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Infrared Spectroscopic Study of NO Reduction by H_2 on Supported Gold Catalysts

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In situ Fourier transform infrared spectroscopy is used to study the reduction of NO by H_2 on Au/SiO_2 and Au/MgO catalysts. On these catalysts, large differences in selectivity toward N_2 formation had been found depending on the nature of the support. These differences are correlated with transient infrared spectral features which appear during reaction. NO by itself does not give rise to a band attributable to NO adsorbed on Au, however, exposure of supported Au to NO renders the catalyst unable to adsorb CO. Preadsorbed CO, on the other hand, is displaced from the Au catalysts by NO. © 1986 Academic Press, Inc.

INTRODUCTION

Gold is generally a poor hydrogenation catalyst due to its weak interaction with molecular hydrogen. However, in a comprehensive kinetic study carried out by Galvagno and Parravano (*1*), supported gold catalysts were found to be surprisingly active for the reduction of NO by H_2. Apparently, a massive support effect was at work, leading to dramatic differences in selectivity toward N_2 formation according to the following overall reactions:

$$2\,NO + 2\,H_2 \rightarrow 2\,H_2O + N_2 \quad (1)$$

$$2\,NO + 5\,H_2 \rightarrow 2\,H_2O + 2\,NH_3 \quad (2)$$

Reaction (1) predominated on Au/MgO and Au/Al_2O_3, whereas reaction (2) was the main reaction on Au/SiO_2. The authors proposed for Au/MgO and Au/Al_2O_3 and increased electron back-donation from the catalyst to the adsorbed NO which would weaken the N—O bond and thereby facilitate the dissociation of NO. On Au/SiO_2, on the other hand, an associative adsorption of NO followed by hydrogenation into NH_3 was postulated.

The present work follows up on this previous study and uses *in situ* IR, a proven technique for probing catalyst surfaces, to investigate the adsorption characteristics of Au/SiO_2 and Au/MgO, and to obtain the mechanistic details of the above reactions on these catalysts. The additional information could then be combined with existing kinetic data to provide better explanations of the experimental results.

EXPERIMENTAL

According to the kinetic study of Galvagno and Parravano (*1*), the selectivity for N_2 formation in NO + H_2 was generally low on Au/SiO_2 but high on Au/MgO. Consequently, two Au catalysts, supported on SiO_2 and MgO, respectively, were used in this study to represent the two extreme cases of N_2 selectivity. The preparation methods and the characterization data for these catalysts are summarized in Table 1. It should be noted that a bimodal distribution of Au particles is present on both catalysts. Neutron activation analysis indicated that, except for a trace amount of Cl (<0.02 wt%), the catalysts were essentially free of impurities, particularly those of other metals.

One hundred milligrams of powdered catalyst was pressed into a 1-in. pellet and

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TABLE 1

Preparation and Characterization of Supported Au Catalysts

	Au/MgO	Au/SiO_2
wt% Au	3.46	6.02
Preparation method	Impregnation	Cation exchange
Precursor salt	$HAuCl_4$	$Au(en)_2Cl_3$
Average particle size (TEM)	80Å[a]	400 Å[a]
Average particle size (WAXS)	80Å[a]	400 Å[a]

[a] Bimodal size distribution.

placed in a high vacuum, IR cell (all Pyrex glass) equipped with NaCl windows and grease-free Teflon vacuum stopcocks. The IR cell was connected to a gas supply system capable of blending and metering different proportions of gases. Only the highest purity gases obtainable from commercial sources were used in this study. To prevent the last trace of impurities in the gas feed from entering the IR cell, a molecular sieve trap cooled in a slurry of dry ice and acetone was placed immediately ahead of the cell.

The cell contained two separate chambers; a front chamber for monitoring the gas phase composition and a back chamber for accommodating the catalyst pellet. The back chamber could be heated up to 623 K. Each of these chambers could be evacuated independently by a combination of diffusion and mechanical pumps. Liquid-N_2 traps were installed at strategic locations to prevent oil vapors from entering the IR cell. A typical experiment would begin with the evacuation of the IR cell, followed by the isolation of the back chamber. The front chamber was then filled with 30 Torr (1 Torr = 133.3 N m^{-2}) of either CO or NO. This procedure allowed the purity of the gases to be checked by their IR spectra. The gas in the front chamber was then expanded through a Teflon stopcock into the back chamber. After the pressures in both chambers were equalized, the back chamber was isolated and the front chamber was evacuated. Subsequent reconnection of the chambers allowed IR spectra of the gas phase and the adsorbed molecules to be obtained separately by scanning the front and the back chamber.

