Reduction of NO by H_2 on $PdO–MoO_3/\gamma-Al_2O_3$ of low molybdena loading

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The catalytic activity and selectivity of three $PdO–MoO_3/\gamma-Al_2O_3$ catalysts containing about 2% Pd and 2% Mo were studied for the reduction of NO by H_2 in the presence of varying amounts of oxygen at temperatures from 50 to 550°C. The results are compared with those for $PdO/\gamma-Al_2O_3$, $PdO–MoO_3/\gamma-Al_2O_3$ containing 2% Pd and 20% Mo, and a commercial Pt–Rh catalyst. In the absence of oxygen, the conversion of NO to N_2 and N_2O is higher on the three catalysts than it is on $PdO/\gamma-Al_2O_3$ at 500 and 550°C. In the presence of oxygen, the yields of N_2 and N_2O are generally lower on two of the $PdO–MoO_3/\gamma-Al_2O_3$ catalysts than on $PdO/\gamma-Al_2O_3$.

Keywords: Reduction of NO; NO_x; $PdO–MoO_3$ catalysts; pollution abatement; automotive catalysts; mixed metal catalysts; MoO_3 catalysts

1. Introduction

The desire to find a substitute for Rh, which is scarce and expensive, in automotive catalysts has generated considerable interest [1–6]. Some bimetallic catalysts containing a base metal and a noble metal have been shown to be effective for the selective reduction of NO. For instance, the activity and selectivity for the reduction of NO by CO and/or H_2 by $PdO–MoO_3/\gamma-Al_2O_3$ have been reported to be comparable to those of Rh in slightly reducing or slightly oxidizing reaction conditions [7,8]. To achieve good activity and selectivity of $PdO–MoO_3/\gamma-Al_2O_3$ and $PtO_2–MoO_3/\gamma-Al_2O_3$, a high loading of at least 20% Mo was used.

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For practical use, it is necessary to reduce the Mo content to minimize possible volatilization of molybdena at high temperatures in gas streams with a high moisture content. Unfortunately, the improved activity and selectivity for reducing NO to N_2 is largely lost when the Mo content is sharply lowered [7]. For example, when NO is reduced by H_2 and CO on $PtO_2–MoO_3/\gamma\text{-}Al_2O_3$ (2% Pt), the selective NO conversion decreased from 60 to 4% when the Mo content was lowered from 30 to 3%, respectively [7]. Since the statistical probability for Pt or Pd being located in close proximity to Mo is high when the surface of the support is highly covered by molybdena and low at low coverage, it is deduced that the poor selectivity at low Mo loadings is due to the absence of contact between Pt and Mo ions. Consequently, preparation procedures resulting in close proximity of the active metals at low concentrations are desirable.

We have described three different procedures for the preparation of the $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts [9]. Examination of the catalysts by temperature programmed reduction (TPR) and X-ray powder diffraction (XRD) has demonstrated that two of the methods resulted in an interaction between finely divided palladium and molybdenum oxides even at low (~ 2%) loadings of the active metals. The catalytic activity for the reduction of NO by CO of $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts containing low concentrations of Pd and Mo was also examined [10]. Three samples were found to be more active than $PdO/\gamma\text{-}Al_2O_3$ at slightly oxidizing conditions (redox ratios $1.1 < R < 1.3$, vide infra) in the temperature range of 300 to 500°C.

Results are reported here of the catalytic activity and selectivity of three $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts for the reduction of NO by H_2. The data are also compared with those of $PdO/\gamma\text{-}Al_2O_3$, $PdO–MoO_3/\gamma\text{-}Al_2O_3$ containing 2% Pd and 20% Mo, and a commercial Pt–Rh catalyst. In the $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalyst containing 20% Mo, the surface of the support is covered with molybdena, so close proximity of Pd and Mo is ensured. Consequently, this catalyst can be used as a model for the catalytic effects due to the Pd–Mo interaction. The data for the Pt–Rh catalyst allow a rough comparison with the current commercial usage.

2. Experimental

Details of the catalyst preparation and experimental methods have been previously described [8,10–13]. A brief summary is presented here for convenience. Catalysts containing only Pd, only Mo, and both of these elements were identified by the symbols of the elements. The numerical suffix gives the concentration of 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 $[Pd(NH_3)_4]Cl_2$, 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 commercial 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 about five to ten times higher in the γ-Al_2O_3 washcoat [1–6]. The monolith was ground and the 80–100 mesh fraction was used for catalytic measurements.

