Highly dispersed MgO-supported model Pd–Mo catalysts prepared from bimetallic clusters: chemisorption and selective catalytic reduction of NO

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Model supported palladium and palladium–molybdenum catalysts prepared from organometallic precursors and previously characterized by a variety of chemical and physical methods were examined by IR spectroscopy of NO chemisorption and tested for their activities as catalysts in the competitive NO + CO + O_2 reaction. The IR results reveal distinctive behavior of the catalyst made from a bimetallic precursor, and the activity results show that this catalyst is more selective for NO reduction than the other catalysts, but its stability is vulnerable to the reaction conditions. The high selectivity is attributed to Pd–Mo interactions, which are inferred to be stronger in the catalyst prepared from a bimetallic precursor than in catalysts prepared from monometallic precursors.

Keywords: bimetallic clusters; NO reduction; Pd–Mo catalysts

1. Introduction

Incorporation of molybdenum oxide into supported platinum or palladium catalysts is known to induce rhodium-like activity for reactions involved in automotive exhaust gas emission control [1,2]. A ten-fold excess of molybdenum oxide relative to the platinum or palladium was needed to obtain this result, although it is thought that much less should be required if contact between the molybdenum oxide and the noble metal could be ensured. Recent work aimed at preparing catalysts with low loadings of molybdenum oxide in close proximity to palladium supports this idea [3–5].

Extending this work, we have prepared a MgO-supported palladium–molybdenum catalyst from an organometallic precursor in which the two metals were initially chemically bound together, thus establishing from the outset the critical interaction presumed to be responsible for the rhodium-like activity [6]. For comparison, a catalyst made from separate Mo and Pd precursors and catalysts made from a Mo precursor and from a Pd precursor were also investigated. We report characterization of these materials by IR spectroscopy of nitric oxide chemisorption and their performance as catalysts for reduction of nitric oxide by carbon monoxide in the presence of oxygen. The principal goal was to determine how interactions between Pd and Mo affect the structure and the catalytic performance.

2. Experimental methods

2.1. Catalysts

Preparation of the catalysts and their characterization by physical and chemical methods including chemisorption, transmission electron microscopy, and extended X-ray absorption fine structure (EXAFS) spectroscopy are described in detail elsewhere [6]. Briefly, the five samples used in these experiments were the support material itself (MgO); 1.0 wt% Mo on MgO (referred to as Mo); 1.0 wt% Pd on MgO (Pd); 1.0 wt% each of Pd and Mo made from monometallic precursors on MgO, (Pd + Mo); and 1.0 wt% Pd and 0.9 wt% Mo from the bimetallic precursor $[Pd_2Mo_2(Cp)_2(CO)_6(PPh_3)_2]$ (Cp is cyclopentadienyl; Ph is phenyl) on MgO (PdMo).

2.2. NO chemisorption

The NO chemisorption experiments were performed in a high-vacuum IR cell equipped with CaF_2 windows. Catalyst powder samples were pressed into a gold wire mesh at 2000 lb/in^2. A chromel–alumel thermocouple was spot-welded to the center of the grid. The sample was fixed onto a transposable probe arm which also allowed resistive heating and liquid-nitrogen cooling of the sample. Spectra were recorded by using a computer-controlled Mattson Cygnus 100 FTIR spectrometer.

Oxygen (99.998%) and hydrogen (99.996%) from Matheson were used without further purification. Nitric oxide (99.0%, Matheson) was purified by trap-to-trap distillation [7]. Depending on its thermodynamic state, the purified product was a white solid, a light-blue liquid, or a colorless gas.

The samples were pretreated in either of two ways before NO adsorption. In the reductive pretreatment, the cell was first evacuated and the sample exposed to 100 Torr of H_2 at 350°C for 30 min; the cell was then evacuated with the sample held at 350°C for 30 min, and finally the sample was cooled to room temperature under vacuum. In the oxidative pretreatment, the cell was first evacuated and the sample exposed to 100 Torr of O_2 at 350°C for 30 min; the sample was then cooled to room temperature in 100 Torr of O_2, and finally the cell was evacuated for 1 h. After either pretreatment the sample was exposed to 0, 1, 3, 10, 30, and then 100 mTorr of NO at room temperature, in order, and the IR spectrum was recorded at each pressure.

