Reduction of NO by CO on $PdO–MoO_3/\gamma$-Al_2O_3 of low molybdena loading

Istvan Halasz [1], Alan Brenner [2]
Department of Chemistry, Wayne State University, Detroit, MI 48202, USA

and

Mordecai Shelef
Scientific Research Staff, Ford Motor Co., Dearborn, MI 48121, USA

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The catalytic activity for the reduction of NO by CO of five $PdO–MoO_3/\gamma$-Al_2O_3 catalysts is compared in the presence of varying amounts of oxygen at reaction temperatures from 25 to 550°C. The samples were prepared by different methods and contain about 2% of Mo and 2% Pd. Results are compared with the activities and selectivities of PdO/γ-Al_2O_3 and $PdO–MoO_3/\gamma$-Al_2O_3 containing 2% Pd and 2% Pd + 20% Mo, respectively. All catalysts showed appreciable activity at temperatures between 300 and 550°C and at stoichiometric ratios, R, of the oxidizing to reducing gases of $0.1 < R < 1.1$. The activity of three $PdO–MoO_3/\gamma$-Al_2O_3 catalysts with low concentrations of Mo and Pd was found to be significantly higher than the activity of PdO/γ-Al_2O_3 at $1.1 < R < 1.3$ and at temperatures between 300 and 500°C. The improved activity is ascribed to the interaction of the active metals.

Keywords: Reduction of NO; PdO catalysts; MoO_3 catalysts; bimetallic catalysts; $PdO–MoO_3$ catalysts; automotive catalysts; automotive pollution control; NO_x

1. Introduction

The catalytic reduction of NO is important in air pollution control [1–8]. Since Rh has the desired activity and selectivity for this reaction, it is one of the components in automotive three-way catalysts [3,5]. However, its high cost and scarce resources [3–6] make it desirable to minimize its use.

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[1] Permanent address: Central Research Institute for Chemistry of the Hungarian Academy of Sciences, PO Box 17, Budapest, Hungary.

[2] To whom correspondence should be addressed.

Earlier studies [9] showed that a $PdO-MoO_3/\gamma-Al_2O_3$ catalyst containing 2% Pd and 20% Mo is quite active and selective for the reduction of NO by CO, by H_2, and by $CO + H_2$ at reaction temperatures from 300 to 550°C and under either slightly reducing or slightly oxidizing reaction conditions. This catalyst tolerated about 10% more oxygen without significant loss of activity or selectivity compared to a commercial Rh based automotive catalyst. Similar results were reported for a $PtO_2-MoO_3/\gamma-Al_2O_3$ catalyst containing 2% Pt and 30% Mo [10].

Nevertheless, it is necessary to lower the Mo content to minimize the expected volatilization of molybdena at high temperatures and especially in the presence of steam [10]. However, it has been reported that the improved activity and selectivity of $PtO_2-MoO_3/\gamma-Al_2O_3$ (2% Pt) is lost when the Mo content is greatly reduced. For example, for the reduction of NO by $H_2 + CO$, the selective NO conversion decreased from 60 to 4% when the Mo content was lowered from 30 to 3% [10]. Since the probability of Pt or Pd being in close proximity to Mo is high when the surface of the support is largely covered by molybdena, it was suggested that the loss of selectivity at low Mo loadings was due to the less intimate contact between Pt and Mo ions. Consequently, an improved method of preparing these catalysts which will encourage close proximity of the active metals at low concentrations is desired.

Three different procedures for the preparation of $PdO-MoO_3/\gamma-Al_2O_3$ catalysts have been reported [9]. Examination of the catalysts by temperature programmed reduction (TPR) and X-ray powder diffraction (XRD) demonstrated that two of the methods resulted in an interaction between finely divided palladium and molybdenum oxides even at low ($\approx 2\%$) loadings of the active metals. The first catalytic study on some of these samples is reported here.

