribute to the activity and selectivity in the reduction of NO by a mixture of H_2 and CO.

3.3. COMPARISON OF THE YIELDS OF N_2 PLUS N_2O OVER DIFFERENT CATALYSTS

Figs. 4, 5, and 6 show the selectivity to N_2 plus N_2O of the catalysts at several temperatures as a function of the redox ratio. For comparison, the selectivities over 2Pd(−)20Mo and 0.16Pt0.03Rh are also shown. The dashed lines at $R = 0.8$ and 1.2 bound the important range of the redox ratio (window) for automotive use. In actual, operating TWC catalysts this window is narrower than these bounds and is maintained by feedback-controlled fuel mixture preparation.

At 300°C (fig. 4), the yields are below 40% on all catalysts near to $R = 1$. However, there is a sharp increase at around $R = 1.2$ on each sample. Except for the commercial 0.16Pt0.03Rh catalyst, the maximum activity covers only a very narrow range of R. These results differ from those reported [13,14] for the reactions of NO with H_2 and NO with CO, for which higher than 80% yields were measured near $R = 1.0$ over most catalysts. In the reduction of NO by a mixture of H_2 and CO at redox ratios of $1.1 < R < 1.2$, the selectivities are better on catalysts 2Pd(−)2.6Mo and 2Pd(+)2Mo(CO) than on the other catalysts (fig. 4).

At 400°C (fig. 5), the selectivity exceeds 50% over the entire $0.8 < R < 1.2$ range on all catalysts. Under slightly reducing conditions at $R \approx 0.9$, the yields over cata-

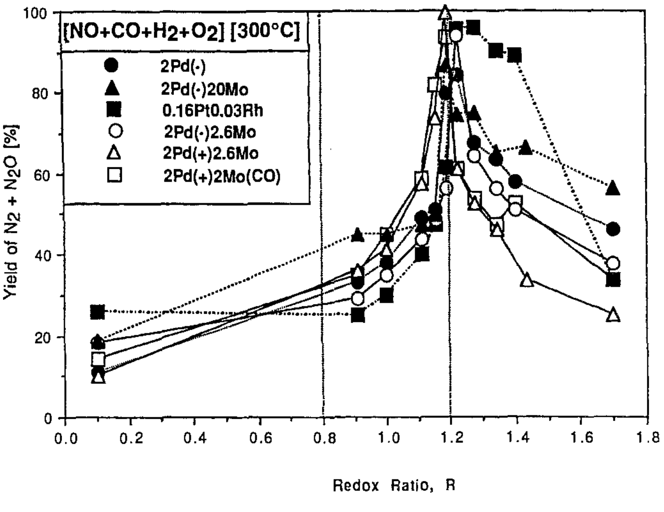

Fig. 4. Effect of O_2 on the yield of N_2 and N_2O on different catalysts at 300°C. Reaction parameters are the same as in fig. 1.

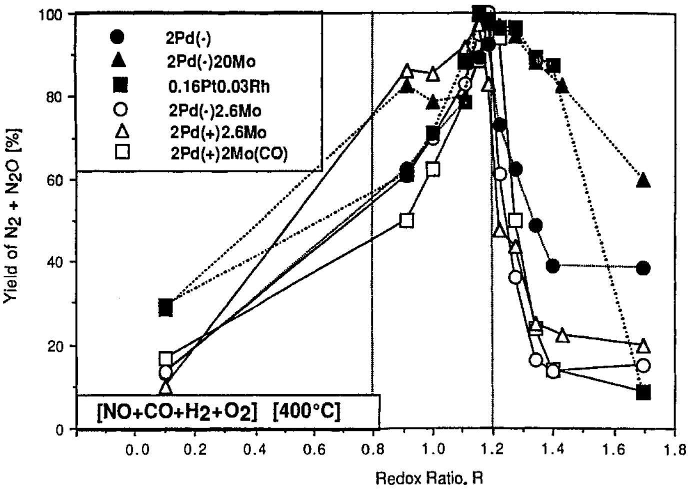

Fig. 5. Effect of O_2 on the yield of N_2 and N_2O on different catalysts at 400°C. Reaction parameters are the same as in fig. 1.

lysts 2Pd(–)20Mo and 2Pd(+)2.6Mo are higher than over the other catalysts including the commercial catalyst containing Rh. However, in the presence of a large excess of oxygen ($1.3 < R < 1.6$) only the catalyst of high Mo loading, 2Pd(–)20Mo, and the commercial catalyst containing 0.16Pt0.03Rh gave high yields.

