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Selective Photocatalytic Reduction of Nitric Oxide by Carbon Monoxide over Silica-Supported Molybdenum Oxide Catalysts

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The photocatalytic reduction of NO by CO over a MoO_3/SiO_2 catalyst (2.5 wt% of Mo), which proceeds under UV irradiation at room temperature, is reported for the first time. N_2 and CO_2 are found to be the major reaction products, and the selectivity of the photoreduction is close to 100%. After completion of photoconversion of a NO–CO mixture and brief evacuation at room temperature, a new portion of the NO–CO mixture admitted to the catalyst can be converted with the same rate as during the first irradiation. It is shown that MoO_3/SiO_2 is an inefficient catalyst for the thermal NO reduction by CO, since heating of a NO–CO mixture at 400 and 500°C yields only small amounts of N_2 and CO_2. A reaction mechanism for the photocatalytic NO reduction by CO over MoO_3/SiO_2 is proposed and discussed.

Key Words: **NO; CO; MoO_x/SiO_2; reduction; UV-irradiation; photocatalysis; molybdenum; silica.**

INTRODUCTION

In view of the growing importance of environmental protection, the catalytic elimination of nitric oxides, mainly NO, has been extensively studied in recent years. A number of published papers report on the use of UV irradiation for accomplishing direct photocatalytic decomposition of NO_x molecules into N_2, N_2O, NO_2, and O_2 over oxide and zeolite catalysts at ambient temperature. Photocatalytic processes for the reduction of global air pollution seems promising, since they may open a means for utilization of solar energy for environmental protection.

Several catalytic systems containing transition metal ions were tested for the direct NO photodecomposition: Ag^+/ZSM-5 (1–3), Cu^+/ZSM-5 (3–5), Cu^+/SiO_2 (6), V^{5+}/porous Vycor glass (7), TiO_2/zeolites (8, 9), and bulk TiO_2 (10). The photocatalytic decomposition of N_2O over Pt/TiO_2 (11) and Zn^{2+}/porous Vycor glass (12) was also reported.

For all the systems applied for NO decomposition, the yields of the reaction products (N_2, N_2O, and O_2) increase linearly with UV-irradiation time indicating that the reaction proceeds catalytically. However, it appears that the photocatalysts studied are not efficient enough, since long irradiation times (typically, tens of hours) are required to attain measurable amounts of the reaction products. The highest N_2 yields (~100 μmol of N_2 per 1 g of the catalyst) were obtained with Ag^+/ZSM-5 after about 20 h of UV irradiation (2, 3), whereas N_2 yields on other oxide systems did not exceed 10–15 μmol of N_2 per 1 g of the catalyst. In addition to N_2, considerable amounts of undesirable toxic by-products (N_2O and NO_2) were also produced. It should be noted that the NO photodecomposition over the above-indicated catalysts occurred only under short wavelength UV irradiation (250–300 nm). However, recent reports (13, 14) indicate the possibility of NO dissociation over TiO_2 with implanted transition metal ions under visible-light irradiation with $\lambda > 450$ nm. Thus, it appears that more effort has to be made to develop efficient catalytic systems for the photodecomposition of nitric oxide molecules.

The well-known method for eliminating nitric oxide admixtures from the exhaust gases, which is widely and successfully used in heterogeneous catalysis, consists in NO reduction by a reducing agent such as carbon monoxide, ammonia, and hydrocarbons. However, rather surprisingly, we were able to find only one publication in the literature using the same approach to a photocatalytic reaction (15). It was found in this work that NO can be reduced by NH_3 to yield N_2 and N_2O (and, probably, H_2O) over a TiO_2 catalyst under UV irradiation at room temperature.

Earlier we had found (16, 17) that Mo^{6+} ions on the surface of Mo/SiO_2 catalysts (1 wt% of Mo) prepared by the impregnation method can be selectively reduced to Mo^{4+} under UV irradiation in the presence of carbon monoxide. For Mo/SiO_2 with low Mo loadings (0.01–0.1 wt%) prepared by grafting molybdenum onto silica by reacting $MoCl_5$ precursor with silanol groups, UV irradiation in CO

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results in more profound reduction of Mo^{6+} to the Mo^{2+} state (18).