Catalytic experiments were done at equal contact times using 0.46 cm^3 of sample. 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. 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]. To check the effect of oxygen, appropriate flows of O_2 in the range from 160 to 360 ml/h were also added to the gas stream.

The NO and NO_x content in the gas stream at the reactor outlet was continuously analyzed using a chemiluminescent analyzer, 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, which was also determined by chemiluminescence. Since neither N_2 nor N_2O were directly analyzed, the selectivity, S, for N_2 and N_2O is calculated from the difference of all NO reacted and NO reduced to NH_3 as reported by Shelef and Gandhi [14],

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

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.

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

Thus, $R = 1, R < 1$, and $R > 1$ correspond to overall stoichiometric, reducing (rich), and oxidizing (lean) gas mixtures, respectively. Except for oxygen the ratios of the reactant gases are fixed, so R is varied by varying the oxygen concentration. For the case $R = 1$, the ratio of gases is $H_2 : NO : O_2 = 1 : 0.1 : 0.45$.

3. Results and discussion

The catalysts were studied at different temperatures and in the presence of varying amounts of oxygen to simulate the conditions present in an internal combustion engine. Figs. 1 and 2 compare the activities of the catalysts at different temperatures, and figs. 3 and 4 show the selectivities of the catalysts at different temperatures. Figs. 5 and 6 give the selectivity to $N_2 + N_2O$ versus redox ratio at low and high temperatures. In addition to the NO and NH_3, the formation of NO_2 was also monitored during the experiments. No measurable NO_2 was detected.

3.1. ACTIVITY AND SELECTIVITY VERSUS TEMPERATURE

In the absence of oxygen, the NO conversion was more than 99% on all catalysts at temperatures over 200°C. Fig. 1 shows that the activity of the 2Pd(−)2.6Mo and 2Pd(+)2.6Mo decreases in the presence of oxygen, although the reaction conditions are still reducing at $R = 0.9$. The activities of the other two catalysts are similar and only at high temperatures is there a slight drop in the activity. The inhibiting effect of oxygen is larger when $R = 1.0$ (fig. 2). Under oxidizing conditions, the activity decreases further. Results observed on the 2Pd(−)2.6Mo are very similar to those reported for the 2Pd(−)20Mo [8].

The inhibiting effect of oxygen suggests that H_2 reacts faster with O_2 than with NO, particularly at high temperatures. The decreased activity of 2Pd(−)2.6Mo and 2Pd(+)2.6Mo compared to that of the 2Pd(−) is reverse to the behavior for the reduction of NO by CO [10]. Nevertheless, both the promoting and inhibiting effects of molybdena indicate interaction between Pd and Mo.

Fig. 3 shows the selectivity versus temperature curves of catalysts in the absence of oxygen. The Mo containing catalysts have improved selectivity at high temperatures compared to 2Pd(−), and this was also observed with 2Pd(−)20Mo and the Rh containing catalyst [8]. Since the activity of all PdO–MoO_3/γ-Al_2O_3 catalysts with low Pd and Mo content is high in an oxygen free gas, catalysts 2Pd(+)2.6Mo

