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Highly Selective Catalytic Reduction of NO by H_2 over Au^0 and Au(I) Impregnated in NaY Zeolite Catalysts

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The NO–H_2 reaction has been studied over Au^0/NaY and Au(I)/NaY catalysts, which were prepared by the mechanical mixing of $AuCl_3$ with NaY zeolite and by the monolayer dispersion of Au(I) species into NaY zeolite, respectively. The precursor samples were reduced in flowing hydrogen at 423 K. The NO–H_2 reaction over these catalysts took place at relatively low temperatures under isothermal conditions from 373 to 673 K. The Au(I)/NaY catalysts were more active toward the above reaction compared with the Au^0/NaY catalysts. The NO selectivity was pointed to the N_2 and N_2O formation, with the former catalysts being more selective to N_2. ***In situ*** **FT–IR study of the NO–H_2 reaction on the gold catalysts demonstrated that NH_3 was detected in the adsorbed NH_4^+ form at 1440 cm^{-1}, along with N_2O at 2240 (2220) cm^{-1} and H_2O at 1645 cm^{-1}. Two characteristic bands due to the vibrations of N–O bond in adsorbed NO were identified. The bands at 1880 cm^{-1} in the spectra of Au^0/NaY were assigned to Au^{n+}–NO ($n \approx 0$) complexes, and the corresponding bands at 1910 cm^{-1} in the spectra of Au(I)/NaY were assigned to Au^{n+} NO ($n = 1$) complexes in cages of zeolite. It was proposed that N_2O and NH_3 formed simultaneously at low to moderate temperatures (<500 K) by the addition of N atom to NO and H atoms, respectively. The presence of adsorbed N atoms was confirmed by the coadsorption of NO/CO/H_2 mixture onto Au(I)/NaY at 423 K, where a band at 2280 cm^{-1} ascribed to isocyanate [NCO] intermediate was developed intensively with time. This band did not deliver when a mixture of NO/CO was admitted alone to the IR cell. Therefore, the H atom promoted the N–O bond fission to form N_{ad} and OH_{ad}. The [NCO] species is the result of a reaction between the adsorbed N atom and gaseous CO.**

1. INTRODUCTION

Au is well known for its inertness among group Ib metals (1), so that on conventional support surfaces, the Au atoms may be considerably less active than precious atoms for adsorption and catalysis. However, in a kinetic study carried out by Galvagno and Parravano (2), supported gold on SiO_2, Al_2O_3, and MgO catalysts were found to catalyze the reduction of NO with H_2. Lee and Schwank (3) followed up on this previous study and used *in situ* IR for probing catalyst surfaces. In agreement with the findings of Galvagno and Parravano, both Au/SiO_2 and Au/MgO were found active for the reaction between NO and excess H_2 at temperatures higher than 573 K. Nevertheless, their IR spectra quality was rather poor to be informative as the spectra were collected at high temperatures. A comment must also be made concerning the high reaction temperature applied and stabilizing high dispersion of gold phase on the oxide surfaces since the sublimation energy of gold is relatively low (4).

It was suggested that further progress could be made by extending the investigations of the NO–H_2 reaction on Au catalysts by changing the nature of the support. Recently, we have reported that Au(I)/NaY catalysts were found to be active in the chemisorption of CO and NO and even surprisingly active in the direct decomposition of NO to N_2 and O_2 (5, 6). The NO decomposition reaction proceeded through the sequential formation of N_2O_3 and N_2O intermediates on Au(I) sites at 300–673 K (5). However, the steady-state activities were not obtained. It is generally presumed that the strongly bound oxygen to the catalyst surface prevents further decomposition of NO (7, 8). Thus, it became evident that steady-state NO decomposition takes place in the presence of some gas-phase reductants to remove an excess oxygen on the catalyst surfaces (9).

We report here the results of NO reduction by H_2 on Au/NaY as an effort to emphasize the catalyst preparation on both activity and selectivity of gold catalysts for this reaction. Although several investigations of NO reduction by H_2 have been reported in the literature, a comprehensive IR study of this reaction was not provided. Therefore, and in view of the current catalysts, an *in situ* infrared spectroscopic investigation of NO + H_2 reaction is required. A temperature-programed desorption (TPD) experiment was carried out to study the affinity of NO decomposition on the gold catalysts.

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2. EXPERIMENTAL

2.1. Catalyst Preparation

Two series of Au (13 wt%) catalysts were prepared by application into NaY zeolite and were noted as Au^0/NaY and Au(I)/NaY to refer to their oxidation states. Since Au(I) sites are crucial for the NO + H_2 reaction, we used this catalyst code to emphasize the moiety of the active gold centers. However, the Au oxidation state 1 is not the prevailing state in Au(I)/NaY but it is a mixture of Au(I) and Au^0 states, while in Au^0/NaY a metallic Au is the only existing state. The Au^0/NaY samples were prepared at room temperature by the mechanical mixing of $AuCl_3$ (Strem Chemicals, 99% purity) with partially dehydrated NaY zeolite (Si/Al = 5.6, surface area = 910 $m^2\,g^{-1}$) at 473 K. The Au(I)/NaY samples were prepared by allowing the physically mixed $AuCl_3$/NaY sample to be exposed to vacuum at 338 K for 72 h. The $AuCl_3$ vapor migrated to be hydrolyzed by trace H_2O in the zeolite. Characterization by XRD, XPS, EXAFS/XANES, and UV-Vis had proved that Au(III) was homogeneously distributed in NaY zeolite and was partially reduced to Au(I) (10, 11).