In another publication (19), we have shown that Mo^{4+} ions on the SiO_2 surface produced by photoreduction can be readily oxidized by NO to the Mo^{6+} state at low temperatures (close to 77 K). It was suggested that NO interaction with Mo^{4+} ions occurs via the formation of intermediate paramagnetic complexes $Mo^{6+}...NO^{2-}$ which were formed by donating two d-electrons of the Mo^{4+} ion to the $\pi^*_{x,y}$-orbital of NO. The complexes were detected and characterized by ESR. The final reaction products were N_2 and N_2O which were produced in a ratio that depended on the NO_{ads}/Mo^{4+} ratio.

These findings prompted us to attempt to combine the Mo^{6+} to Mo^{4+} photoreduction by CO and the Mo^{4+} to Mo^{6+} oxidation by NO in one photocatalytic process. The aim of this study was to find out whether it would be possible to photocatalytically convert NO–CO mixtures to nontoxic reaction products under UV irradiation of Mo/SiO_2 catalysts and to determine the principal characteristics of the process such as efficiency, compositions of the products, and characteristic irradiation times.

EXPERIMENTAL

The catalyst containing 2.5 wt% of Mo^{6+} on SiO_2 was prepared by impregnating a silica gel with an $(NH_4)_6Mo_7O_{24}$ aqueous solution. A commercial KSK-2-5 silica gel ($S_{sp} = 300\ m^2/g$) contained as impurities Al_2O_3 (1.02%), Fe_2O_3 (0.16%), and CaO (1.45%). The material was ground in a sapphire mortar, and the fraction with particle size of 0.3–0.5 mm was then used as a support. The impregnated catalyst was dried in air at 80°C.

The pretreatment of a catalyst sample (~1 g) was carried out in a quartz reactor suitable for *in situ* UV irradiation connected with a closed evacuable circulation setup. The catalyst was subjected to the following sequence of treatments: (1) evacuation to 10^{-3}–10^{-4} Torr at 150°C for 1 h; (2) slow raising of the temperature to 800°C during 1 h and heating of the sample under vacuum at this temperature for 1 h; (3) heating in a circulating oxygen flow at 800°C for 1 h; (4) evacuation at 800°C for 2 h; (5) admission of oxygen at 800°C followed by lowering of the temperature to 500°C and final evacuation for 0.5 h.

Nitric oxide was obtained by solid-state thermal decomposition of a KNO_2–Fe_2O_3–Cr_2O_3 mixture according to the procedure described in Ref. (20). The NO thus produced was purified by passing through a trap cooled to −150°C to reduce possible admixture of N_2O and stored in a glass cylinder connected to the vacuum setup. The admixture of N_2O in NO was found mass-spectroscopically to be 2%. Carbon monoxide taken from a gas cylinder was purified from oxygen by passing through a column filled with Cr^{2+}/SiO_2. The oxygen admixture in the purified CO was below 0.1%. ^{13}C-labeled carbon monoxide used in this study contained 92 at.% ^{13}C.

The MoO_3/SiO_2 catalyst was irradiated at ambient temperature in a circulating flow of NO–CO mixtures by full light of a DRSh-1000 (1 kW) high-pressure mercury lamp through a water filter to reduce heating of the sample. The working volume of the circulation unit was 880 cm^3. After accomplishing the photoreaction, the light beam was switched off, and the catalyst was either evacuated at room temperature for 15–30 min or subjected to thermal treatment in O_2 at 500°C for 30 min followed by evacuation at this temperature.

Total pressures of the gaseous reactants and products were measured with a capacity-type manometer VDG with an accuracy of about 3%. The composition of gaseous mixtures above the catalyst was determined using a monopole-type MKh-7304 mass spectrometer connected with the circulation unit of the evacuable setup through a leak valve.