After an evacuation to remove most of the moisture and the volatile impurities from the catalyst pellet, the pellet was pretreated at 473 K in 50 Torr of flowing H_2 for 2 h. It was then cooled to room temperature in H_2 atmosphere.

All IR spectra were collected on a Digilab FTS-20 FTIR spectrometer at a spectral resolution of 1 cm^{-1}.

RESULTS AND DISCUSSION

Ideally, for an *in situ* IR study of a reaction to be informative, the reactive forms of the adsorbed reactant molecules must be IR active, so that the progress of reaction can be followed closely by observing the changes in the IR spectra of the adsorbed species. However, in the reactions between NO and H_2 over supported Au, this ideality is quite difficult to achieve as will be indicated later.

The exposure of both Au/MgO and Au/SiO_2 to 30 Torr of NO at room temperature did not produce any IR band that could be assigned to NO chemisorption on Au. The same conclusion was also true at other temperatures (298–603 K). The spectra did not show any adsorbed species except for a weak band at 1629 cm^{-1} on Au/SiO_2. This band could easily be removed by evacuation and was due to NO adsorption on SiO_2. The band assignment was confirmed by adsorbing NO on blank SiO_2 which had been pretreated the same way as the catalysts. Exposure of NO to similarly pretreated blank MgO failed to result in any detectable chemisorbed species in the spectral region of interest.

In view of the absence of IR active adsorbed NO species on Au, it was decided to check the adsorption capability of Au in these catalysts by adsorbing other gases. CO was selected for this purpose because previous work (*2–9*) had consistently indi-

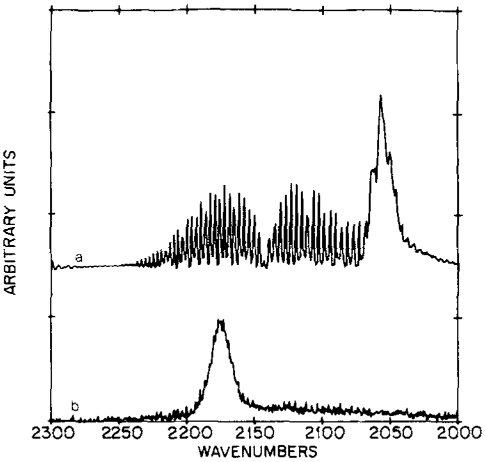

FIG. 1. Absorbance IR spectra (in arbitrary units) of (a) CO adsorption on reduced Au/SiO_2, (b) CO adsorption on unreduced Au/SiO_2.

cated that CO at partial pressures of several Torrs could adsorb on Au at room temperature, producing a single IR band in the range of 2120–2080 cm^{-1}. Both Au/SiO_2 and Au/MgO that had previously been exposed to NO were found to lose their ability for CO readsorption, even after the catalysts were subjected to evacuation followed by H_2 pretreatment at 473 K for 2 h. The only way to restore the CO chemisorption capability of Au was to treat the NO exposed catalysts in H_2 at 603 K for 2 h.

In order to elucidate this phenomenon further, fresh catalyst pellets were used and exposed first to CO before NO adsorption. These experiments were conducted to compare the relative strengths of adsorption of CO and NO on the Au surface.