2.2. Activity Measurements

The activity measurements studies were made at atmospheric pressure using a mixture of 4810 ppm of NO and 1% of H_2 balanced with He, in a steady-state flow mode. A Pyrex glass tubular reactor containing 200 mg of the sample was used in these runs. Catalytic experiments were done at equal contact times $W/F = 0.47$ g s cm^{-3}, where W is the catalyst weight and F flow rate in milliliters per second. Prior to each series of runs, the samples were reduced by flowing hydrogen (10 ml min^{-1}) at 423 K for 1 h. The NO and products in the gas stream at the reactor outlet were continuously analyzed using on-line gas chromatograph (Ohkura GC-103) with thermal conductivity detector. Two separation columns were used. The first column was packed with porapak-N (4 m long, $\phi = 4$ mm) for N_2O and NH_3 separation, while the other was packed with 5A molecular sieve (2 m long, $\phi = 4$ mm) for N_2 and NO separation. He was used as a carrier gas with flow rates equal to 25 ml min^{-1} for the former column and 15 ml min^{-1} for the latter. The columns temperature was 363 K. The NO conversion has been evaluated as the percentage of NO converted to reduced products i. e., N_2 and N_2O. The selectivity, S, for N_2 and N_2O is calculated from the corresponding yield, Y, as follows:

$$Y_{N_2} = \frac{2N_2}{NO_{\text{inlet}}}$$

$$Y_{N_2O} = \frac{2N_2O}{NO_{\text{inlet}}}$$

$$S_{N_2}\% = \frac{Y_{N_2}}{(Y_{N_2} + Y_{N_2O})} \times 100$$

$$S_{N_2O}\% = \frac{Y_{N_2O}}{(Y_{N_2} + Y_{N_2O})} \times 100.$$

2.3. In Situ FT-IR (Fourier Transform Infrared) Spectroscopic Study

The powdered catalyst (15–20 mg) was pressed into a pellet and placed in an IR cell equipped with NaCl windows. The IR cell (dead volume = 94.8 cm^3) was connected to a circulation manifold (dead volume = 402.2 cm^3) equipped with gas supply reservoirs. NO gas was purified prior to use by passing through a molecular sieve trap cooled in a slurry of dry ice, acetone, and small amount of liquid N_2. This procedure served to remove NO_2 and N_2O. Hydrogen (99.99%) was used without further purification. A typical experiment would begin with evacuation of the IR cell at 423 K to remove the moisture and the volatile impurities from the catalyst pellet. The pellet was pretreated at 423 K in 50 Torr of H_2 for 2 h. A liquid-N_2 trap was installed during the static reduction of the catalyst pellet to prevent the evolved H_2O from reoxidizing the pellet. A mixture of NO and H_2 (H_2/NO = 4), with a total pressure of 68 Torr, was introduced to the catalyst pellet, so that *in situ* infrared spectra can be taken of species adsorbed on the catalyst surface. All IR spectra were collected on a Shimadzu FTIR-4100 spectrometer at a spectral resolution of 2 cm^{-1} with the coaddition of 50–100 interferograms.

2.4. TPD Study

TPD experiments were conducted in a fixed-bed reactor using 50 mg of the sample. NO gas (5 Torr) was admitted onto the catalyst bed at 300 K for 15 min, after which time the system had equilibrated. Following this, the system was evacuated until a base pressure of 2×10^{-7} Torr was attained. TPD started by increasing the temperature linearly with the rate of 5 K min^{-1} and scan time 10 s. The desorbed gases were analyzed by ANELVA AQA-100 quadrupole mass spectrometer and gave the following elution traces: NO (mass 30), N_2O (mass 44), N_2 (mass 28), and O_2 (mass 32).

3. RESULTS

3.1. Activity versus Time and Temperature

Figure 1 shows the NO conversion to reduced products in the NO–H_2 reaction, i.e., N_2 and N_2O, as a function of time-on-stream after various reaction temperatures were applied to Au(I)/NaY catalysts. Interestingly, the reaction began at relatively lower temperatures, such as 373 K. All the conversions were in the steady state and did not decay for hours. The specific rates for NO reduction to N_2 and N_2O under the steady-state conditions over the gold catalysts as a function

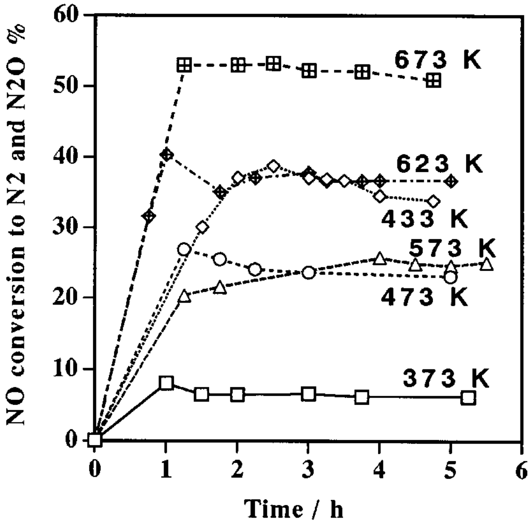

FIG. 1. Conversion of NO to N_2+N_2O as a function of time-on-stream in the NO–H_2 reaction over Au(I)/NaY at various reaction temperatures.

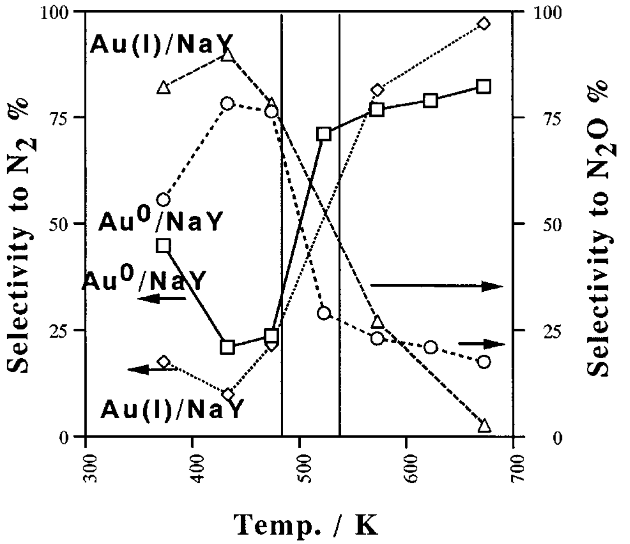

FIG. 2. Comparison of the NO selectivity to N_2 and N_2O on the gold catalysts as a function of reaction temperatures.

of reaction temperature are compared in Table 1. The rates of N_2 and N_2O formation on Au(I)/NaY are almost twice as high as those on Au^0/NaY in the temperature range 433–623 K, and the difference in rates increased almost five times at 673 K. There is a common rate trend accompanying the two catalysts in the temperature range 373–623 K. The specific rates first increased to 433 K, where substantial amounts of N_2O were detected, followed by a drop at 433–473 K and passed through a very broad minimum values for temperatures between 473 and 573 K. The specific catalytic activities of both catalysts were increased by increasing the reaction temperature above 573 K, i.e., 623 K. As the reaction temperature is further increased to 673 K, the rate of NO reduction increased again with Au(I)/NaY, while it sharply decreased with Au^0/NaY. On testing the structure stability of the catalysts that might result in the catalytic activity variations in Table 1, we found that the subsequent measurements of rates at lower temperatures following the reaction at 673 K reproduced the original values. Therefore, such variations are related to thermodynamically favorable products distribution as shown below.