RESULTS AND DISCUSSION

In blank experiments, no products were observed during UV irradiation of gaseous NO–CO mixtures in the presence of the silica support without molybdenum. No reaction occurred when MoO_3/SiO_2 was exposed to a NO–CO mixture at room temperature in the absence of UV irradiation.

Figure 1 shows the drop in the total pressure and the gas-phase compositions during UV irradiation of the

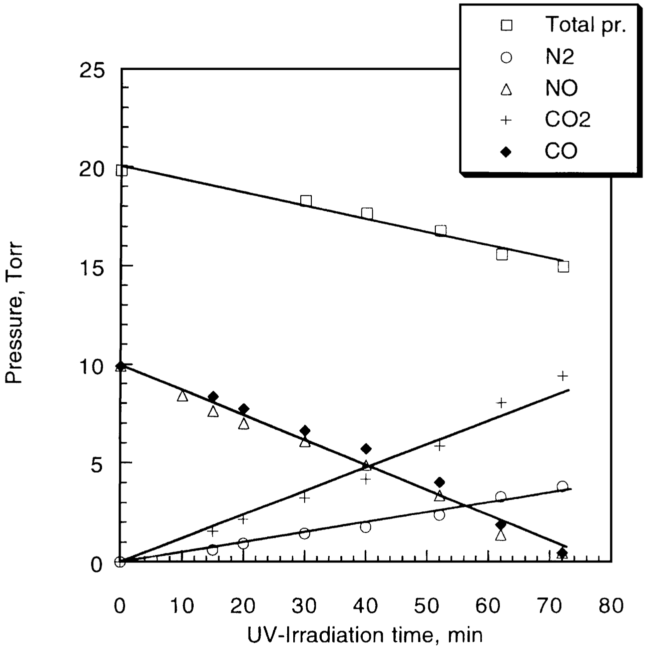


FIG. 1. Total pressure and partial pressures of NO, CO, N_2, and CO_2 vs time during UV irradiation of 1 g MoO_3/SiO_2 in the presence of a NO : CO = 1 : 1 mixture. Initial NO and CO pressures 9.9 Torr, (NO + CO)/Mo = 4. First irradiation.

MoO_3/SiO_2 catalyst in the presence of a NO : CO = 1 : 1 mixture as a function of irradiation time. Initial NO and CO pressures in this experiment were 9.9 Torr.

Partial pressures of CO_2 and NO were determined by measuring the intensities of their parent peaks in mass spectra at $m/e = 44$ and $m/e = 30$, respectively. Since the masses of CO and N_2 molecules are the same ($m/e = 28$), they cannot be directly discriminated from the mass-spectroscopic data by their parent peaks. Therefore, the following procedure was applied to determine partial pressures of these gases. Assuming that one CO molecule consumed yields one CO_2 molecule, CO partial pressures, $P(\mathrm{CO})$ were calculated by the equation $P(\mathrm{CO}) = P_0(\mathrm{CO}) - P(\mathrm{CO_2})$, where $P_0(\mathrm{CO})$ stands for initial CO pressure, and $P(\mathrm{CO_2})$ is CO_2 partial pressure. The contribution of nitrogen molecules to the $m/e = 28$ peak in mass spectra was then calculated, and N_2 partial pressures were thus found.

Figure 1 clearly demonstrates the occurrence of photocatalytic NO reduction by carbon monoxide to yield N_2 and CO_2. After irradiation for 72 min, virtually all NO and CO have been consumed, and N_2 and CO_2 become largely dominant in the gas phase. The ratio of the initial total pressure of the NO–CO mixture to the final pressure of the reaction products is found to be 1.3. This value is very close to the ratio of 1.33 that one may expect to observe for a selective NO reduction process described by the following:

$$\mathrm{CO} + \mathrm{NO} \rightarrow 1/2\ \mathrm{N_2} + \mathrm{CO_2}. \qquad [1]$$

Also, the CO_2/N_2 ratio in the reaction products, which was roughly estimated from the above experiment as 2.4 ± 0.3, and the similarity in the CO and NO pressure drop during the irradiation agree within experimental error with the above reaction equation.