2. Experimental

2.1. PREPARATION OF CATALYSTS

The catalysts were prepared by impregnation of Pd and Mo salts onto $\gamma-Al_2O_3$ followed by calcination in a porcelain or quartz crucible in air or in a stream of pure O_2. The compounds used were $(NH_4)_2MoO_4$ (pure grade) from Climax Molybdenum Co., $Mo(CO)_6$ (pure grade) from Alfa Inorganics, and $PdCl_2$ (nominal composition > 59% Pd) from MCB. The $\gamma-Al_2O_3$ was 80–100 mesh of sample 8801K Catapal from Conoco. The surface area and average pore diameter after calcination at 500°C were 203 m^2/g and 7 nm, respectively [9,11].

A detailed description of the preparation methods as well as of the TPR and XRD characterization of samples is given in ref. [9]. For convenient comparison, some data are summarized in table 1. Catalysts containing only Pd, only Mo, and

Table 1
Summary of physical and chemical characteristics of the catalysts (data are from ref. [9])

Name of sample	Notation in ref. [9]	Weight% of		Size of crystallites [a] (nm)	
		Mo	Pd	MoO$_3$	PdO
2Pd(−)	P2	0	2.0	–	5.3
20Mo	M2	20.7	–	55.1	–
2Pd(−)20Mo	MP1	20.2	2.0	33.9	na [b]
2Pd(−)2.6Mo	MP5	2.6	2.0	< 3.5	8.0
2Pd(+)2.6Mo	MP6	2.6	2.0	< 3.5	< 3.5
2Pd(+)1.8Mo(coad)	MP7	1.8	2.0	< 3.5	< 3.5
2Pd(−)2Mo(CO)	MP8	2.0	2.0	< 3.5	5.9
2Pd(+)2Mo(CO)	MP9	2.0	2.0	< 3.5	4.5

[a] Diameter as prepared.
[b] Not measurable (see ref. [9]).

both elements are identified by the symbols of the elements. The numeric suffix gives the concentration of the elements. The (−) or (+) signs show that the Pd was deposited using an anionic solution of $H_2[PdCl_2(OH)_2]$ or a cationic solution of $[Pd(NH_3)_4]Cl_2$. 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 (coad) suffix denotes that a mixture of the Pd and Mo salts was adsorbed on the alumina.

Sample 2Pd(−) was prepared by incipient wetness. Appropriate amounts of $PdCl_2$ were dissolved in hot water containing 4 vol% of HNO_3. The catalyst was dried at 120°C for 2 h and then calcined in air at 500°C for 2 h. Sample 20Mo was also prepared by incipient wetness. The $(NH_4)_2MoO_4$ was dissolved in hot water. The drying and oxidizing procedures were the same as those for 2Pd(−).

Samples 2Pd(−)20Mo and 2Pd(−)2.6Mo were prepared similarly to the 2Pd(−), except that the solution of palladium was taken up by $MoO_3/\gamma\text{-}Al_2O_3$ containing appropriate amounts of Mo.

For 2Pd(+)2.6Mo, the necessary amount of $PdCl_2$ was mixed with the required amount of water and HNO_3 (20 vol%) was added until a yellow (later reddish) precipitate was obtained. The mixture was heated and aqueous NH_4OH (10 vol%) was added until the precipitate disappeared and the solution became colorless. After evaporating excess water, the solution of $[Pd(NH_3)_4]Cl_2$ was added to the appropriate amount of $MoO_3/\gamma\text{-}Al_2O_3$ containing 2.6% Mo. The material was then treated in the same manner as 2Pd(−).

Sample 2Pd(+)1.8Mo(coad) was prepared by coadsorption of the metal ions. $PdCl_2$ was dissolved in hot HNO_3 (4 vol%). After adding $(NH_4)_2MoO_4$, NH_4OH (10 vol%) was added to the mixture until the precipitate disappeared, forming $[Pd(NH_3)_4]Cl_2$. After concentrating by evaporation, the solution was added to the $\gamma\text{-}Al_2O_3$. The drying and oxidizing procedures were the same as for 2Pd(−).