TABLE 1

Rates of Nitric Oxide Reduction by Hydrogen on the Gold Catalysts at Various Temperatures

	Rate (10^{-2} · mol[a] NO/g[b]-Au · min)	
Temp. (K)	Au(I)/NaY	Au/NaY
373	1.08	1.01
423	4.35	2.93
474	3.04	2.00
573	3.22	1.95
623	4.49	3.89
673	6.69	1.45

[a] Moles of NO that have been converted to N_2O and N_2.

[b] Au content was determined by ICP analysis. Rates were normalized to a total gram gold content in the samples.

3.2. Products Distribution versus Reaction Temperature

Figure 2 shows the selectivity of NO in the NO–H_2 reaction on gold catalysts versus the temperature. It should be stressed that distribution of products N_2 and N_2O depends on the reaction temperature. The NO selectivity to N_2O and N_2 is 100% in the range of temperatures applied in this study, i.e., 373–673 K. No NH_3 is ever detected at the outlet, although this clearly counts against the results of Galvagno and Parravano (2) for the same reaction on Au supported on Al_2O_3, SiO_2, and MgO catalysts. The product distributions are somewhat similar in behavior on both types of catalysts. N_2O was produced as an important product at 433 K. By increasing the reaction temperature, the NO selectivity to N_2O drops steeply on both Au^0/NaY and Au(I)/NaY catalysts with corresponding increase in the selectivity to N_2. The selectivity to N_2 was 97% on Au(I)/NaY at 673 K and 82.4% on Au^0/NaY at 673 K.

4. IN SITU FT-IR STUDY OF THE NO–H_2 REACTION

The effects of the reaction temperature against time on the infrared species observed during the NO–H_2 reaction over Au^0/NaY and Au(I)/NaY are shown in Figs. 3–7 . The spectra obtained were subtracted from background for each spectrum. All the bands seen in these spectra are due to vibrations of adsorbed N_2O at 2240 (2220) cm^{-1} (12), and NO in Au–nitrosyl complexes: Au^{n+}–NO ($n=1$) at 1910 cm^{-1} (13, 14), Au^{n+}–NO ($n \approx 0$) at 1880 cm^{-1} (13, 14), Au–NO^-

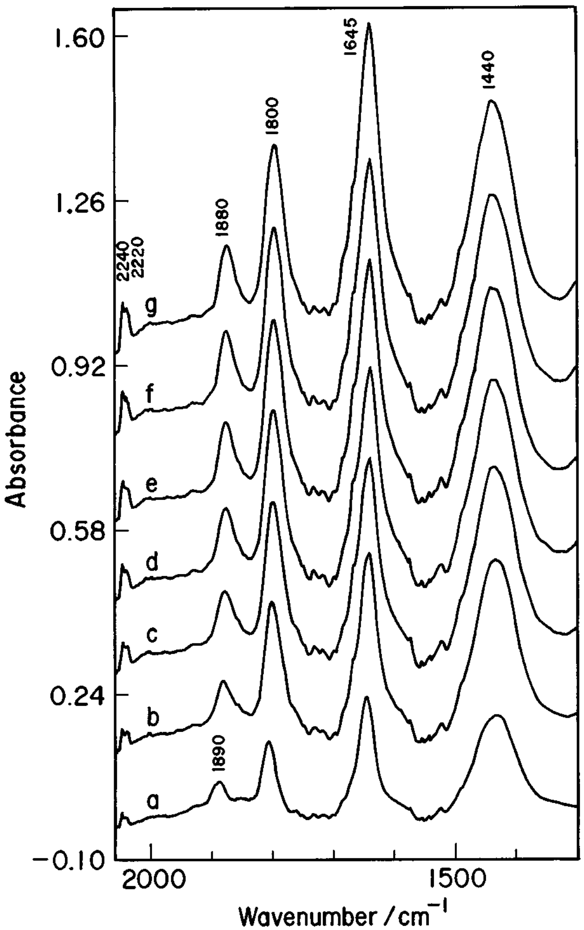

FIG. 3. *In situ* FT-IR spectra from NO–H_2 reaction on Au^0/NaY at 433 K. The sample was exposed to reactant gases for (a) 5 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 75 min, (f) 90 min, and (g) 120 min.

at 1800 cm^{-1} (15). H_2O has a band at 1645 cm^{-1} (16) and adsorbed NH_4^+ at 1440 cm^{-1} (16). No form of adsorbed NH_3 molecules at 1620 cm^{-1} was detected. The hydrogen bonded to surface hydroxyl, caused by H_2O, masked the NH bands in the high-frequency regime beyond recognition. The detection of adsorbed H_2O species upon the admission of NO–H_2 mixture onto the gold samples at low to moderate temperatures (<423 K) is a crucial evidence that N_2O is not the result of NO dissociation but is a reduced product. Once the bands of product species N_2O and NH_4^+ formed, their intensities gradually increased with time to reach certain maxima then showed no further changes. This indicates that the reaction equilibrium was attained at a given time, and furthermore, these species did not undergo further reaction.

4.1. *Au^0/NaY*

As shown in Fig. 3, when the Au^0/NaY catalyst was contacted with a mixture of NO–H_2 at 433 K, the bands of product species N_2O and NH_4^+ were produced, along with the H_2O bands at 1645 cm^{-1}. It is noteworthy to mention that the bands due to monomeric Au–nitrosyl complexes at 1880 and 1800 cm^{-1} are seen only in the spectra of Au^0/NaY at 433 K. Therefore, NO did not completely dissociate at this temperature. These bands conceivably could be assigned to adsorbed NO in Au^{n+}–NO ($n \approx 0$) complexes by analogy with the NO band on Ag^+/NaY and on Cu^+/ZSM-5 (13). From the observed gradual peak shift to lower frequency with reaction time, i.e., from 1890 to 1880 cm^{-1}, it is concluded that the NO bond order is weakened due to charge transfer from Au^{n+} ($n \approx 0$) to $NO^{\delta+}$. The charge donation from Au^{n+} ($n \approx 0$) to $NO^{\delta+}$ centers is almost complete as the observed IR frequency is slightly higher than that of free NO at 1876 cm^{-1}. The 1800 cm^{-1} band is likely to be assigned to NO^- vibration.