In the experiment of Fig. 1, the number of CO + NO molecules converted over one Mo atom of the catalyst sample (turnover number, TON) is equal to four. Thus, already from this experiment, we can conclude that NO reduction by CO over MoO_3/SiO_2 is really a photocatalytic process. Certainly, TON = 4 is not a limit value. After removal of the gaseous mixture by brief evacuation at room temperature and admission of a new portion of the NO : CO = 1 : 1 mixture, the photocatalytic reaction proceeds with the same rate as during the first irradiation (Fig. 2). Thus, Fig. 2 provides a good evidence for photocatalytic character of the NO reduction by CO. The same procedure repeated several times did not lead to a marked decrease in the photocatalytic activity of the MoO_3/SiO_2 catalyst.

Figure 3 shows the kinetics of CO_2 accumulation and NO consumption during UV irradiation of the MoO_3/SiO_2 catalyst in the presence of a NO : CO = 1 : 2 mixture. The initial total pressure in this experiment was 32 Torr and the (NO + CO)/Mo ratio was 6 : 1. The CO_2 partial pressure grows nearly linearly up to irradiation times of 40–45 min and then tends to level off due to practically full consumption of NO by the reaction.

The next step of this study was to check whether another plausible product of the NO photoreduction, N_2O,

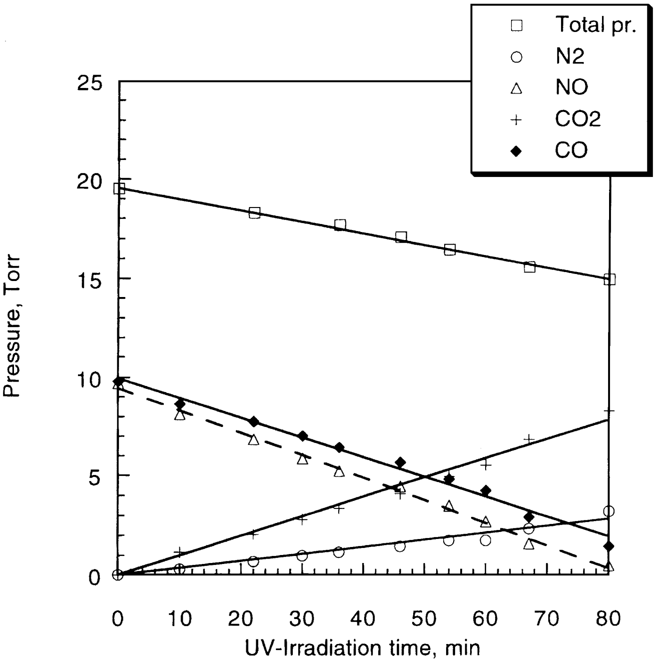


FIG. 2. Total pressure and partial pressures of NO, CO, N_2, and CO_2 vs time during UV irradiation of 1 g MoO_3/SiO_2 in the presence of a NO : CO = 1 : 1 mixture. Initial NO pressure 9.7 Torr, initial CO pressure 9.8 Torr, (NO + CO)/Mo = 4. Second irradiation.