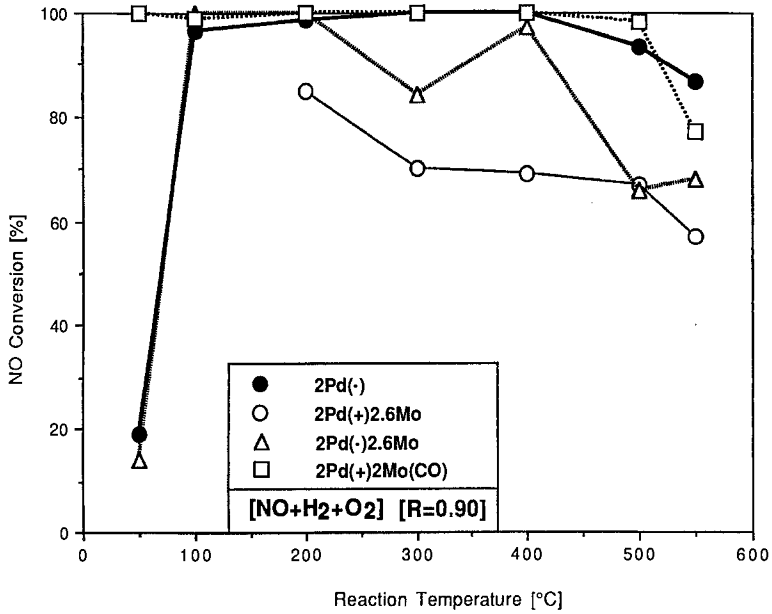

Fig. 1. Activity versus reaction temperature for the different catalysts. Reaction conditions: 0.1% NO + 0.3% H_2 in He plus added O_2 to give $R = 0.9$ (R is the stoichiometric ratio of oxidizing to reducing gases); total pressure = 1.0×10^5 Pa; SV ≈ 60 000 h^{-1}.

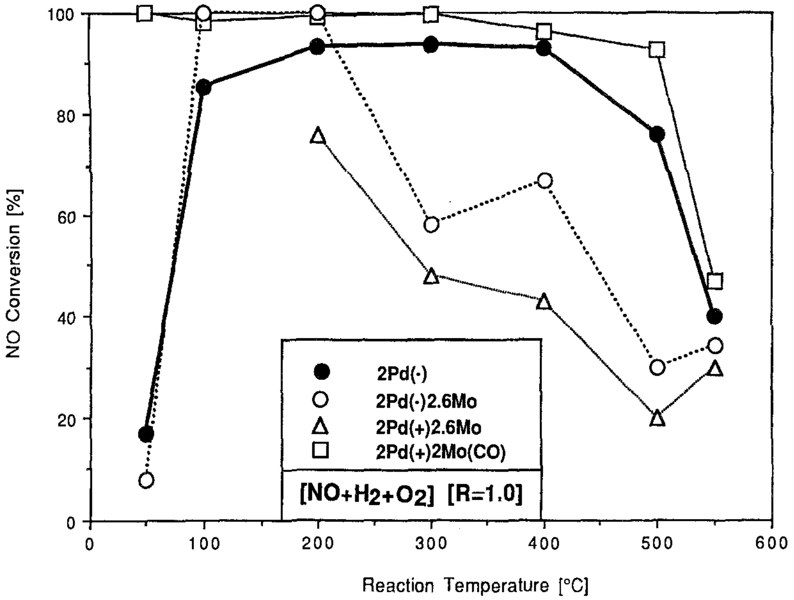

Fig. 2. Comparison of the activity of different catalysts at $R = 1.0$ redox ratio. Reaction parameters are the same as in fig. 1.

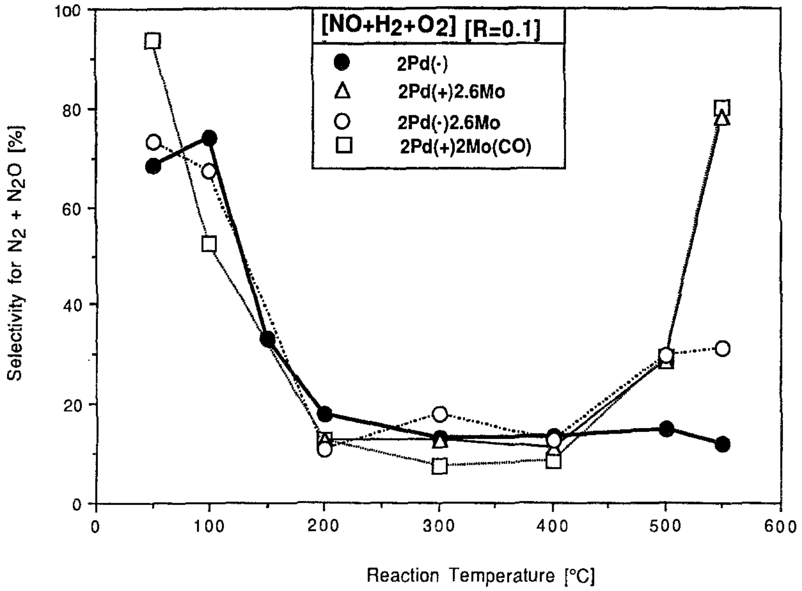

Fig. 3. Comparison of the selectivity of different catalysts in the absence of oxygen. Reaction parameters are the same as in fig. 1.

and 2Pd(+)2Mo(CO) convert NO selectively to N_2 and N_2O with high (~ 80%) yields at 550°C.