When the NO–H_2 reaction temperature was raised to 473 K, the spectra obtained resembled those collected over a Au^0/NaY catalyst at 433 K except that the bands at 1880 and 1800 cm^{-1} have completely vanished, as shown in Fig. 4. Thus, the slightly upscale shift of the band at 1880 cm^{-1} from that of gaseous NO indicates that the structure contributing this bond is weakly attached on the surface and is rapidly removed by increasing the temperature. Consequently, it appears more reasonable to propose that this form of adsorbed NO and the NO species at 1800 cm^{-1} are

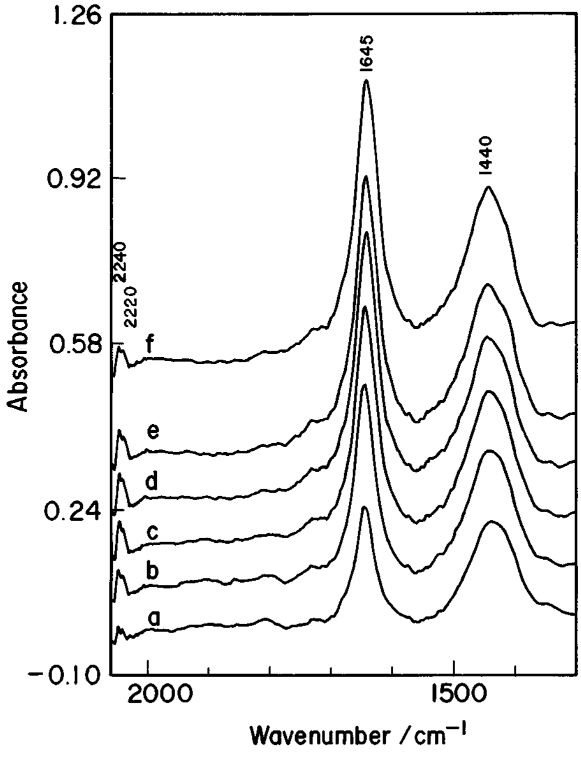

FIG. 4. *In situ* FT-IR spectra from NO–H_2 (H_2/NO = 4) reaction on Au^0/NaY at 473 K. The sample was exposed to reactant gases for (a) 5 min, (b) 15 min, (c) 30 min, (d) 45 min, (e) 60 min, and (f) 120 min.

the ones that dissociate. The relative peaks intensity ratio NH_4^+/H_2O decreased from 8 to 5.3 by raising the temperature and became invariant with time after 30 min. Thus, the concentration of NH_4^+ species decreased with raising the temperature from 433 to 473 K.

4.2. Au(I)/NaY

Shown in Fig. 5 are the IR spectra of NO–H_2 reaction on Au(I)/NaY at 373 K. It is interesting to note that the bands of reduced species N_2O and NH_4^+ were produced at this relatively low temperature. The Au–NO bands were broad and ill defined. The N–O bond order at 1910 cm^{-1} became stronger by the positive frequency displacement above the vibrational frequency of free NO than the corresponding one at 1890–1880 cm^{-1} in the spectra of Au^0/NaY (Fig. 3). The 1910 cm^{-1} band would thus be assigned to a partially positive NO species on Au(I)/NaY. However, it is conceivable that the removal of one antibonding electron by coordinating to Au(I) site is contributing bonding mode to NO at 1910 cm^{-1}. The weak bands at about 1850 cm^{-1} are possibly assigned to NO vibrations in Au–$NO^{\delta-}$ structure.

Figure 6 shows the IR spectra of NO–H_2 reaction over Au(I)/NaY at 433 K. By comparing these spectra with those in Fig. 5, the changes in the Au(I)-nitrosyl features were not significant. Since the band at 1910 cm^{-1} did not diminish at this temperature as the 1890–1880 cm^{-1} band did in the spectra of Au^0/NaY at the same temperature, it must be noted that the NO molecule is accommodated as a positively charged state in the sodalite cavity in Au(I)/NaY. Weak IR bands characteristic of $Au(NO)_2$ species at 1817 and 1736 cm^{-1} could be detected. The bands for dinitrosyl species are analogous to those on Cu/ZSM-5 (13). However, it is a relatively less important species under our reaction conditions. On the other hand, the data shown in Fig. 6 demonstrate pronounced differences in the intensity ratios NH_4^+/H_2O compared to the analogies in Fig. 3. These ratios varied from 1.82 to 0.94 over 2 h reaction time on Au(I)/NaY, while it varied from 0.8 to 0.66 over the same time on Au^0/NaY. Therefore, the activation of molecular hydrogen is facilitated better on Au(I)/NaY than on Au^0/NaY under the same experimental conditions.

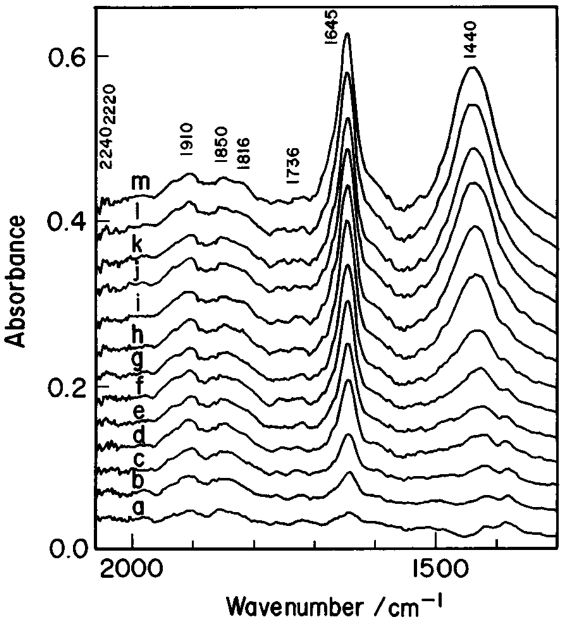

FIG. 5. *In situ* FT-IR spectra from NO–H_2 (H_2/NO = 4) reaction on Au(I)/NaY at 373 K. The sample was exposed to reactant gases for (a) 5 min, (b) 10 min, (c) 20 min, (d) 30 min, (e) 45 min, (f) 60 min, (g) 80 min, (h) 105 min, (i) 120 min, (j) 150 min, (k) 175 min, (l) 210 min, and (m) 240 min.