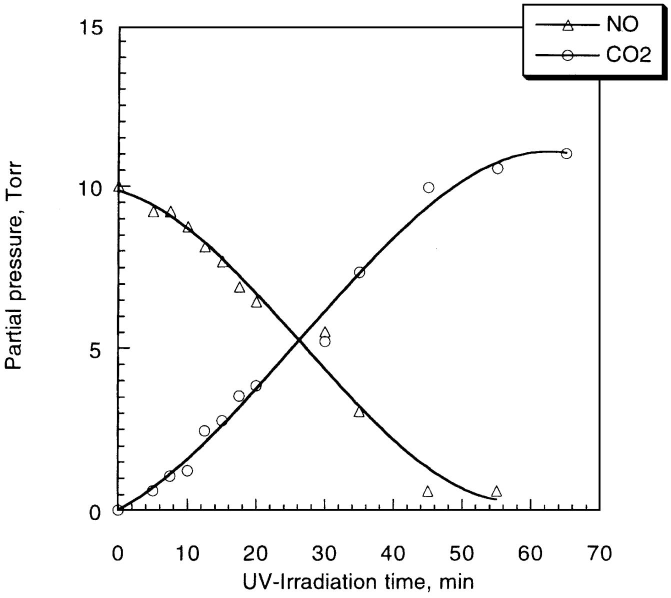


FIG. 3. Partial NO and CO_2 pressures vs time during UV irradiation of 1 g MoO_3/SiO_2 in the presence of a NO : CO = 1 : 2 mixture. Initial NO pressure 10 Torr, initial CO pressure 22 Torr, (NO + CO)/Mo = 6.

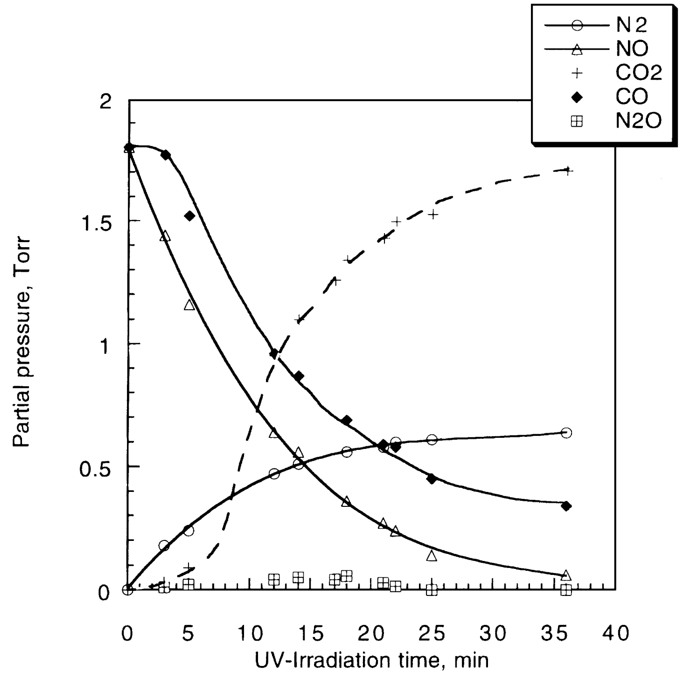


FIG. 4. Partial pressures of NO, CO, N_2, CO_2, and N_2O vs time during UV irradiation of 1 g MoO_3/SiO_2 in the presence of a NO : $^{13}CO = 1:1$ mixture. Initial NO and ^{13}CO pressures 1.8 Torr, $(NO + CO)/Mo = 0.3$.

was formed in measurable amounts along with dinitrogen. Since the masses of N_2O and CO_2 molecules are the same ($m/e = 44$), these gases cannot be directly discriminated in mass spectra by their parent peaks. Therefore, a mixture of 1.8 Torr ^{13}CO and 1.8 Torr NO was taken for the experiment. The use of ^{13}C-labeled carbon monoxide enabled us to easily discriminate ^{13}CO ($m/e = 29$) and N_2 ($m/e = 28$) as well as $^{13}CO_2$ ($m/e = 45$) and N_2O ($m/e = 44$) by their parent peaks. The results are presented in Fig. 4. In this run, UV irradiation was performed under static conditions, and the $(^{13}CO + NO)/Mo$ ratio was 0.3.

Figure 4 shows that the N_2O yield is negligibly small as compared to that of N_2. Moreover, it is even hard to judge from the experimental data of Fig. 4 whether N_2O is produced at all because of the experimental uncertainty in measuring the $m/e = 44$ peak intensities. Thus we can conclude that the photocatalytic reduction of NO to N_2 proceeds with a selectivity close to 100%, i.e., it is a highly selective process.