As fig. 4 illustrates, the selectivity is very high on all catalysts in the presence of some oxygen ($R = 1$). A significant decrease in selectivity to about 60% occurs at redox ratios of $R > 1.5$, and at 500°C the selectivity further decreases to 10%. This drop in selectivity at 500°C was also observed on $PdO/\gamma\text{-}Al_2O_3$ and 2Pd(−)20Mo [8]. The change may reflect different mechanisms for NO reduction [8,15].

Mo has a different effect on the *activity* of Pd in catalyst 2Pd(+)2Mo(CO) than in the other two bimetallic catalysts, and the Mo has a different effect on the *selectivity* of Pd in sample 2Pd(−)2.6Mo than in the other two catalysts. These different effects suggest that there is an interaction between the Pd and Mo even at low concentration of the active metals. However, this by itself does not always improve the activity and selectivity of the catalysts. Similar conclusions obtain from the results for the reduction of NO by CO [10].

3.2 EFFECT OF OXYGEN ON THE ACTIVITY AND SELECTIVITY

The activity of all of the $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts decreases with increasing amount of oxygen. A sharp drop in the conversion of NO occurs near $R = 1$. The drop usually begins at $R > 0.9$ and ends at $R < 1.1$. This decrease in activity resembles that observed on 2Pd(−) for the reduction of NO by H_2 [8], but is different from the reduction of NO by CO where the activity usually starts to drop at redox ratios of $R > 1.1$ [10]. Generally, the initially low selectivity to $N_2 + N_2O$ of all

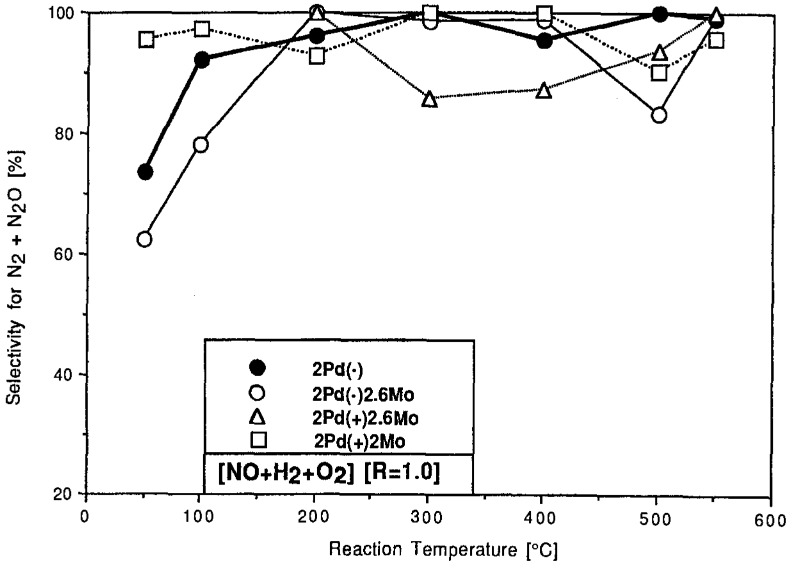

Fig. 4. Comparison of the selectivity of different catalysts at $R = 1.0$ redox ratio. Reaction parameters are the same as in fig. 1.

$PdO–MoO_3/\gamma$-Al_2O_3 catalysts increases with increasing R to nearly 100% at redox ratios of $R > 1$.

Since the activity and selectivity of $PdO–MoO_3/\gamma$-Al_2O_3 changes with reaction temperature and redox ratio, the selectivity of NO to $N_2 + N_2O$ at 300 and 500°C is shown in figs. 5 and 6, respectively. Also shown are data for 2Pd(–), 2Pd(–)20Mo, and 0.16Pt0.03Rh at the same reaction conditions. The dashed lines at $R = 0.8$ and 1.2 highlight the more important redox ratio range (window) around stoichiometry.