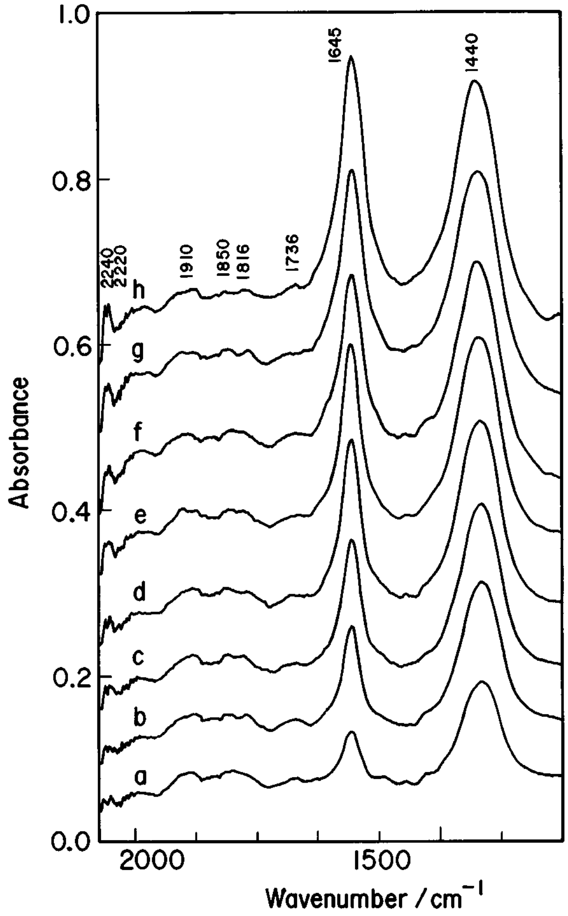

FIG. 6. *In situ* FT-IR spectra from NO–H_2 (H_2/NO = 4) reaction on Au(I)/NaY at 433 K. The sample was exposed to reactant gases for (a) 5 min, (b) 10 min, (c) 20 min, (d) 45 min, (e) 60 min, (f) 90 min, (g) 120 min, and (h) 180 min.

Upon increasing the NO–H_2 reaction temperature to 573 K, the bands responsible for both N_2O and NH_4^+ species were not produced (Fig. 7). Also, the Au(I)–NO bands have not developed. The H_2O band intensity decreased due to the intense scattering of the infrared beam by the sample and/or desorption of H_2O from the sample at high temperatures. To check up the generation of N_2O and NH_4^+

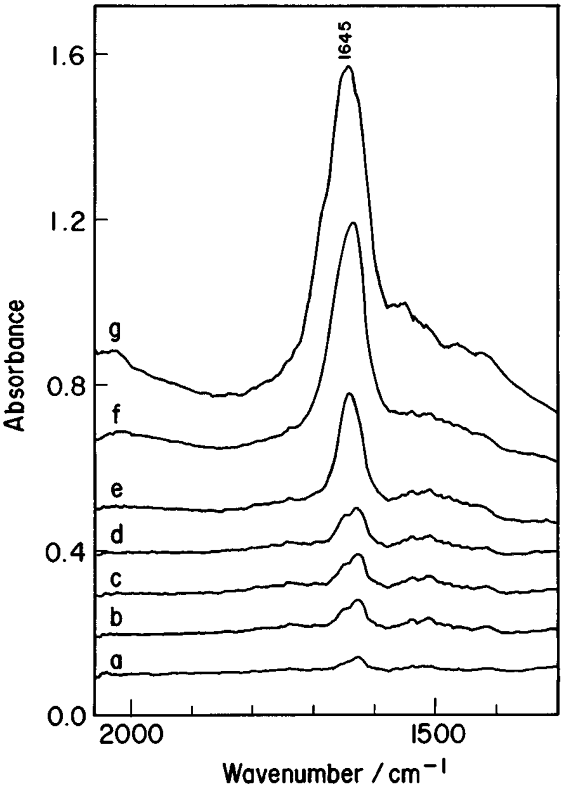

FIG. 7. *In situ* FT-IR spectra from NO–H_2 (H_2/NO = 4) reaction on Au(I)/NaY at 573 K. The sample was exposed to reactant gases for (a) 30 min, (b) 60 min, (c) 105 min, (d) after (c) cooling to 474 K, (e) after (d) cooling to 423 K, (f) after (e) cooling to 373 K, and (g) after (f) cooling to 298 K.

species on Au(I)/NaY at 573 K, the spectra were collected on cooling the sample (Figs. 7e–7g). No bands appeared at 2240(2220) and 1440 cm^{-1}; the only ones detected were those for H_2O at 1645 cm^{-1}. Therefore, the production of NH_3 and N_2O essentially ceased and the selectivity was directed only to N_2 at temperatures >573 K, in agreement with the product distribution data given in Fig. 2. This is in direct contrast to the catalytic behavior of Pt and Pd catalysts in NO–H_2 reaction, where significant NH_3 formation is observed up to temperatures as high as 1033 K (17).

5. DISCUSSION

5.1. Catalytic Performance of Au-Supported Catalysts in NO–H_2 Reaction

Although the dissociation of molecular H_2 is rather difficult on Au (18), it has been reported that the H_2–D_2 exchange reaction proceeded on Au/SiO_2 and Au/MgO at the temperature used in NO–H_2 reaction, i.e., 573 K (2). The activity of Au/SiO_2 was about an order magnitude higher than that of Au/MgO. In a parallel study by Schwank, *et al.* (19), the CO adsorption on Au/MgO gave a band that was shifted to a significantly lower wavenumber in comparison to the band position on Au/SiO_2. Lee and Schwank (3) plausibly concluded that an interaction of gold with oxide supports can, under certain conditions, modify the chemistry of supported gold, and the active sites in Au/SiO_2 and Au/MgO for NO–H_2 reaction are not necessarily zero-valent metallic gold. This suggests that the presence of a small fraction of Au^{n+} in the gold catalysts is necessary in the activation of molecular H_2 as well as NO.

The data in Table 1 and Fig. 2 showed that the Au(I)/NaY catalysts are more active and selective than the Au^0/NaY catalysts in the NO–H_2 reaction, especially at 673 K. This is due to the presence of charged Au cations in pores of the former catalysts since larger Au particles are expected to be segregated and exposed to external zeolite at the prevailing temperatures, thereby leading to the activity decrease. Thus, the dispersion state of Au atoms is related to changes of the chemical states of these atoms. The presence of charged Au atoms was confirmed by the *in situ* IR spectra of the NO–H_2 reaction. From the relative NO band shift above that of free NO, it is concluded that stronger charged Au atoms were generated in Au(I)/NaY preparations than in Au^0/NaY preparations. The charged Au atoms are expected to be located in the pores of NaY zeolite in the former catalysts for the following reasons: First, their characteristic NO bands at 1910 cm^{-1} did not diminish at 473 K. On the contrary, the corresponding bands at 1890–1880 cm^{-1} in the spectra of Au^0/NaY disappeared completely at 423 K. Second, according to the IR data the reaction equilibrium was attained on Au^0/NaY faster than on Au(I)/NaY (Figs. 3 and 6). Third, the activities of both catalysts at 673 K were dramatically different.