2.3. *Catalytic activity*

The activity was evaluated in a microreactor, as follows: Approximately 10 mg of catalyst was mixed with approximately 40 mg of α-Al_2O_3 (surface area 10.5 m^2/g) and placed between quartz-wool plugs in a quartz tube within a tube furnace. The inside diameter of the tube was 4 mm and the catalyst bed was 4–5 mm long. A feed gas containing 0.05 mol% NO, 0.5 mol% O_2, and 1.05 mol% CO in He was passed through the tube at a rate of 100 cm^3/min while the furnace temperature was ramped to a final set temperature of either 400 or 300°C at a rate of 8°C/min. The concentration of NO and CO_2 was monitored continuously by using chemiluminescence (Beckman 951) and NDIR (Beckman 845) detectors, respectively. When the final set temperature was reached, the feed CO concentration was lowered in steps, and the NO, NO_x, O_2, CO, and CO_2 concentrations were measured by using the chemiluminescence detector for NO and NO_x and a gas chromatograph (Varian 3700 with Supelco Carboxen 1000 column and thermal conductivity detector) for O_2, CO, and CO_2. (In the subsequent discussion, the ratio, $R \equiv [CO]/([NO]+2[O_2])$, is used as the independent variable rather than feed CO concentration, and concentrations are plotted relative to the feed gas.)

3. Results and discussion

3.1. *NO chemisorption*

There was no sign of NO adsorption on either the MgO or Mo samples upon NO exposure after either the oxidative or reductive pretreatment. In particular, the dinitrosyl bands typically observed at about 1700 and 1800 cm^{-1} in the spectrum of molybdenum oxide were not seen in the spectrum of the Mo sample, even after a pretreatment in 100 Torr of H_2 at 500°C for 1 h [8]. This result could reflect the low Mo loading and correspondingly high dispersion of Mo-containing species, which might not exhibit usual molybdenum oxide behavior [6].

Bands associated with chemisorbed NO were, however, found for all the Pd-containing samples; spectra of the (Pd + Mo) and PdMo samples are reproduced in fig. 1. There is no difference between the spectra of the (Pd + Mo) and Pd samples, and both sets of spectra, following the reductive pretreatment, match spectra of reduced palladium supported on silica [9,10]. By comparison with results obtained for NO chemisorbed on clean Pd single crystals [10], the sharp peaks at 1740 and at 1550 cm^{-1} following the reductive pretreatment are assigned to NO chemisorbed on (111) Pd crystal planes whereas the sharp peak at 1670 cm^{-1} following the reductive pretreatment is assigned to NO chemisorbed on (100) Pd crystal planes.

In the case of the PdMo sample following the reductive pretreatment, there is an additional band at 1800 cm^{-1}. Several plausible explanations are proposed for this band. One possibility is that it may be the 1800 cm^{-1} dinitrosyl band for NO on molybdenum oxide, present in (bimetallic) particle form in this sample rather than as a highly dispersed Mo-containing species [6]. In this case, the other dinitrosyl band, at 1700 cm^{-1}, would fall in the valley between the 1740 and 1670 cm^{-1} bands for NO on Pd, making them somewhat less well resolved than in the spectrum of the (Pd + Mo) sample, as seems to be the case.

Another possible explanation is that as a result of the smaller particle size in the PdMo sample [6] there exist relatively many of some new sites characterized by weaker adsorption than on the Pd (111) and (100) planes. Yet another possibly distinct explanation is suggested by the spectra recorded for the Pd and (Pd + Mo) samples following the oxidative pretreatment, in which an additional band at 1800 cm^{-1} also appears. In this case, the 1800 cm^{-1} band may be associated with adsorption on oxidized Pd. (Note, however, that yet another band also appears in the spectrum of the PdMo sample at wavenumbers greater than 1800 following the oxidative pretreatment.)

As a test of this last possibility, all the samples were examined by XPS to determine whether Pd in the PdMo sample is more likely to be in an oxidized state or more difficult to reduce than in the other samples. Unfortunately, interference with Mg prevented such a determination.