At 300°C (fig. 5), PdO/γ-Al_2O_3 was found to be almost as effective for the selective reduction of NO as the commercial Pt–Rh catalyst. In the presence of oxygen, most $PdO–MoO_3/\gamma$-Al_2O_3 catalysts, including 2Pd(–)20Mo, convert NO into N_2 and N_2O with lower yields than PdO/γ-Al_2O_3. An exception is 2Pd(+)2Mo(CO). All catalysts show higher selectivity in the redox window at 300°C than at other temperatures. At 400°C the results are similar to those in fig. 5. However, the maximum yields are higher, the selectivity drops more steeply at $R > 1$, and the selectivity of catalyst 2Pd(–)20Mo exceeds that of 2Pd(–) when $R > 1$.

At 500°C (fig.6), the maximum selectivity is at $R = 0.9$ for all catalysts and there is a steep drop in the selectivity at $R = 1$. The selectivity of the commercial 0.16Pt0.03Rh catalyst drops less. The changes in selectivity near $R = 1$ roughly parallel the changes in activities for all samples, included 0.16Pt0.03Rh. The partitioning of H_2 between the two oxidants, NO and O_2, probably determines the con-

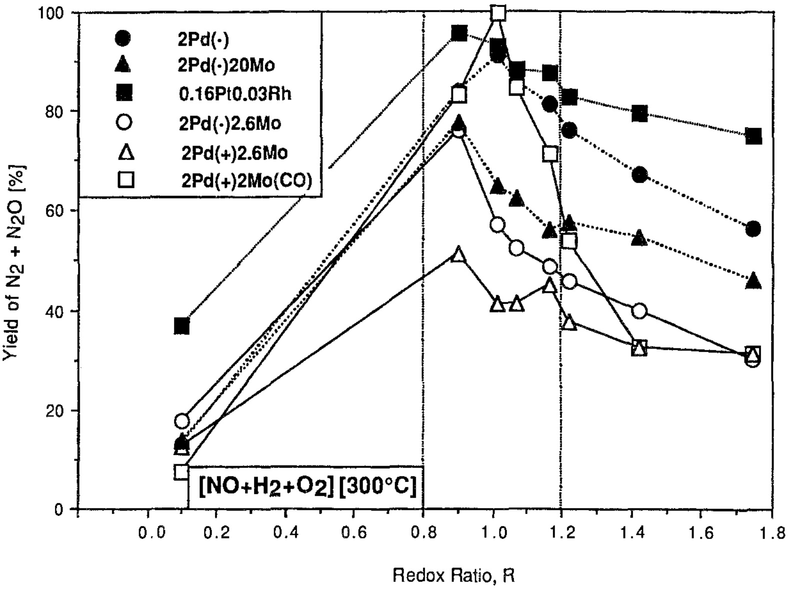

Fig. 5. Effect of O_2 on the activity of different catalysts at 300°C. Reaction parameters are the same as in fig. 1.

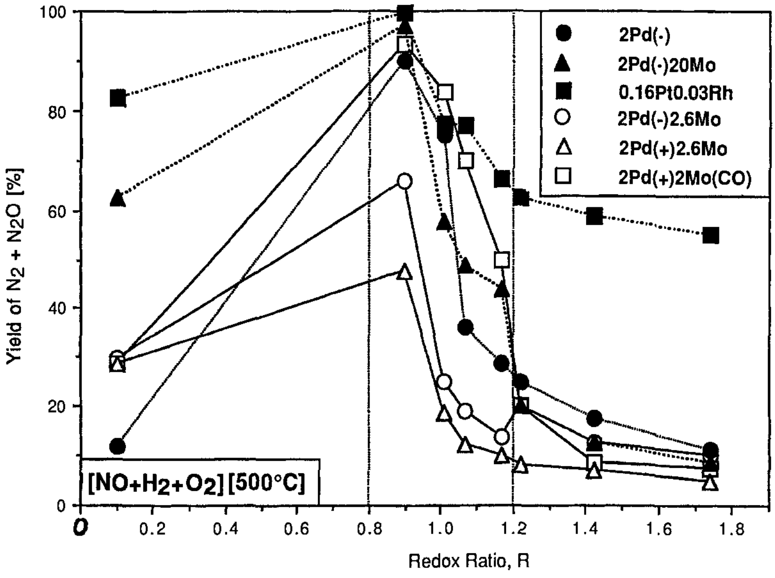

Fig. 6. Effect of O_2 on the activity of different catalysts at 500°C. Reaction parameters are the same as in fig. 1

version of NO [16]. At $R < 1.0$, there is ample H_2 to reduce both NO and O_2. At $R > 1.0$, the H_2 reacts mainly with the O_2.