Another interesting feature of the above-described experiment is the existence of an induction period in the CO_2 production which is clearly seen in Fig. 4. Possibly, this effect is associated with the accumulation of some surface reactive intermediates during the first few minutes of irradiation. It appears also that some nitrogen-containing species are held by the catalyst surface, since the NO partial pressure is markedly lower than that of carbon monoxide. Obviously, a thorough kinetic and spectroscopic study of the initial stages of the NO photoreduction is necessary. That will be the subject of further work.

In contrast to the selective photocatalytic reduction of NO which readily occurs at room temperature, heating of an NO : CO = 1 : 1 mixture in the presence of MoO_3/SiO_2 at 400°C results in the production of only small amounts of N_2 and CO_2 (Fig. 5). The NO conversion after heating for 1 h at 400°C was about 6%. When temperature was raised to 500°C, the rate of NO consumption and that of CO_2 formation slightly increased. However, under these conditions, one cannot rule out that some CO_2 is produced by direct CO decomposition via the Boudouard reaction $2\,CO \rightarrow C + CO_2$. Thus, it follows that although MoO_3/SiO_2 is a good photocatalyst, it is an inefficient catalyst for the thermal reaction.

The results obtained in this work as well as those of our earlier studies (16, 17, 19) allow us to propose the following reaction mechanism for the photocatalytic NO reduction. The first step is the photoreduction of supported Mo^{6+} ions by carbon monoxide to yield Mo^{4+} ions and CO_2 via transient formation of a charge-transfer excited triplet state:

$$\sim Mo^{6+}=O^{2-} + h\nu \rightleftharpoons (\sim Mo^{5+}-O^{-})^* \qquad [2]$$

$$(\sim Mo^{5+}-O^{-})^* + CO \rightarrow \sim Mo^{4+} + CO_2. \qquad [3]$$

Here $\sim Mo^{6+}=O^{2-}$ denotes one of the two molybdenyl

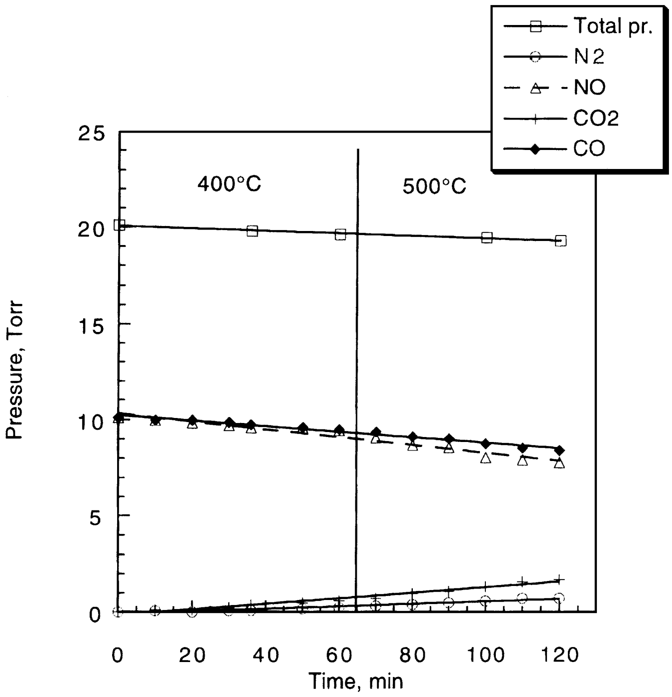
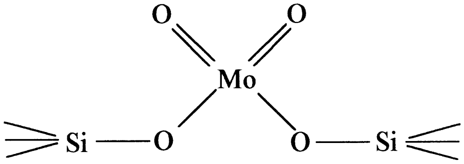


FIG. 5. Total pressure and partial pressures of NO, CO, N_2, and CO_2 vs time of heating at 400 and 500°C of 1 g MoO_3/SiO_2 in the presence of a NO : CO = 1 : 1 mixture. Initial NO and CO pressures 10.1 Torr, $(NO + CO)/Mo = 4$.

bonds of a tetrahedrally coordinated Mo^{6+} ion on the silica surface:



The mechanism of photoreduction of silica-supported Mo^{6+} ions was considered in our previous publications (16, 17).