When a gas mixture of NO/H_2/CO was admitted onto an Au(I)/NaY pellet at 473 K and collected the IR spectra on cooling the gold catalyst, a characteristic strong carbonyl IR absorbing band at 2188 cm^{-1} was detected. This band was reasonably assigned to a CO vibration of carbonyl coordinated Au(I) site (20). Besides the IR investigation in this study, we are inclined to consider that Au(I) sites could be formed in pores of zeolite under the net redox atmosphere used in the NO/H_2 reaction. As the oxidation affinity of NO is higher than that of H_2O as a side product, the latter has a minimal effect on changing the oxidation state of Au atoms. Thus, the difference in catalytic activities in Table 1 must be discussed in terms of the presence of a dual Au(I) and Au^0 site in Au(I)/NaY and a unique Au^0 site in Au^0/NaY, which is exposed to the surface as big particles especially at high temperatures (Table 1). However, the Au(I) sites in general are very remarkable in NO dissociation (5). Au(I) and Au^0 must exist next to each other since it is highly unlikely that Au(I) ions were located neither within the crystal structure of metallic Au particles nor as isolated small patches. Metal ions have been proven to be present in macroscopic inter-

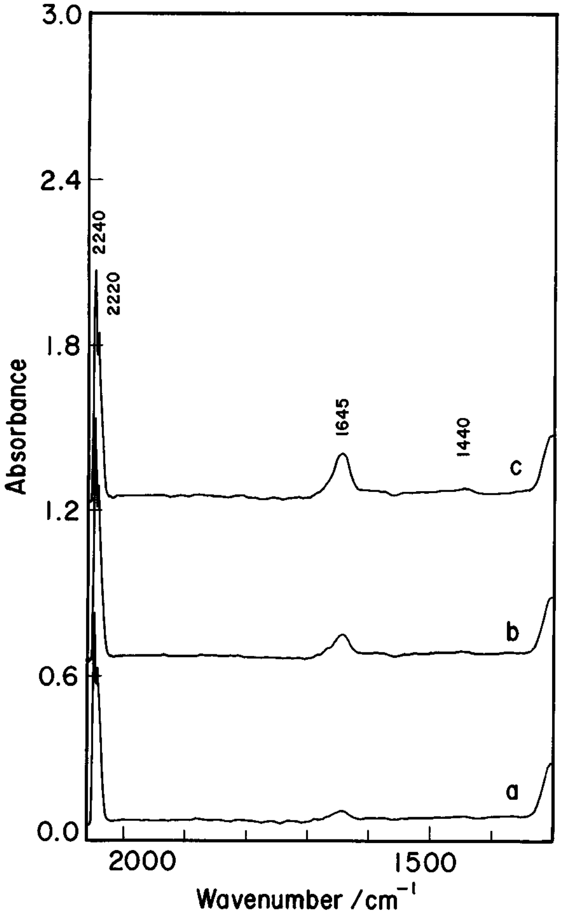

FIG. 8. *In situ* FT-IR spectra from N_2O–H_2 reaction on Au(I)/NaY at 433 K as a function of reaction time, (a) 30 min, (b) 60 min, and (c) 120 min.

faces between metals and oxidic materials (21, 22). Thus, it is suggested that Au(I) ions exist at the interface between metallic Au particles and interior walls of NaY zeolite.

The decline in activity of NO conversion between 433 and 573 K has been previously reported for the same reaction on Pt/ZSM-5 (23), which was attributed to the lack of available hydrogen because of the simultaneous formation of NH_3. The NH_3 is presumably produced by the addition of hydrogen atoms to N atoms derived from NO dissociation. Although, NH_3 was not observed in the reaction products over the gold catalysts due to a H_2 dissociation process less efficient than that on Pt, adsorbed NH_4^+ species was detected in the IR spectra of the NO + H_2 reaction at temperatures lower than 573 K. It appears likely that small amounts of NH_3 that are converted in the presence of H^+ were produced, from polarized H_2O to adsorbed NH_4^+ species at 1440 cm^{-1}. However, a mass balance of $70 \pm 10\%$ on N_2 was obtained at temperatures lower than 573 K. This value has increased to $90 \pm 10\%$ by increasing the reaction temperature over ≈ 573 K. Thus, it was confirmed that the gaps among the NO conversions to $N_2O + N_2$ in the temperature range 433–573 K are linked by adsorbed NH_4^+ and N_2O species. Although, the concentration of NH_4^+ species was decreased then vanished by raising the temperature to 573 (Figs. 5–7), the presence of strongly adsorbed N_2O species onto Au(I) sites in cages of zeolite has been confirmed from NO-TPD results in the same temperature region, as is presented below.

5.2 Reaction Mechanism

5.2.1. At temperatures <573 K. The *in situ* spectra of $N_2O + H_2$ reaction over Au/NaY at 423 K are shown in Fig. 8. It is observable that the NH_4^+ bands cannot be produced by the above reaction according to the following equation:

$$N_2O + 4H_2 \rightarrow 2NH_3 + H_2O.$$

Recently, it has been reported that there is a direct correlation between concentration of NH_4^+ and NO_x conversion over vanadia–titania catalysts (24), and NH_4^+ are active species for the NO–NH_3 to produce N_2. Figure 9 illustrates the spectra resulting from NO + H_2 reaction on Au(I)/NaY at 423 K in sequential treatment. After the reaction proceeded for 2 h (Fig. 9a), the system was evacuated shortly for 5 min (Fig. 9b). As a result, the N_2O bands have disappeared leaving the bands of H_2O and NH_4^+. Following this, NO (40 Torr) was introduced first for the purpose of interacting with adsorbed NH_4^+ species. As can be seen, the N_2O bands developed to a lesser extent with a negligible decrease in the concentration of NH_4^+ species (Figs. 9c–9e). The conclusion from this result is unlikely to be that the dissociation of adsorbed NH_4^+ species via series of NH_x intermediates is a major reaction path for producing N_2O under these experimental conditions according to the following equation:

$$NH_x + NO \rightarrow N_2O + x/2H_xO.$$

The subsequent addition of H_2 (160 Torr) to the reactor at the same temperature caused the development of N_2O and NH_4^+ bands with time again (Figs. 9f–9k). This result unequivocally shows that the H_2 adsorption is dissociative, and therefore H atoms must have been involved in a common reaction pathway to produce N_2O and NH_4 simultaneously.