Chemisorption of CO

Figure 1 (spectrum a) shows the infrared spectrum obtained after exposing a hydrogen pretreated Au/SiO_2 pellet to 30 Torr of CO. In addition to the clearly resolved rotational fine structure of gas-phase CO, a strong, single band with the absorption maximum at about 2060 cm^{-1} was observed. Decreasing the gas-phase pressure to 5 Torr reduced the intensity of this band significantly. Upon evacuation of the gas phase to 10^{-5} Torr, the band disappeared completely. This indicates that the adsorption of CO on Au/SiO_2 is reversible at room temperature. However, the fact that the band appeared at much lower wavenumbers compared to the CO gas phase implies that we were dealing with a chemisorbed, rather than physically adsorbed CO species. Furthermore, there was a slight shift (3–5 cm^{-1}) to higher wavenumber when the surface coverage was reduced. This shift, which is opposite in direction to group VIII metals, is typical for group IB metals (*10*). While the strength of adsorption and the coverage dependent band shifts were characteristic for Au, the observed CO band position on the reduced Au/SiO_2 pellet was significantly lower than the previously reported wavenumbers (*2–9*). In view of this rather unusual band position, an unreduced Au/SiO_2 pellet was exposed to CO. A band was found at 2175 cm^{-1} (Fig. 1, spectrum b), in perfect agreement with the results on unreduced Au obtained by Kavtaradze and Sokolova (*5*) and Yates (*8*). This band could easily be removed by evacuation. The pellet was then reduced *in situ* by H_2, following precisely the procedure used by Yates (*8*). The band at 2060 cm^{-1} was immediately reproduced after readsorbing CO on the reduced Au/SiO_2 catalyst.

Figure 2 shows the infrared spectra of

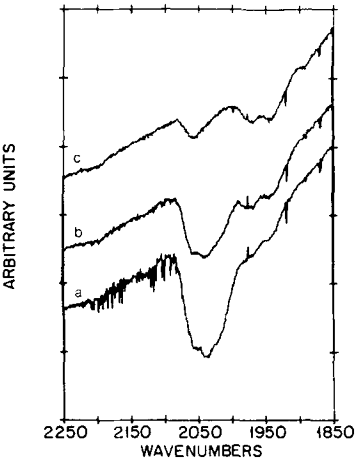

FIG. 2. Transmission IR spectra (in arbitrary units) of CO adsorption on reduced Au/MgO. (a) 15 Torr, (b) 5 Torr, (c) <1 Torr.

CO chemisorbed on Au/MgO as a function of gas phase CO pressure. At a pressure higher than 15 Torr, a broad band at around 2040 cm^{-1} appeared, comprising a high frequency shoulder at 2060 cm^{-1} and additional shoulder at wavenumbers lower than 2000 cm^{-1}. As the pressure was reduced, the band at 2040 cm^{-1} decreased in intensity much faster than that of the high frequency band at 2060 cm^{-1}, and the low frequency shoulders developed into a doublet with maxima at 1970 and 1940 cm^{-1} (Figs. 2b and c). After evacuation at 10^{-5} Torr, all the bands disappeared completely. A small shift to higher wavenumber with decreasing CO coverage, which is typical for group IB metals, was again observed for the high frequency band. As in the case of Au/SiO_2, the band positions were significantly lower than the previously reported values.

The appearance of the two low frequency shoulders may be assigned to bridge-bonded or multiply bonded adsorbed CO species. A more in-depth discussion of these features is presented elsewhere (*40*).

There are a number of reasons for IR bands of adsorbed species to appear at lower wavenumbers than expected. Particle size effects alone do not seem to be a dominant factor. Although ν_{CO} usually decreases with the decrease in metal particle size for group VIII metals, the reverse trend has been observed for Cu, a group IB metal (*11*). Furthermore, there was a large difference in the average Au particle size between the two supported Au catalysts of this study and yet ν_{CO} on both catalysts were shifted almost equally to wavenumbers much lower than that expected from an extended Au surface.

In the IR study of CO adsorption on Au electrodes (*12*), the CO stretching frequency was found to vary as a function of the electrode potential. In addition, the linearly adsorbed species could be completely transformed into the bridged species when the electrode was adequately polarized. By analogy, the oxide support in the Au catalysts may possess a similar function as the electrodes in the electrocatalytic experiment. For supported Au, the action of regulating the electrode potential is effectively replaced by the various combinations of metal particle size and the reactivity of the support. In Au/MgO, where smaller Au particles are dispersed over a more reactive oxide support, the interactions between CO and Au are probably more complex, resulting in more complex IR spectra.