Fig. 6 shows that NO is reduced selectively to N_2 and N_2O with over 80% yields at 500°C in the redox window on all catalysts, with the exception of 2Pd(–). Very

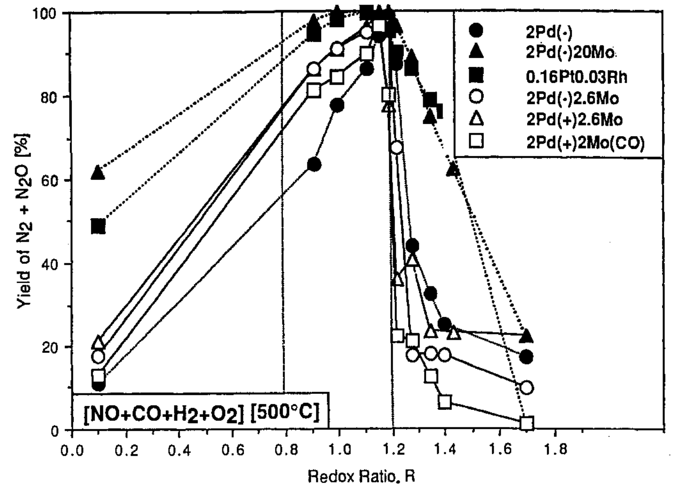

Fig. 6. Effect of O_2 on the yield of N_2 and N_2O on different catalysts at 500°C. Reaction parameters are the same as in fig. 1.

similar results were also observed at 550°C and the yields were >90%. The improved yields on the $PdO–MoO_3/\gamma$-Al_2O_3 compared to PdO/γ-Al_2O_3 are, again, tentatively ascribed to the interaction between Pd and Mo.

Figs. 4, 5, and 6 indicate that, using slightly oxidizing reaction conditions ($1.0 < R < 1.2$), the fresh $PdO–MoO_3/\gamma$-Al_2O_3 catalysts, including those containing only 2% Mo, are about as effective for the selective reduction of NO as is a commercial Rh containing catalyst at temperatures from 300 to 550°C. The Mo containing catalysts are slightly superior at low temperatures. At high temperatures and at redox ratios $R > 1.3$, only the fresh 2Pd(–)20Mo catalyst appears to be competitive with the commercial catalyst.

4. Conclusions

(1) Fresh $PdO–MoO_3/\gamma$-Al_2O_3 catalysts containing relatively low loadings of Mo (2% Pd and 2% Mo) are active and selective for the reduction of NO by a mixture of H_2 and CO under slightly oxidizing conditions ($1.0 < R < 1.2$) at temperatures from 300 to 550°C. At lower temperatures, the selectivity to N_2 and N_2O are somewhat higher on 2Pd(+)2.6Mo than on a commercial Pt–Rh catalyst.

(2) The differences between the catalytic activity and selectivity of the monometallic catalyst 2Pd(–) and the bimetallic catalysts of low molybdena content, 2Pd(–)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)2Mo(CO), are similar to the differences observed between the activity and selectivity of 2Pd(–) and the bimetallic catalyst of high molybdena loading, 2Pd(–)20Mo [2]. The results indicate that there is probably an interaction between the Pd and Mo in the bimetallic catalysts leading to improved yields of N_2 and N_2O compared to the yields on PdO/γ-Al_2O_3.

(3) The effect of O_2 on the activity and selectivity of catalysts is quite different in the reduction of NO by H_2 [14], by CO [13], and by a mixture of H_2 and CO. Results with the mixture of reductants cannot be inferred directly from the results with the single reductants.

These results must not be overinterpreted to mean that the catalysts studied in this work are close to being ready for practical application. The results show, nevertheless, that a lower cost automotive catalyst should be pursued. Much more work is needed to ascertain stability against volatilization, resistance to spatial separation of the components and clarification of other durability issues. More effort is also needed to study the interaction of noble metals and base metal oxides on the fundamental level.

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