The similarity of the results for the PdMo sample following the reductive treatment, on the one hand, and for the Pd or (Pd + Mo) samples following the oxidative

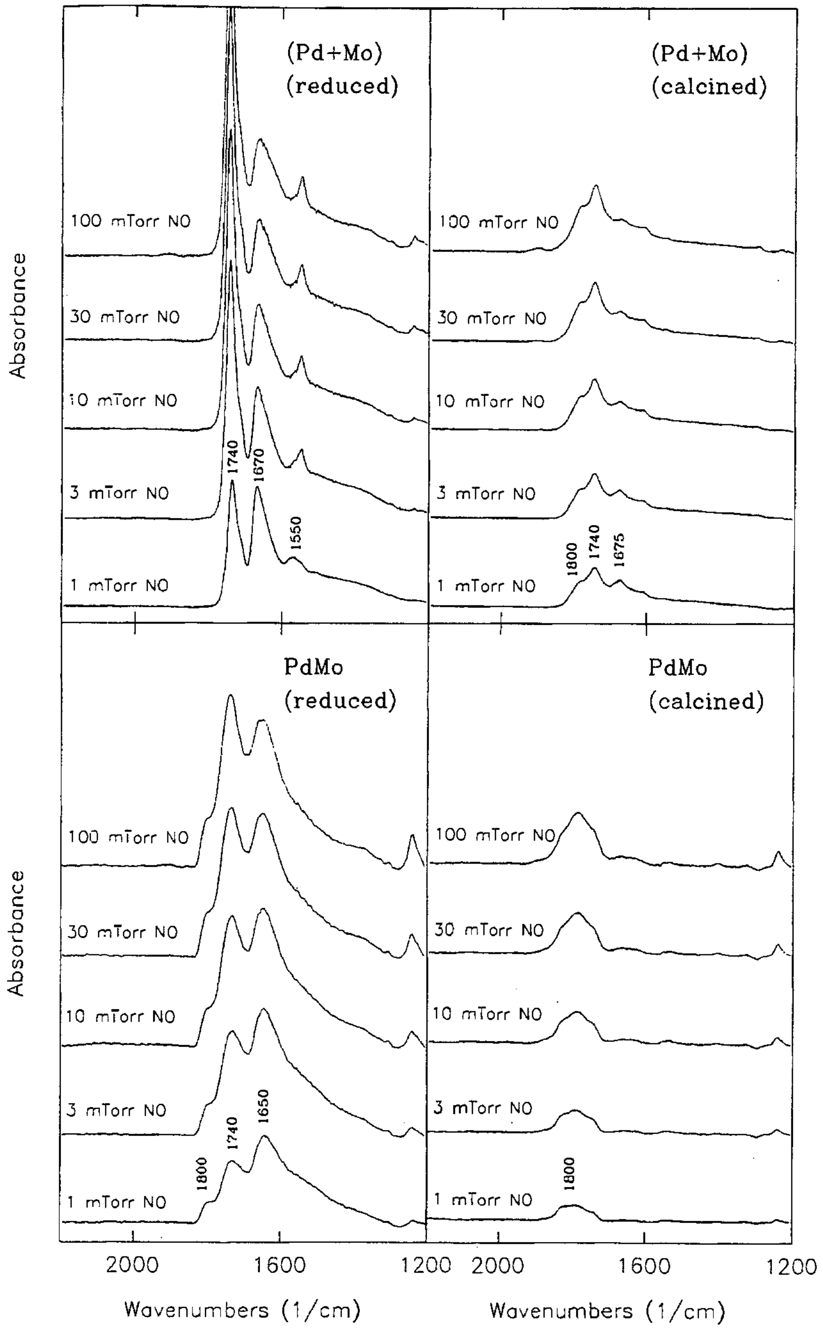

Fig. 1. FTIR spectra of NO chemisorbed on the (Pd + Mo) and PdMo samples at room temperature following the reductive and oxidative pretreatments. (Spectra are normalized to the evacuated-cell spectrum.)

pretreatment, on the other hand, suggest the possibility that Pd in the PdMo sample might have undergone oxidation in the course of the NO chemisorption measurement, since dissociative adsorption of NO on Pd is known to proceed more easily on smaller than on larger particles [11–13]. To test this idea, the NO chemisorption measurements with the PdMo sample following the reductive pretreatment were also performed at −100°C, so that NO dissociation would be slower than at room temperature. There was no difference found between the spectra at the two temperatures, however, and thus there is no evidence for the suggested oxidation of Pd in the PdMo sample by NO.