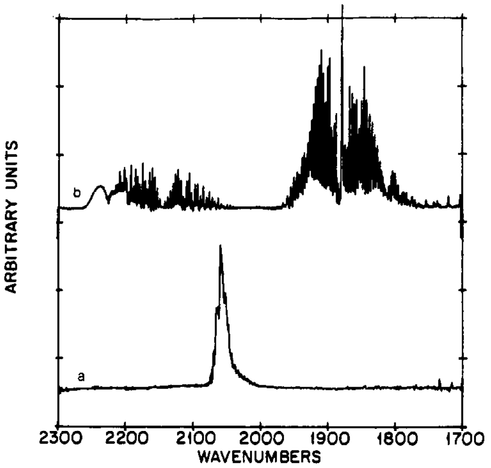

FIG. 3. Absorbance IR spectra (in arbitrary units) of (a) CO chemisorbed on Au/SiO_2, (b) displacement of adsorbed CO on Au/SiO_2 by NO(g).

Displacement of CO Adsorbed Species by NO

After the preadsorption of CO on the supported Au catalysts, the cell was evacuated to approximately 1 Torr. The purpose was to drastically reduce the intensity of gas phase CO but to keep the IR band for CO adsorption on Au distinctively visible (Fig. 3a). At that moment, 30 Torr of NO was introduced to the IR cell at room temperature. The resulting spectrum on Au/SiO_2 (Fig. 3b) showed an almost immediate displacement of adsorbed CO by NO. A similar result was also obtained on Au/MgO. Although the disappearance of the CO adsorbed species was accompanied by a simultaneous increase in the intensity of gas phase CO, a small amount of N_2O and CO_2 was also detected in the gas phase spectrum containing both NO and CO. However, the overall spectrum was still devoid of IR features attributable to NO adsorption on Au.

The appearance of N_2O and CO_2 was the result of a Au-catalyzed reaction between CO and NO. According to Cant and Fredrickson (*13*), the reaction could only proceed to a limited extent because its rate is inhibited by N_2O in the products. These observations, together with the preponderance of gas phase CO after introduction of NO led us to believe that only part of the adsorbed CO was removed by the reaction between CO and NO. The majority of CO was physically displaced from the catalyst surface simply because the affinity of Au for NO is stronger than that for CO. An evacuation after the displacement experiment did not restore the capability of Au to readsorb CO. Instead, a H_2 treatment at 603 K for 2 h was necessary to regenerate the catalysts. This indicates that a strongly bound surface species was left on Au after the exposure to NO. Whatever the nature of this species might be, its IR spectrum was not detectable under our experimental conditions.

Generally, NO adsorption on metals gives rise to IR bands in the range 2100–1700 cm^{-1} (*14–17*). However, to the best of our knowledge there is no previous report concerning the IR spectrum of NO on Au in the literature.

There are several possible explanations for the absence of a NO band on Au in the region 2100–1700 cm^{-1}. First, a small NO coverage below the detection limits of IR can be ruled out as an explanation because the entire Au surface was incapacitated for CO readsorption after the exposure to NO. This indicates that the coverage of NO was at least as extensive as that of CO and the latter had been shown to produce detectable IR bands. Second, the adsorbed species could be a linear species with very low extinction coefficient. This is rather unlikely in view of the more polar nature of NO and the relatively large extinction coefficient of gas phase NO. Third, NO could be adsorbed parallel to the Au surface. The N═O stretch in this configuration is IR inactive according to the metal-surface selection rules (*18*). Finally, NO might undergo dissociative chemisorption on the Au surface. Although this is not conceived as probable according to the prediction of Broden *et al.* (*19*), the rule was generalized without any data on Au. Furthermore, an exception to the rule has already been found in the case of Cu, where dissociative chemisorption of NO could occur even at a low temperature of 80 K (*20, 21*). In general, dissociative chemisorption of NO depends strongly on coverage, temperature, and nature of metal. Thermal desorption spectra suggest that residual oxygen adatoms from NO dissociation are difficult to remove from metal surfaces, often requiring very high temperatures for desorption (*22, 23*).

In summary, although the adsorbed species of NO on Au was not detected by IR spectroscopy, its presence was verified by the inhibiting effect of NO on CO readsorption, and by the reaction between CO and NO at room temperature, which formed a detectable amount of N_2O and CO_2. Since N_2O formation probably requires the pairing of molecularly adsorbed NO and nitrogen adatoms (*24*), some NO dissociation on Au seems to occur under the experimental conditions. The dissociative chemisorption probably proceeded via an adsorption precursor in which the NO axis was parallel to the surface. Such an adsorption mode is IR inactive according to the metal-surface selection rule (*18*).