From the TPD measurements of NO adsorption on Au(I)/NaY catalysts (Fig. 10), the associative adsorption of NO molecules was deduced in the temperature range where the parallel formation of N_2O and NH_4^+ species was observed in the IR spectra at temperatures lower than 573 K. The N_2O formation should primarily involve the NO dissociation. For the N–O bond to be broken it is anticipated that it will be necessary to first weaken the bond through the addition of an electron into the antibonding orbital of the N–O bond. According to the spectral features in Fig. 9 it

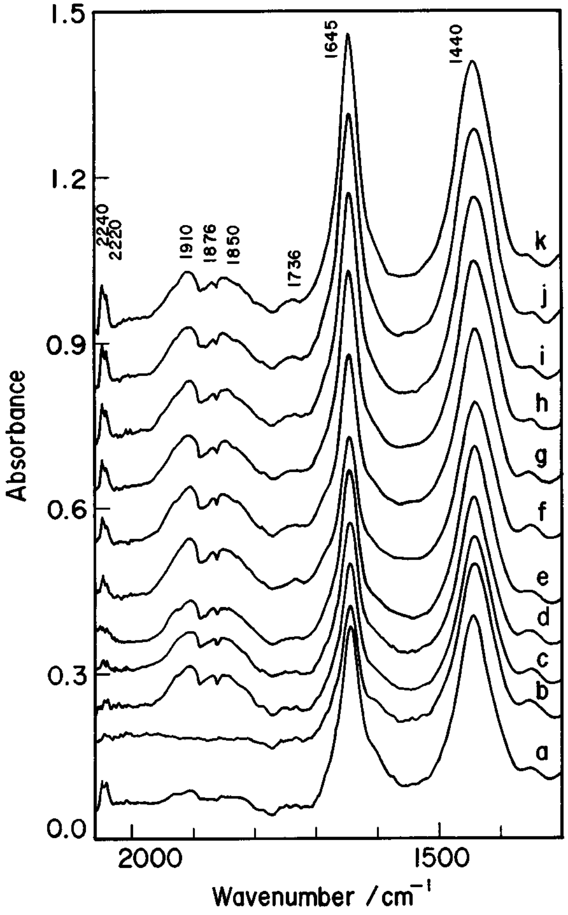

FIG. 9. *In situ* FT-IR spectra of adsorbed species on Au(I)/NaY at 423 K. (a) The sample was exposed to NO (17 Torr) + H_2 (51 torr) for 2 h; (b) the sample was evacuated for 5 min after (a); after (b) the sample was exposed to NO (40 Torr) for (c) 20 min, (d) 60 min, and (e) 180 min; after (e) the sample was exposed to NO (40 Torr) + H_2 (160 Torr) for (f) 5 min, (g) 15 min, (h) 25 min, (i) 35 min, (j) 50 min, and (k) 1 h.

seems reasonable that an electron from a H atom weakened the N–O bond, thereby causing to N–O bond dissociation at these temperatures.

Kokes (25) has suggested that the NO–H_2 reaction proceeds via the formation of $(HNO)_x$, a solid species that decomposes readily to yield N_2O, NH_3, and H_2O. Our data agree in general with Kokes' findings, the following reaction paths seem reasonable, and, in particular, close homogeneous analogies to it have developed at low to moderate temperatures (<573 K):

$$(1)\quad H_2 \rightarrow 2H_{ad}$$

$$(2)\quad NO_g \rightarrow NO_{ad}$$

$$(3)\quad NO_{ad} + H_{ad} \rightarrow N_{ad} + OH_{ad}$$

$$(4)\quad N_{ad} + NO_{ad} \rightarrow N_2O_g$$

$$(5)\quad N_{ad} + 3H_{ad} \rightarrow NH_{3,ad}$$

$$(6)\quad NH_{3,ad} + H^+(HCl, H_2O) \rightarrow NH^+_{4,ad}$$

$$(7)\quad H_{ad} + OH_{ad} \rightarrow H_2O.$$

Hecker and Bell have postulated (26) that the NO dissociation proceeds with the assistance of an adsorbed H atom. We have, however, confidently probed the reaction pathway 3 by the IR spectra recorded in sequential NO/CO/H_2 additions over Au(I)/NaY at 423 K (Fig. 11). The NO/CO (CO/NO = 4) mixture was introduced first to the catalyst pellet at 423 K. After 1 h contact time, the interaction between NO and CO did not produce additional bands (Fig. 11a). As soon as H_2 (CO/H_2 = 1) was admitted to the system, a band at 2280 cm^{-1} was produced, which systematically increased in intensity with time (Figs. 11b–11g). This band is assigned to isocyanate–[NCO] intermediates (27). It became apparent from this result that a reaction occurs between NO and H_2 to produce surface N atoms, and therefore H atoms promoted the NO dissociation according to step 3, in full agreement with the assumption proposed by Hecker and Bell (26). Adsorbed N atoms interacted with gaseous CO (bands at 2176 and 2120 cm^{-1}) to form an isocyanate complex:

$$\text{Au–N} + \text{CO} \leftrightarrow \text{Au–NCO}.$$

5.2.2. At temperatures >573 K. When the temperature of the Au(I)/NaY catalyst exceeded 573 K, the NO molecule dissociated mainly to produce N_2O and N_2 regardless of the H-assistant role, as shown in Fig. 10. The desorption of N_2O

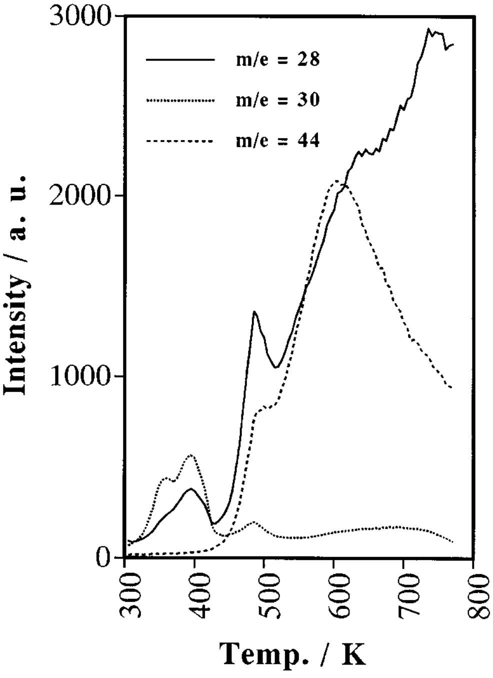

FIG. 10. TPD profiles of NO decomposition on Au(I)/NaY to form N_2 ($m/e = 28$), NO ($m/e = 30$), and N_2O ($m/e = 44$).