For samples 2Pd(−)2Mo(CO) and 2Pd(+)2Mo(CO), the γ-Al_2O_3 was first impregnated with the appropriate amounts of $H_2[PdCl_2(OH)_2]$ or $[Pd(NH_3)_4]Cl_2$, respectively. The materials were then treated as sample 2Pd(−). In the second step, $Mo(CO)_6$ vapor was adsorbed on both samples. The catalysts were then heated in flowing O_2 at 500°C for 2 h.

2.2. ACTIVITY MEASUREMENTS AND ANALYSIS

Catalytic experiments were done at equal contact times for all catalysts using 0.46 cm^3 of sample. The samples were contained in a fused quartz reactor (10 mm i.d.) of the flow-through type. The sample was supported on a porous quartz frit and covered with quartz wool. Catalysts were 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 the starting reaction temperature of 550°C. To avoid a systematic error, the sequential reaction temperatures were chosen randomly. For catalytic measurements, a flow of 27 ml/h NO and 270 ml/h CO was mixed with He (27.2 ℓ/h) to achieve a total pressure of 1 atm (1×10^5 Pa). The ratio of the gases and the space velocity (SV $\approx 60\,000$ h^{-1}) were chosen to approximate the conditions in an automotive exhaust [1–6]. For checking the effect of oxygen, appropriate flows of O_2 in the range from 60 to 300 ml/h were also added to the gas stream. The gas flow was controlled by Brooks mass flow controllers. The reactor system is constructed of stainless steel with bellows seal valves. Data points represent the average of two to five measurements carried out by a random variation of oxidizing and reducing conditions. The data scatter was $\approx 5\%$ of the average values. Details of the reactor system have been described elsewhere [11–14].

The NO and NO_x content in the gas stream at the reactor outlet were continuously analyzed using a Thermo Electron model 10A chemiluminescent NO–NO_x gas analyzer, and it was compared with the NO content at the reactor inlet to calculate the conversion of NO. Details of the analysis have been reported [9].

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 to reducing components in the gas mixture and is given by the following formula. The coefficients are determined by the number of electrons transferred,

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

Thus, $R = 1$ corresponds to a stoichiometric mixture, $R > 1$ represents an oxidizing (lean) mixture, and $R < 1$ corresponds to a reducing (rich) mixture. Except for oxygen, the ratios of the reactant gases are fixed, so R is varied by varying the oxygen concentration. For typical reaction conditions, $R = 1$ when the ratios of the gases are CO : NO : O_2 = 1 : 0.1 : 0.45.

3. Results and discussion

Due to the different operating conditions of internal-combustion engines, the exhaust temperature varies. The common temperature range in catalytic converters is from 300 to 500°C [3–6]. In addition, the catalyst has to be able to reduce nitrogen oxides under slightly oxidizing conditions since the oxidation of CO and hydrocarbons also occurs [1–6]. Hence, the activity of the catalysts was studied at different temperatures and in the presence of varying amounts of oxygen.

3.1. ACTIVITY VERSUS TEMPERATURE

Figs. 1, 2, and 3 compare the activity as a function of temperature of the catalysts in the presence of different amounts of oxygen. In the absence of oxygen (fig. 1), the activity of all samples increased monotonically with increasing temperature until ≈ 100% conversion was achieved. The activity of most