In Situ IR Study of NO Reduction by H_2

For the *in situ* IR study of the reactions between NO and H_2, a mixture of NO in excess H_2 at a total pressure of about 100 Torr was exposed to the catalyst pellet in the IR cell (90 cm^3) at room temperature. The cell was then heated up slowly to 573 K. When pure SiO_2 or pure MgO pellets that had been pretreated in the same man-

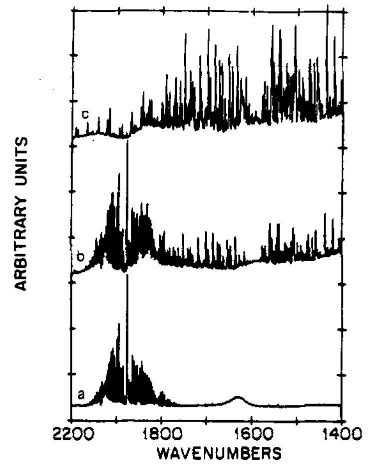

FIG. 4. Absorbance IR spectra of *in situ* NO reduction by H_2 at 603 K on Au/SiO_2 (spectral region 1400–2000 cm^{-1}) as a function of reaction time. (a) Start of reaction, (b) after 5 min, (c) after 35 min.

ner as the Au catalysts were used instead of the catalysts, no reaction took place over a period of more than 1 h at 603 K.

In agreement with the findings of Galvagno and Parravano (*1*), both Au/SiO_2 and Au/MgO were very active for the reactions between NO and excess H_2 at temperatures higher than 573 K. In fact, the NO in the IR cell was completely reacted within 30 to 35 min.

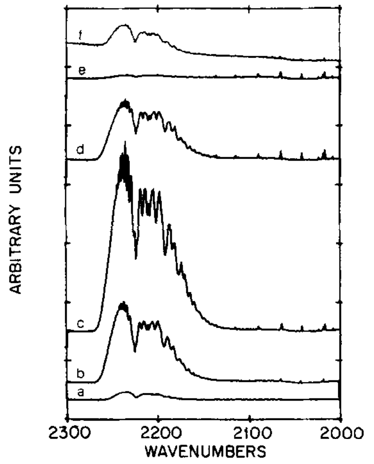

FIG. 5. Absorbance IR spectra of *in situ* NO reduction by H_2 at 603 K on Au/SiO_2 (spectral region 2000–2300 cm^{-1}) as a function of reaction time. (a) Start of reaction, (b) after 5 min, (c) after 10 min, (d) after 15 min, (e) after 35 min, (f) after cooling to 338 K at the end of reaction.

Figures 4–6 show the infrared spectra of the *in situ* reactions between NO and H_2 at different stages of the experiment on Au/SiO_2. Figure 4 displays the spectral region from 2000 to 1400 cm^{-1} where the gas phase vibrations of NO, NH_3, and H_2O occur. Figure 5 shows the range of 2300 to 2000 cm^{-1}, the region for the N_2O gas phase. Finally, Fig. 6 shows the spectral region from 2700 to 2400 cm^{-1} to 2400 cm^{-1} where some infrared active transient species were detected. In the remaining spectral regions that were not obscured by the total absorption of infrared radiation by the oxide carrier, no interesting spectral features were detected.

Heating the reactant mixture in the presence of Au/SiO_2 up to a temperature of 573 K did not cause any significant reaction. At 603 K, NO started reacting as evidenced by a decrease in the intensity of the NO gas phase spectrum accompanied by the appearance of gas phase NH_3 and H_2O (Fig. 4b). Most of the NO gas phase disappeared within 10 min. After 35 min, the NO gas was completely consumed and intense NH_3 and H_2O gas phase spectra were formed (Fig. 4c). As soon as NO started reacting, N_2O began to form in the gas phase (Fig. 5b), reaching a maximum after approxi-

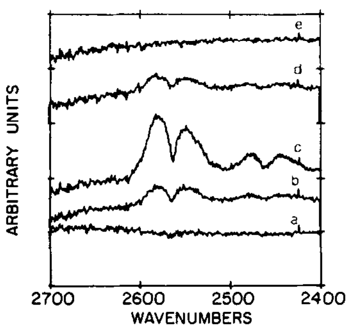

FIG. 6. Absorbance IR spectra of *in situ* NO reduction by H_2 at 603 K on Au/SiO_2 (spectral region 2400–2700 cm^{-1}) as a function of reaction time. (a) Start of reaction, (b) after 5 min, (c) after 10 minutes, (d) after 15 minutes, (e) after 35 min.