3.2. *Catalytic performance*

Results of the temperature sweep activity measurements are reproduced in the left portion of fig. 2 for the MgO, (Pd + Mo), and PdMo samples, and results of the *R* sweep measurements at 400°C for the same samples are reproduced in the right portion of fig. 2. In both cases, there was no significant difference between the

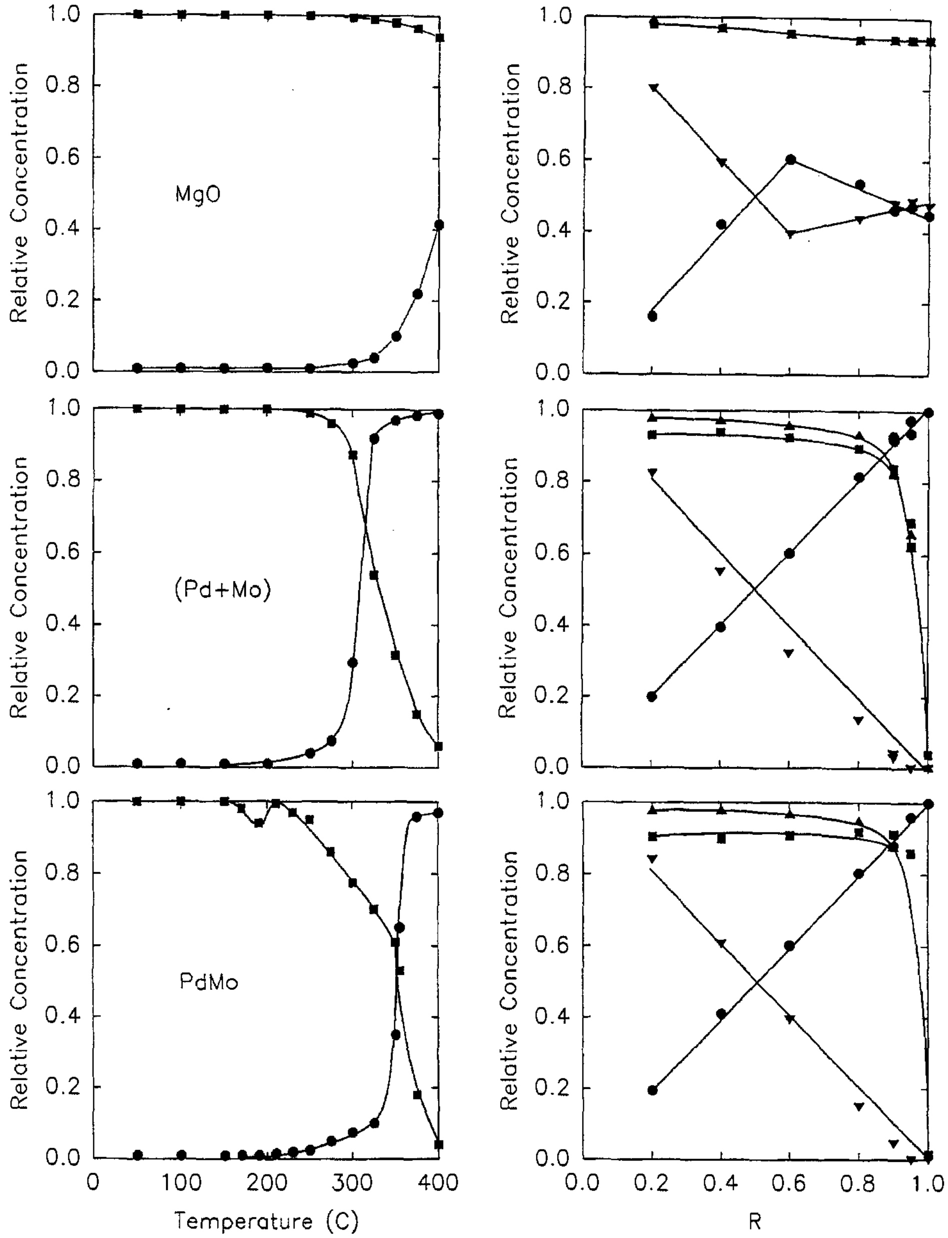

Fig. 2. Temperature sweep (left side) and R sweep (right side) activity measurements for the MgO (top), (Pd + Mo) (middle), and PdMo (bottom) samples. The R sweep measurements were performed at 400°C. Symbols: (●) CO_2; (■) NO; (▼), O_2; (▲), NO_x. Lines are to guide the eye.

MgO and Mo samples or between the (Pd + Mo) and Pd samples. It is clear that the MgO support material provides a substantial fraction of the activity needed for CO oxidation for $R > 0.6$ and essentially all the activity required even for $R < 0.6$ at 400°C. The effect of Pd is to enable NO reduction very near $R = 1$ and also to catalyze the oxidation of NO, probably to give NO_2, for $R < 1$. The selectivity of the PdMo sample for NO reduction at 400°C is no better than that of the (Pd + Mo) (or Pd) sample, and all are relatively poor, which is typical of Pd catalysts [15,16]. The temperature sweep result for the PdMo sample differs from those of the other samples, however, in that up to about 350°C, the NO conversion is greater (rather than less) than the CO conversion, suggesting that this sample may exhibit a better selectivity than the others at temperatures somewhat lower than 400°C.