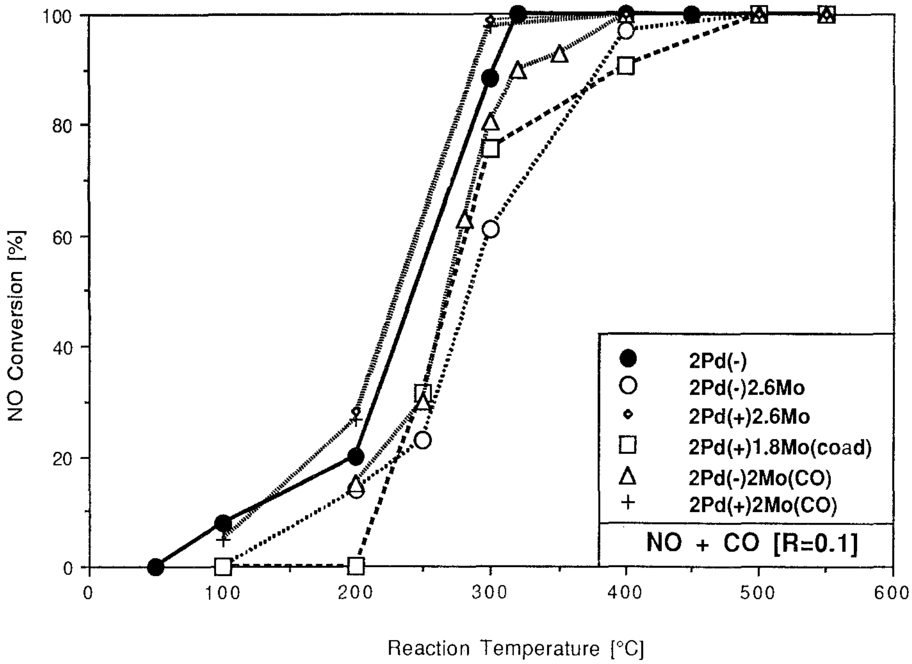

Fig. 1. Comparison of the activity of different catalysts in the absence of oxygen. Reaction conditions are 0.1% NO + 1% CO in He, total pressure = 1.0×10^5 Pa, SV ≈ 60000 h^{-1}. R is the stoichiometric ratio of oxidizing to reducing gases.

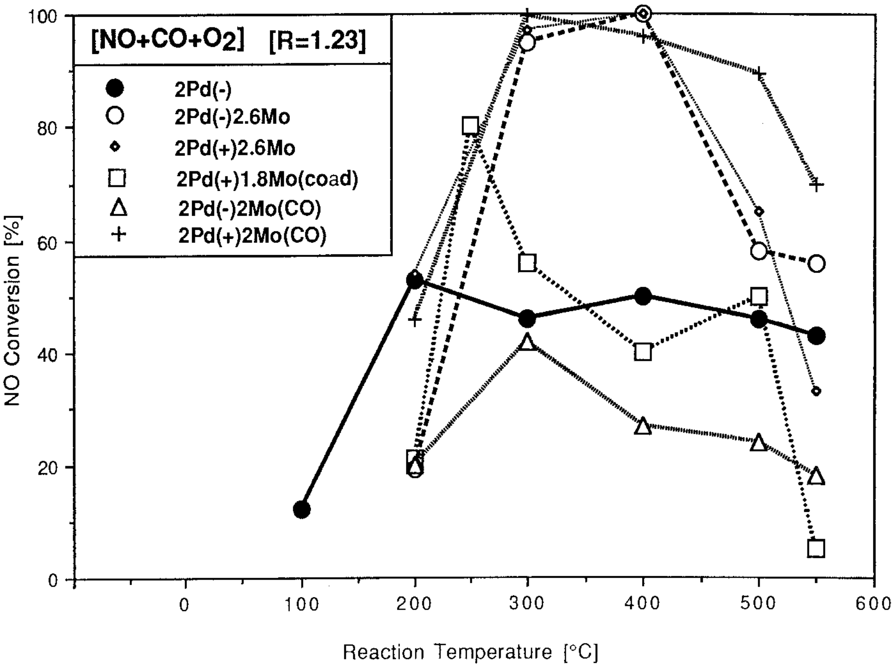

Fig. 2. Comparison of the activity of different catalysts at $R = 1.23$. Reaction conditions are the same as in fig. 1.