mately 10 min (Fig. 5c). Then, the intensity of the N_2O gas phase spectrum began to decrease (Fig. 5d). There seems to be a correlation between the decrease in the N_2O intensity and the depletion of NO in the gas phase. After 35 min, no detectable quantity of N_2O remained in the gas phase (Fig. 5e). The growth and the decay of N_2O suggests that N_2O was an intermediate product in the reduction of NO by H_2 on these Au catalysts. However, when the reaction temperature was lowered to 338 K at the end of the reaction, a small amount of N_2O reappeared, possibly an indication of an equilibrium condition between N_2O and NH_3/H_2O. N_2O was not detected in the kinetic study of Galvagno and Parravano (*1*) but that could be due to a longer residence time used in their reactor. Indeed, Otto *et al.* (see references cited in (*23*)) found that the reduction of N_2O by H_2 was faster than the reduction of NO by H_2. However, the reaction did not proceed until all the NO had been consumed.

The background infrared spectrum of the Au/SiO_2 sample showed no infrared band in the region of 2700 to 2400 cm^{-1} after exposure to the NO/H_2 mixture at 298 K (Fig. 6a). With the onset of the reaction at 603 K, some transient infrared spectral features appeared (Fig. 6b). After 10 min of reaction, these spectral features reached a maximum in intensity (Fig. 6c) followed by a gradual decrease in intensity (Fig. 6d) and a total disappearance after 35 minutes at 603 K (Fig. 6e). Cooling to room temperature did not recreate any of these species. The growth and the decay of these species appears to parallel that of N_2O, except for the reappearance of N_2O upon cooling at the end of the reaction. Before attempting an assignment of the infrared bands in the region of 2700 to 2400 cm^{-1}, the results obtained on Au/MgO will be discussed.

Au/MgO gave similar results compared to Au/SiO_2, namely a depletion of NO at 603 K after 10 min, appearance of NH_3 and H_2O bands, and growth and decay of N_2O. However, there was no spectral feature whatsoever observed in the range of 2700 to 2400 cm^{-1}. This difference between Au/MgO and Au/SiO_2 rules out that the appearance of bands in the region of 2700 to 2400 cm^{-1} was due to adsorption of N_2O on the catalyst.

It seems likely that the presence of these transient spectral features on Au/SiO_2 in the region 2700–2400 cm^{-1} was related to the high selectivity of this catalyst to produce NH_3. On the Au/MgO catalyst, which has high selectivity for N_2 formation, these transient species were either absent or present in a concentration below the detection limit.

The identification of the transient species at 2700–2400 cm^{-1} is extremely difficult, for the fact that the oxides and particularly the hydrides of N_2 are not strong absorbers of IR radiation in this region of interest. An analogy with the IR spectra of hydroxyl amines is also absent. Although resemblance with some of the minor features of the higher oxides of N_2 (N_2O_4, N_2O_5) was noted (*25*), the more prominent features which are characteristic of these oxides were absent from our spectra. Furthermore, these nitrogen oxides are thermally unstable compounds that could not possibly exist at the reaction temperature. It is equally improbable that these highly oxidized products of N_2 could be formed under the net reducing atmosphere used in the $NO + H_2$ reactions.

The IR spectra of adsorbed molecules of common oxides and hydride of nitrogen including hydroxylamines (*14*) also failed to provide a good match for the transient species. Regardless of this, we are still inclined to consider the transient species as a precursor to NH_3 formation because it was only detected on Au/SiO_2, the Au catalyst noted for its selectivity towards NH_3 formation. However, the composition of the transient species is conceivably more complicated than the NH_x species that were suggested for the NO/H_2 reaction on Ru (*26*).