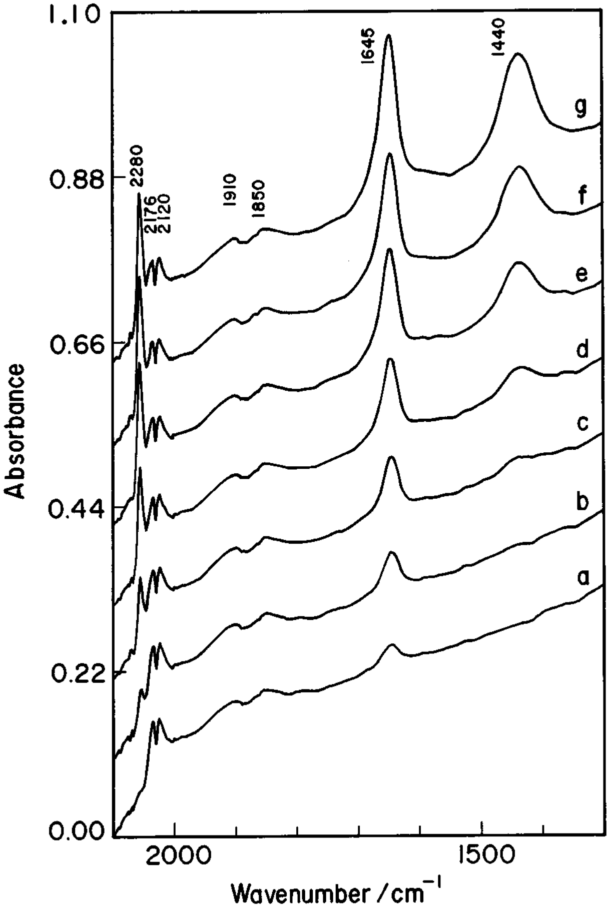

FIG. 11. *In situ* FT-IR spectra of adsorbed species on Au(I)/NaY at 423 K. (a) The sample was exposed to NO (17 Torr) + CO (51 Torr) for 1 h; then H_2 (50 Torr) was introduced to the reaction mixture for (b) 5 min, (c) 20 min, (d) 30 min, (e) 45 min, (f) 90 min, and (g) 120 min.

at 615 K implies the existence of stable Au(I) cations in the zeoliote cages. The formation of N_2O was reported to be correlated to the existence of Cu(I) on Cu/Al spinel catalyst in the NO decomposition reaction (28). However, the very broad N_2O desorption peak at this temperature is likely the result of a diffusion limited process from the sodalite cage into the gas phase. The temperature at which N_2O started to decay almost coincided with the temperature of increased NO selectivity to N_2, e.g., 573–673 K (Fig. 2). This indicates that N_2O is a reaction intermediate to N_2 in the NO–H_2 at temperatures higher than 573 K. The formed N_2 desorbs immediately from the Au sites and new vacancies were created. The oxygen atoms left on the surface were removed from the catalyst by hydrogen to form H_2O according to the subsequent steps:

$$(1)\quad NO_g \rightarrow NO_{ad}$$

$$(2)\quad H_{2,g} \rightarrow 2H_{ad}$$

$$(3)\quad 2NO_{ad} \rightarrow N_2O_{ad} + O_{ad}$$

$$(4)\quad N_2O_{ad} + 2H_{ad} \rightarrow N_{2,g} + H_2O$$

$$(5)\quad 2H_{ad} + O_{ad} \rightarrow H_2O.$$

6. CONCLUSIONS

(1) The NO–H_2 reaction took place on gold catalysts at temperatures as relatively low as 373–673 K. The NO selectivity to dinitrogen-containing products (N_2O and N_2) was rather high unless it is 100% especially at temperatures above 500 K. NH_3 was not detected at the outlet, although the band of adsorbed NH_4^+ at 1440 cm^{-1} grew in the *in situ* FT-IR spectra of the above reaction up to 500 K. NH_3 was produced with small amounts, which react subsequently with H_2O to produce NH_4^+.

(2) The *in situ* FTIR spectra of NO + H_2 reaction on Au(I)/NaY revealed that the bands of NO^{x+} coordinating Au^{n+} sites appeared at 1910 cm^{-1}, at such a location above the frequency of free NO at 1876 cm^{-1}. The corresponding bands from Au^0/NaY were located at 1880 cm^{-1}. Therefore, the band at 1910 cm^{-1} was assigned to vibrations of NO in Au(I)–NO complexes in cages of NaY zeolite, while those at 1880 cm^{-1} were assigned to NO vibrations in Au^{n+}–NO ($n \approx 0$) complexes on the external zeolite or near by regions of the zeolite surface.

(3) The NO-TPD profiles from Au(I)/NaY catalyst revealed the associative adsorption of NO up to 573 K. At these temperatures, the NO molecule was dissociated to N_{ad} and OH_{ad} by the aid of H atom in the NO + H_2 reaction. This interpretation is completely consistent with the observation of a band at 2280 cm^{-1} ascribed to adsorbed [NCO] species when a mixture of NO/CO/H_2 was adsorbed on Au(I)/NaY at 432 K. However, the coadsorption of only NO/CO did not produce this species. The [NCO] species is formed by a reaction between adsorbed N atom and gaseous CO.

(4) The dissociative adsorption of NO occurred at temperatures higher than 573 K. The N_2O is proposed as the intermediate species in the NO + H_2 reaction under the same NO dissociation conditions. The formation of N_2 by the decomposition of adsorbed NH_4^+ species via series of NH_x intermediates was not considered a major reaction path. This is because the reaction between NO and NH_4^+ species did not yield the development of N_2O bands at 423 K on one hand and the decrease in the NH_4^+ concentration was not associated with a corresponding increase in either N_2O or N_2 compositions on the other hand.

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