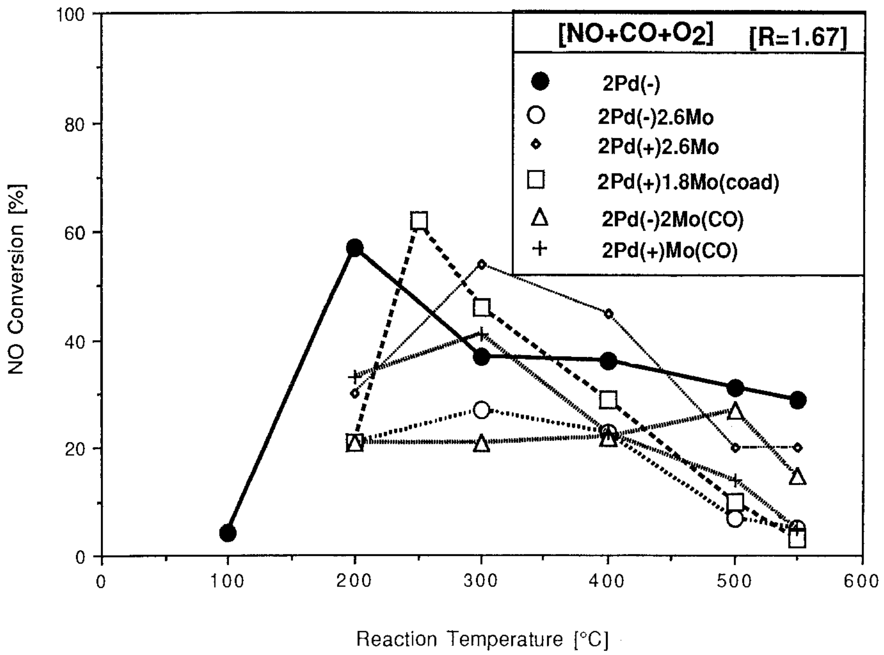

Fig. 3. Comparison of the activity of different catalysts at $R = 1.67$. Reaction conditions are the same as in fig. 1.

PdO–MoO$_3$/γ-Al$_2$O$_3$ samples is similar to that of PdO/γ-Al$_2$O$_3$. At the same conditions, MoO$_3$/γ-Al$_2$O$_3$ gave an NO conversion of only 25% at 550°C (table 1, sample 20Mo).

When oxygen is added to the reaction mixture at redox ratios $R < 1.0$ (not shown), the low temperature activity (< 300°C) of every PdO–MoO$_3$/γ-Al$_2$O$_3$ catalyst increased by about 30%. This behavior was also reported to be typical for PdO/γ-Al$_2$O$_3$ [9]. NO conversions over 99% were measured on the PdO–MoO$_3$/γ-Al$_2$O$_3$ catalysts (fig. 1) at redox ratios of $0.1 < R < 1.0$ and at reaction temperatures from 300 to 500°C. At reducing conditions, the activities of the catalysts are even closer to each other (< 10% difference in conversions) in the entire temperature range of fig. 1. These results indicate that the activity is determined by the presence of Pd under reducing conditions.

In contrast, significant differences were observed between the activities of the different samples at slightly oxidizing conditions. The differences are particularly noticable at redox ratios from 1.1 to 1.3. A typical example for the activity versus temperature curves in this range is shown in fig. 2. The appreciably higher activity of samples 2Pd(−)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)2Mo(CO) in the temperature range from 300 to 500°C and the low activity of 2Pd(−) points to a similar effect due to the presence of both Pd and Mo as reported for a PdO–MoO$_3$/γ-Al$_2$O$_3$ catalyst containing 20% Mo [9].