Upon repeating the temperature sweep measurement for the original PdMo sample, it was found that the result did not reproduce the original measurement but instead was comparable to that of the (Pd + Mo) sample. Starting with a fresh PdMo sample and performing the temperature sweep measurement up to 300°C, the original result (up to 300°C) was obtained once again, but the CO and NO conversions were found to change over a period of several hours at 300°C, as shown in fig. 3. A much more rapid and proportionally smaller increase in CO conversion was found in the case of the (Pd + Mo) sample at 300°C, whereby the CO_2 concentration stabilized within minutes.

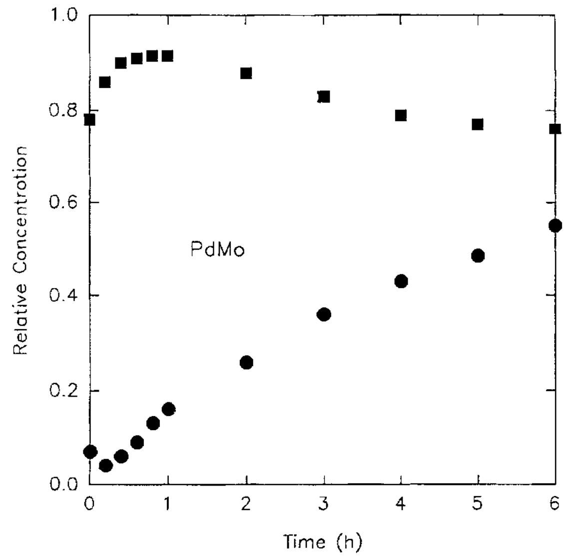

Fig. 3. Time dependence of the CO_2 (●) and NO (■) concentrations for the PdMo sample after sweeping the temperature to 300°C.

The R sweeps measured at 300°C after 1 h for the (Pd + Mo) sample and 6 h for the PdMo sample are shown in fig. 4. Even though the PdMo sample had become considerably less selective for NO reduction after 6 h at 300°C, it still exhibited somewhat better selectivity than the (Pd + Mo) sample for $R > 0.4$. Since the activity of the PdMo sample is not stable at this point, it is likely that the difference in selectivity between the catalysts would continue to diminish at increasing times on stream.

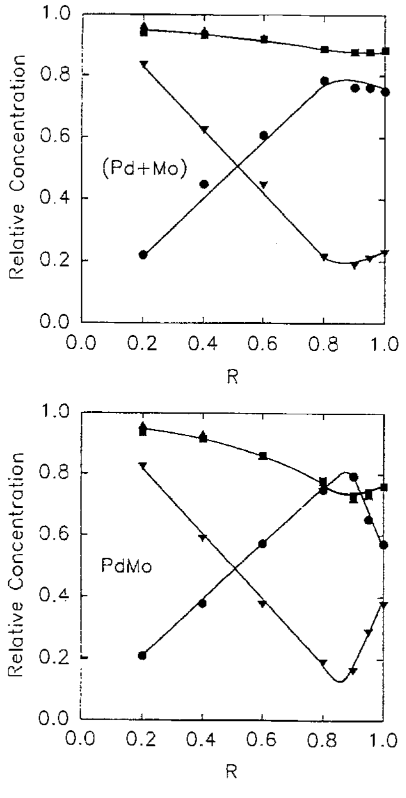

Fig. 4. R sweep activity measurements for the (Pd + Mo) (top) and PdMo (bottom) samples performed after 1 and 6 h, respectively, at 300°C. Symbols: (●) CO_2; (■) NO; (▼), O_2; (▲) NO_x. Lines are to guide the eye.

4. Conclusions

The previously known promotional effect of molybdenum oxide on palladium for selective NO reduction has been demonstrated with catalysts containing minimal molybdenum oxide that were prepared from a molecular bimetallic precursor. This catalyst is more selective than one prepared from a combination of monometallic precursors. However, the catalyst prepared from the bimetallic precursor lacks stability under typical reaction conditions. The initial selectivity of the catalyst made from the bimetallic precursor is attributed to the Pd–Mo interactions, which are suggested to become less as the catalyst functions. Future efforts will be aimed at assessing the extent to which the lack of stability is a function of the support material.

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