The reaction mechanism for the reduction of NO by H_2 is usually system-specific

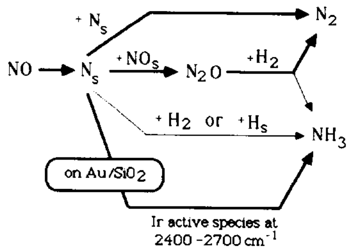

FIG. 7. Proposed reaction pathways of the H_2 reduction of NO on Au catalysts. The subscripts "s" denote adsorbed species.

and cannot be generalized for all metal catalysts. Kokes (*27*) initially proposed that the reaction proceeds through an adsorbed HNO complex, which can either decompose to N_2O or hydrogenate directly to NH_3. The same intermediate or its oligomers were also postulated by several other authors (*28, 29*). Echigoya *et al.* (*30*) suggested that most of the N_2 is formed by the decomposition of N_2O which is a reaction intermediate. All of the above mechanistic formulations tacitly assumed the associative chemisorption of NO. Recent views (*24, 26, 31, 32*), however preferred a dissociative chemisorption of NO, whereby the surface nitrogen atoms can either pair up with other nitrogen containing species on the surface to form N_2O or N_2, or undergo hydrogenation to the end product of NH_3 via a series of NH_x intermediates. The formation of N_2 by the decomposition of NH_3 or the reaction between NO and NH_3 are usually not considered as major reaction paths.

Generally, the reactions between NO and H_2 over catalytic surfaces are very complex, and numerous reaction intermediates and mechanisms have been proposed. While the present study, in agreement with previous work (*1*), confirms the influence of the support of the selectivity of Au catalysts, it does not allow us to arrive at definitive conclusions with regards to the reaction mechanism. However, based on the combination of past and current experimental data, the following reaction scheme (Fig. 7) is given as a phenomenological explanation.

Although the dissociative chemisorption of NO has not been established in the literature, it is the most probable explanation for the formation of N_2O under the reaction conditions and also in the reaction between NO and CO at room temperature. Although the dissociation of molecular H_2 is difficult on Au (*33*), it is not totally impossible at the temperature used in the NO + H_2 reaction (*34*). Indeed, Galvagno and Parravano (*1*) had reported that both Au/SiO_2 and Au/MgO were more active in H_2–D_2 exchange at 573 K than in the reduction of NO by H_2 at the same temperature. Furthermore, the activity of Au/SiO_2 was about an order of magnitude higher than that of Au/MgO. A more efficient activation of H_2 on Au/SiO_2 seems to be the main reason for this catalyst to form NH_3 preferentially in the reactions between NO and H_2. There does not seem to be any difference in the modes of NO chemisorption (i.e., associative vs dissociative) on Au when the support is SiO_2 or MgO. This is a totally different viewpoint from the original hypothesis of Galvagno and Parravano (*1*).

It has to be emphasized that the high activity of Au/MgO and Au/SiO_2 for this reaction is rather surprising considering the low catalytic activity of metallic gold. One might be tempted to argue that traces of other metals, rather than gold, are responsible for the observed activity. However, the effect is so massive that a considerable amount of impurities would be required to justify the observed activity. Careful analysis of the catalysts, using atomic absorption, neutron activation analysis and photoelectron spectroscopy did not reveal any significant metal impurity. In fact, the only significant impurity found was 0.02 wt% of chlorine in the case of Au/MgO. The same Au/MgO catalyst was proven to be totally inactive in the hydrogenolysis of cyclopropane up to a temperature of 623 K (*35*). Similarly, Au/SiO_2 was totally inactive for ethane hydrogenolysis up to 503 K (*36*). This lack of activity indicates the absence of group VIII metal impurities such as rhodium, palladium or iridium. Furthermore, blank experiments were carried out on SiO_2 and MgO pellets at different times in between experiments with gold. These blank runs showed quite convincingly that there was no extraneous or internal source of impurities in our infrared cell.

This leads to the conclusion that an interaction of gold with oxide supports can, under certain conditions, modify the chemistry of bulk gold. One might suggest that the active sites in the Au/MgO and Au/SiO_2 catalysts are not necessarily zero-valent metallic gold. Indeed, EXAFS data for Au/MgO catalysts indicated the presence of highly dispersed gold carrying a formal charge of +1 in addition to metallic gold (*37*, *38*). This result is supported by transmission electron microscopy on Au/MgO, showing a large fraction of highly dispersed gold particles together with large particles. Similarly, a Mössbauer study on supported gold catalysts indicated an *s*-electron density at the gold nucleus lower than that of the gold metal (*39*).

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