Although it appears that there is a strong interaction between the Mo and Pd in the three PdO–MoO$_3$/γ-Al$_2$O$_3$ catalysts, some results of fig. 2 are surprising considering earlier studies of such catalysts [9,10]. In the first case, the preparation method for the 2Pd(−)2.6Mo sample was the same as reported for a PtO$_2$–MoO$_3$/γ-Al$_2$O$_3$ catalyst containing 3% Mo [10]. The comparison of the activity of 2Pd(−)2.6Mo to that of 2Pd(−) indicates that, unlike the case of Pt–Mo, at low metal loadings Pd–Mo catalysts prepared by this method behave as if there is close proximity between the two elements. However, the TPR and XRD results [9] indicated a strong interaction between palladium and molybdenum oxides in all of the PdO–MoO$_3$/γ-Al$_2$O$_3$ catalysts studied here except for 2Pd(−)2.6Mo. In a second case, the most active catalyst, 2Pd(+)2Mo(CO), was prepared using a solution of [Pd(NH$_3$)$_4$]Cl$_2$, while the least active catalyst, 2Pd(−)2Mo(CO), was prepared using a solution of H$_2$[PdCl$_2$(OH)$_2$]. However, both the particle sizes (table 1) and the TPR curves [9] of these samples were found to be similar to each other. In contrast, both the particle sizes (table 1) and the TPR curves [9] are different for samples 2Pd(−)2.6Mo and 2Pd(+)2.6Mo, although their respective methods of preparation mirror those of 2Pd(−)2Mo(CO) and 2Pd(+)2Mo(CO). Nevertheless, the activity curves of samples 2Pd(−)2.6 and 2Pd(+)2.6 resemble each other. Thus, the catalytic activity does not necessarily correlate with characterization data.

Fig. 3 indicates that the activity of the PdO–MoO$_3$/γ-Al$_2$O$_3$ catalysts decreases at redox ratios of $R > 1.3$. A similar, but less precipitous, decrease in activity of PdO–MoO$_3$/γ-Al$_2$O$_3$ (20% Mo) was also observed [9].

3.2. EFFECT OF OXYGEN ON THE ACTIVITY

Figs. 4 and 5 show examples of the change in activity with the redox ratio, R. Fig. 4 compares the samples at 400°C which is found to be the optimum temperature for the best catalyst, 2Pd(+)2Mo(CO). Fig. 5 shows the activities at 550°C which simulates hot conditions in an automotive catalytic converter. For comparison, the activity curves of samples 2Pd(−) and 2Pd(−)20Mo (from ref. [9]) are also shown in both figures. The solid lines at $R = 0.8$ and $R = 1.2$ mark the more important composition window between slightly oxidizing and slightly reducing conditions.

As noted, most catalysts, including PdO/γ-Al$_2$O$_3$, have high activity under reducing conditions but the activity decreases sharply at higher R values. Since the relative amount of oxygen exceeds the amount of nitric oxide at $R > 0.3$, the inhibiting effect of oxygen cannot be attributed to the prevention of dissociative NO adsorption by the stronger adsorption of oxygen. The partitioning of CO between the two oxidants, O$_2$ and NO, determines the selectivity for reduction of NO at $R \geqslant 1$ [15]. The NO reduction at $R > 1$ depends on the relative rate ($\alpha = k_1/k_2$) of the two competitive reactions, CO + NO (rate constant k_1) and CO + O$_2$ (rate constant k_2). For most catalysts $k_2 \gg k_1$, so the activity for reduction of NO decreases abruptly as soon as the concentration of oxygen exceeds the stoichiometrically equivalent concentration of carbon monoxide.