Then the Mo^{4+} ions interact with NO molecules as follows:

$$\sim Mo^{4+} + NO \rightarrow \sim Mo^{6+}...NO^{2-} \quad [4]$$

$$\sim Mo^{6+}...NO^{2-} + NO \rightarrow \sim Mo^{6+}{=}O^{2-} + N_2O \quad [5]$$

$$\sim Mo^{4+} + N_2O \rightarrow \sim Mo^{6+}{=}O^{2-} + N_2. \quad [6]$$

A key step of this reaction scheme is the formation of the intermediate complex $\sim Mo^{6+}...NO^{2-}$ by reaction [4] which arises from a two-electron transfer from a strong-donor Mo^{4+} ion to an NO molecule. This paramagnetic complex gives an ESR signal with $g_{\parallel} = 2.075$, $g_{\perp} = 1.996$, and $A_{\perp}^{N} = 15$ G when NO is adsorbed at 77 K on MoO_3/SiO_2 photoreduced in a CO atmosphere (19).

The next step of the NO reduction scheme is reaction [5], which yields N_2O and regenerates the Mo^{6+} ion. Most likely, it is followed by fast N_2O decomposition over Mo^{4+} yielding N_2 (reaction [6]), since no or very little N_2O was found in the gas phase under stationary UV irradiation of MoO_3/SiO_2 in the presence of a NO–CO mixture (Fig. 4).

However, when 1 g of the MoO_3/SiO_2 catalyst sample, which had been preliminary photoreduced in CO and then evacuated at room temperature for 30 min, was exposed to nitric oxide in the absence of UV irradiation, fast NO consumption was followed by N_2 and N_2O evolution into the gas phase in comparable amounts (Fig. 6). In this run, the number of Mo^{4+} in the catalyst was $4.6 \cdot 10^{19}$ (as determined from the amount of CO_2 produced by photoreaction [3]), and the same number of NO molecules was allowed contact with the photoreduced sample. It should be noted that, in this experiment, the fast drop of the NO partial pressure during the first minute of reaction could not be followed correctly due to instrumental limitations.

The rates of N_2 and N_2O formation decrease continuously with time. They are nearly zeroed as the Mo^{4+} concentration in the catalyst sample becomes very low, since both NO and N_2O molecules consume Mo^{4+} by reactions [4] and [6].

The switching on of UV light has no effect on the N_2 evolution and NO consumption, but causes the N_2O concentration in the gas phase to slightly increase, probably because of its desorption due to heating of the catalyst by the light beam.

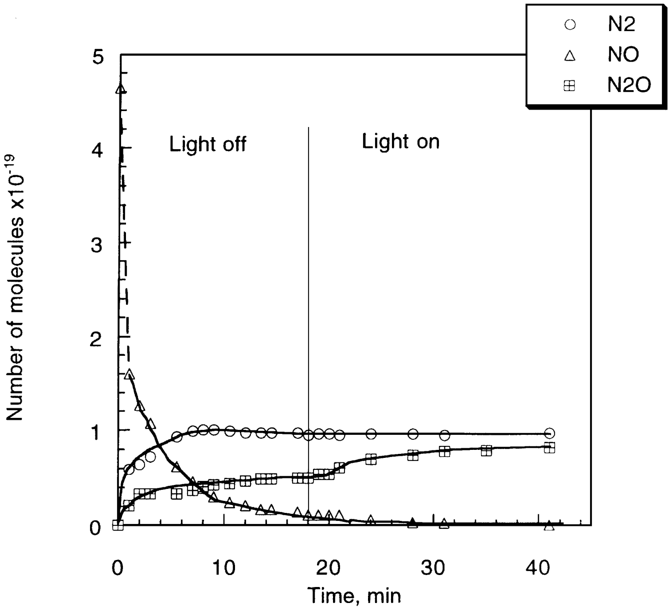


FIG. 6. Gas-phase composition vs time after NO admission on the preliminary photoreduced MoO_3/SiO_2 catalyst. Initial number of NO molecules is 4.6×10^{19}; 1 g of MoO_3/SiO_2 was photoreduced in CO for 2 h and outgassed at room temperature for 30 min.