As reported earlier [8], the yield of $N_2 + N_2O$ in an oxidizing environment ($R > 1$) is higher on the catalyst of high molybdena content, 2Pd(−)20Mo, than on 0.16Pt0.03Rh at 550°C. The yields on all other samples at 550°C resemble those shown in fig. 6 for $R > 0.9$. However, significantly higher (~ 80%) N_2 and N_2O selectivity was observed on catalysts 2Pd(+)2.6Mo and 2Pd(+)2Mo(CO) than on the 2Pd(−) (~ 10%) in the absence of O_2 ($R = 0.1$) at 550°C.

4. Conclusions

(1) The bimetallic catalysts 2Pd(−)2.6Mo, 2Pd(+)2.6Mo, and 2Pd(+)-2Mo(CO), are all active in the reduction of NO by H_2 above 200°C in the absence of oxygen. When oxygen is present, the activity of the former two catalysts is about 20 to 30% lower than the activity of $PdO/\gamma\text{-}Al_2O_3$ even at slightly reducing ($R = 0.9$) conditions. Under oxidizing conditions ($R > 1.0$), the activity decrease is steeper.

(2) The selectivity of the above three $PdO-MoO_3/\gamma\text{-}Al_2O_3$ catalysts for producing N_2 and N_2O (instead of NH_3) in the absence of oxygen is low below 400°C and similar to the selectivity of $PdO/\gamma\text{-}Al_2O_3$. At 500 and 550°C, only little NH_3 is produced on catalysts 2Pd(+)2.6Mo and 2Pd(+)2Mo(CO). The overall selectivity to

$N_2 + N_2O$ of all catalysts is higher than 60% over the temperature range from 200 to 550°C in the presence of O_2 at redox ratios up to $R = 1.5$.

(3) In the presence of oxygen, catalyst 2Pd(+)Mo(CO) is similar to 2Pd(−) in its ability to selectively reduce NO to $N_2 + N_2O$, while the selectivities of catalysts 2Pd(−)2.6Mo and 2Pd(+)2.6Mo were lower. At 500 and 550°C in the absence of oxygen, the selectivities to $N_2 + N_2O$ on the $PdO–MoO_3/\gamma\text{-}Al_2O_3$ catalysts are higher than on $PdO/\gamma\text{-}Al_2O_3$.

(4) The differences between the activities and selectivities of the $PdO–MoO_3/\gamma\text{-}Al_2O_3$ and $PdO/\gamma\text{-}Al_2O_3$ catalysts show that even at low loadings there is an observable effect of the molybdena.

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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 Combust. 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 (Akademie Verlag, Berlin, 1984) p. 119.
[6] J.T. Kummer, J. Phys. Chem. 90 (1986) 4747.
[7] H.S. Gandhi, H.C. Yao, H.K. Stepien, in: *Catalysis Under Transient Conditions*, ACS Symp. Ser., No 178, eds. A.T. Bell and L. Hegedus (Am. Chem. Soc., Washington, 1982) p. 143.
[8] I. Halasz, A. Brenner and M. Shelef, Appl. Catal., submitted.
[9] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, Appl. Catal., in press.
[10] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, Catal. Lett., submitted.
[11] A. Kadkhodayan and A. Brenner, J. Catal. 117 (1989) 331.
[12] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, J. Catal 126 (1990) 109.
[13] I. Halasz, A. Brenner, M. Shelef and K.Y.S. Ng, Catal. Lett. 6 (1990) 349.
[14] M. Shelef and H. S. Gandhi, Ind. Eng. Chem. Prod. Res. Dev. 11 (1972) 2.
[15] H. Muraki and Y. Fujitani, Ind. Eng. Chem. Prod. Res. Dev. 25 (1986) 414.
[16] S.J. Tauster and L.L. Murrel, J. Catal. 53 (1978) 260.