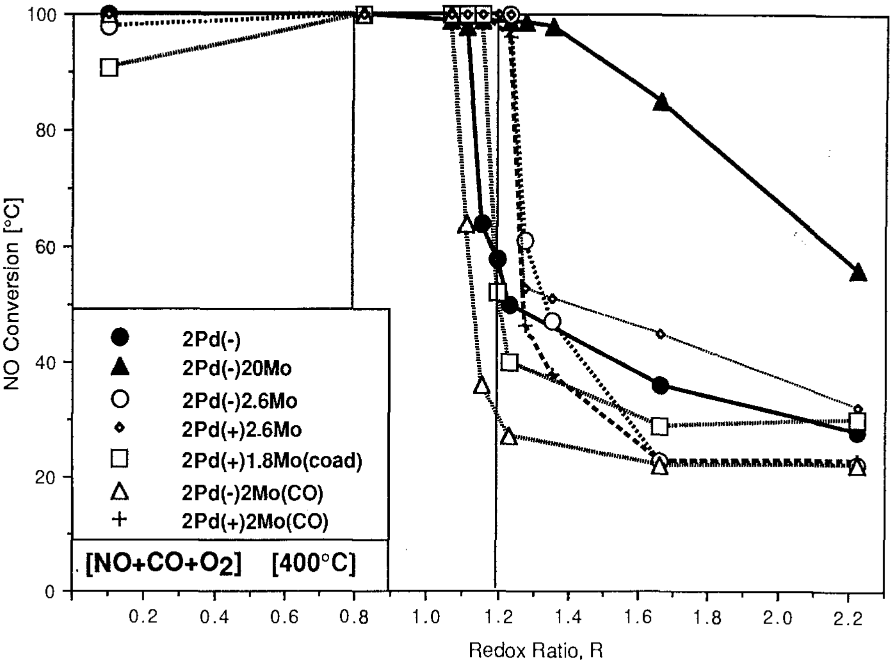

Fig. 4. Effect of O$_2$ on the activity of different catalysts at 400°C. Reaction conditions are the same as in fig. 1.

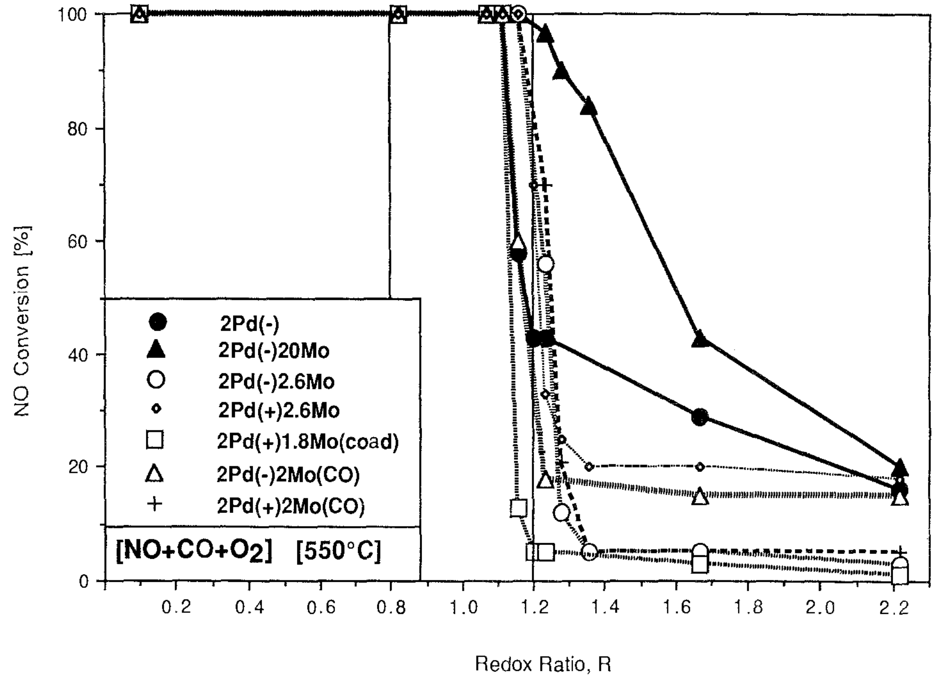

Fig. 5. Effect of O_2 on the activity of different catalysts at 550°C. Reaction conditions are the same as in fig. 1.

Palladium belongs to this group of catalysts. However, for some catalysts $k_2 \leqslant k_1$, so the activity for NO reduction does not decrease as steeply when $R > 1$. Examples of this group are Rh, Ir, and 2Pd(–)20Mo (which contains a high loading of Mo) [9].