The following mass-balance equation can be applied to the reaction scheme [4]–[6],

$$N(NO)_0 - N(NO) = N(\sim Mo^{6+}...NO^{2-}) + 2\,N(N_2O) + 2\,N(N_2), \quad [7]$$

where the symbol N denotes the number of the corresponding molecules in the gas phase or the number of the surface complexes.

Since all NO is consumed by the catalyst at the end of the run, we can calculate the final concentration of the surface paramagnetic complex $[\sim Mo^{6+}...NO^{2-}]$ by putting into Eq. [7] the following values found in the experiment of Fig. 6: $N(NO)_0 = 4.6 \cdot 10^{19}$, $N(N_2O) = 0.8 \cdot 10^{19}$, and $N(N_2) = 1.0 \cdot 10^{19}$. This gives $N(\sim Mo^{6+}...NO^{2-}) = 1.0 \cdot 10^{19}$ per 1 g of the catalyst, i.e., the concentration that, in principle, can be measured by the ESR technique. This finding may provide a way to determine the rate constants of elementary steps [4]–[6] in the proposed reaction mechanism by comparing the number of NO molecules consumed with those of the reaction products and the concentration of the intermediate $\sim Mo^{6+}...NO^{2-}$ complex as a function of time. The corresponding measurements are being carried out.

It was also found in this study that the rate of NO consumption by Mo^{4+} and the N_2/N_2O ratio in the reaction products are strongly dependent on the presence of chemisorbed CO on the surface of the photoreduced catalyst. When MoO_3/SiO_2 preliminary photoreduced in CO was heated in a vacuum at 150°C for 20–30 min, and the same amount of NO as that in the experiment of Fig. 6 was then admitted onto the catalyst at room temperature, all NO was consumed within 1 min (a minimum time required to detect NO mass-spectroscopically in our experiments), and the N_2/N_2O ratio was about 20 times higher than that in the experiment of Fig. 6.

It is known from IR spectroscopic studies (21, 22) that CO molecules form carbonyl complexes of different compositions with Mo^{4+} ions, which are produced by photoreduction of Mo^{6+} in excess CO. The thermal stability of the complexes depends on the number of CO molecules bonded to Mo^{4+}. Some of them can be destroyed by simple evacuation at room temperature as it was done in the experiment of Fig. 6, whereas the most stable complexes decompose only upon heating in a vacuum at temperatures above 100°C. Thus, it appears that the presence of one or several CO molecules in the coordination sphere of Mo^{4+} strongly affects the rates of reactions [4]–[6].

CONCLUSION

The present work clearly demonstrates the efficiency of silica-supported molybdenum oxide as a catalyst for selective photoreduction of NO by CO at room temperature. To the best of our knowledge, it is the first report on the possibility of using MoO_3/SiO_2 as a selective and efficient photocatalyst for the conversion of NO–CO mixtures to nontoxic products (N_2 and CO_2). It is found that in a closed circulation setup, NO–CO mixtures can be fully photoconverted to N_2 and CO_2 with a selectivity close to 100%.

In addition, the results of this study led us to propose a reaction mechanism which is partly based on and agrees with previous studies on the photoreduction of MoO_3/SiO_2 in the presence of CO and on the interaction of NO with photoproduced Mo^{4+}. It appears that a detailed kinetic study of NO consumption and accumulation of the reaction products under UV irradiation combined with ESR measurements of the concentration of the intermediate Mo–nitrosyl complex might allow one to obtain some quantitative characteristics such as rate constants of the elementary steps and their activation energies.

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