Fig. 4 shows that 2Pd(–)2.6, 2Pd(+)2.6, and 2Pd(+)2Mo(CO) can tolerate about 20% more oxygen than 2Pd(–) before the activity drops sharply. At 550°C (fig. 5), some slight differences remain. Unlike 2Pd(–)20Mo, the three $PdO-MoO_3/\gamma-Al_2O_3$ catalysts with low molybdena lose activity abruptly at $R > 1.3$. In the case of 2Pd(–)20Mo, it is surmised [9] that the large amount of molybdena covers some of the active sites of Pd, thereby decreasing k_2 relative to a $PdO/\gamma-Al_2O_3$ catalyst (e.g., sample 2Pd(–)). This increases α. A similar increase in α (and for selectivity at $R > 1.3$) might occur if the Pd content of 2Pd(–)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)2Mo(CO) were lowered.

The activity is highly dependent on reaction conditions and probably is also influenced by the $PdO-MoO_3$ interface. Thus, turnover frequencies (TOF) have limited meaning. However, for the purpose of comparison to other catalysts, a rough value of TOF can be calculated. From the crystallite data in table 1 and assuming spherical geometry, a typical dispersion of the Pd of about 0.35 is calculated. Based on the reaction conditions, it follows that at 100% conversion, TOF = 0.02 s^{-1} (based on exposed Pd). Examination of figs. 1–3 shows that the temperature dependence (E_a) of the activity is strongly affected by the value of R and that for a given value of R, E_a is also not constant so values of E_a are of limited use.

4. Conclusions

(1) The bimetallic catalysts 2Pd(−)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)2Mo(CO) have appreciable activity for the reduction of NO by CO at temperatures from 300 to 500°C and at redox ratios of $R < 1.3$. Under oxidizing conditions at $1.1 < R < 1.3$, their activity is higher than the activity of a PdO/γ-Al_2O_3 catalyst, 2Pd(−).

(2) At reaction temperatures from 300 to 500°C, the activities of 2Pd(−)2.6Mo, 2Pd(+)2.6, and 2Pd(+)2Mo(CO) decrease at a redox ratio of about $R = 1.3$, while the activity of 2Pd(−), decreases abruptly near $R = 1.1$. Activity trends suggest that the oxygen tolerance of the bimetallic catalysts might be further improved by lowering the Pd concentration.

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References

[1] J. Wei, in: *Advances in Catalysis*, eds. P.D. Eley, H. Pines and P.B. Weisz (Academic Press, New York, 1975) p. 57.
[2] M. Shelef, Catal. Rev. Sci. Eng. 11 (1975) 1.
[3] J.T. Kummer, *Prog. Energy Combustion Sci.* 6 (1980) 177.
[4] W.F. Egelhoff Jr., in: *The Chemical Physics of Solid Surfaces and Heterogeneous Catalysis*, eds. D.A. King and D.P. Woodruff (Elsevier, Amsterdam, 1982) ch. 9, p. 397.
[5] K.C. Taylor, in: *Catalysis – Science and Technology*, Vol. 5, eds. J.R. Anderson and M. Boudart (Akademia Verlag, Berlin, 1984) p. 119.
[6] J.T. Kummer, J. Phys. Chem. 90 (1986) 4747.
[7] L.D. Pfefferle and W.C. Pfefferle, Catal. Rev. Sci. Eng. 29 (1987) 219.
[8] Z.R. Ismagilov, M.A. Kerzhentsev and T.L. Susharina, Russian Chem. Rev. 59 (1990) 973.
[9] I. Halasz, A. Brenner and M. Shelef, Appl. Catal., submitted.
[10] H.S. Gandhi, H.C. Yao and H.H. Stepien, in: *Catalysis Under Transient Conditions*, ACS Symp. Ser., Vol. 178, eds. A.T. Bell and L. Hegedus (Am. Chem. Soc., Washington, 1982) p. 143.

[11] A. Kadkhodayan and A. Brenner, J. Catal. 117 (1989) 331.
[12] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, Appl. Catal., in press.
[13] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, J. Catal. 126 (1990) 109.
[14] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, Catal. Lett. 6 (1990) 349.
[15] S.J. Tauster and L.L. Murrel, J. Catal. 53 (1978) 260.