# Studies of the selective reduction of nitric oxide by carbon monoxide in the presence and absence of hydrogen over Au/NaY catalysts

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The selective reduction of NO with CO in the presence and absence of hydrogen over Au/NaY catalysts has been studied by *in* situ FTIR spectroscopy and under steady-state conditions in a flow mode in the temperature range 473–723 K. The NCO intermediates found by FTIR absorption at 2280–2240 cm<sup>-1</sup> after contacting, at 423–573 K, an Au/NaY catalyst with an NO-CO-H<sub>2</sub> mixture shows a dependence on the presence of H<sub>2</sub> which functions in N—O dissociation in this temperature region. Removal of NCO groups from the catalyst with time at 473 K, proposed to be limited by the prerequisite reaction between adsorbed NCO and NO in the gas phase, to form N<sub>2</sub> and CO<sub>2</sub> is accelerated with increasing temperatures. The effect of adding H<sub>2</sub> to an NO-CO-He stream on the conversions of both NO and CO to, respectively, N<sub>2</sub> and CO<sub>2</sub> were found to be consistent with a temperature-dependent mechanism. The yields of N<sub>2</sub> and CO<sub>2</sub> were increased in the presence of hydrogen, when NCO complexes were present on the gold catalyst, up to 573 K. Above this temperature, where direct NO + CO is the only competing reaction, the presence of hydrogen reduced conversion. The activities of the gold catalysts were maintained even at temperatures as high as 723 K, suggesting that a large fraction of partially charged Au<sup>1</sup> cations were stabilized by the framework of NaY zeolite. This species, after pumping off the reacting mixture gases at 473 K and collecting the spectra on cooling the gold catalyst, gave a characteristic carbonyl IR absorption band at 2188 cm<sup>-1</sup>, reasonably assigned to a CO vibration of carbonyl coordinated to Au<sup>1</sup>.

Noble metals and transition-metal oxides have been found to be capable of catalysing reduction of NO by CO with the formation of isocyanate (-NCO) surface intermediates under a variety of conditions.<sup>1-6</sup> For instance, the formation of NCO intermediates in the reaction of NO with CO is established for a variety of supported catalysts, including  $Pd/Al_2O_3$ ,<sup>1,2</sup>  $Ir/Al_2O_3$ ,<sup>1</sup>  $Pt/Al_2O_3$ ,<sup>1</sup> On the other hand, no previous report on the catalysis of NO + CO reaction over gold could be found in the literature, in agreement with our earlier FTIR results where neither the bands of NCO complexes, nor of product species, were found in FTIR spectra of this reaction over Au/NaY. $^{6}$  The low activity of Au for most catalytic reactions has generally been attributed to its lack of a partially filled d band under the usual experimental temperatures and as a consequence an inability to chemisorb simple molecules such as CO, NO, H<sub>2</sub>. Surprisingly, when H<sub>2</sub> was added to the reacting gases (NO + CO) over Au/NaY at 423 K, the formation of complexes between NO and CO was evidently observed by FTIR in the region 2280-2240 cm<sup>-1</sup>.<sup>6</sup> These bands were ascribed to adsorbed -NCO intermediates in different oxidation states on the gold sites. It was concluded that hydrogen assisted dissociation of N-O bonds and that a reaction between adsorbed N atoms and gaseous CO to form -NCO groups occurred; therefore,  $H_2$  promoted the coadsorption of NO and CO on Au/NaY. In a recent study by Dumpelmann et al.,<sup>7</sup> the positive role of adding hydrogen to a reaction mixture of NO and CO over Pt/Al<sub>2</sub>O<sub>3</sub> and Rh/Al<sub>2</sub>O<sub>3</sub> catalysts was studied, although -NCO intermediates were identified on these catalysts also in the absence of hydrogen.1-5

In view of the relative inertness of gold surfaces in chemisorption and catalysis, the important role of hydrogen in the NO-CO-H<sub>2</sub> reaction on Au/NaY at relatively low temperatures appears to be of significant interest. The objective of the current study was to obtain more insight into the surface chemistry of the NCO species and, in particular, to clarify the importance of these incorporated intermediates in the NO-CO- $H_2$  reaction on the Au/NaY catalysts.

## Experimental

#### **Catalyst preparation**

Since the catalyst preparation method has been described elsewhere,<sup>8,9</sup> only a brief description will be given here. The Au/NaY (Au 5 wt.%) samples were prepared at room temperature by the mechanical mixing of AuCl<sub>3</sub> (Strem Chemicals, 99% purity) with partially dehydrated NaY zeolite (Si/Al = 5.6, surface area = 910 m<sup>2</sup> g<sup>-1</sup>) at 473 K, under a nitrogen atmosphere. The mixture sample was allowed to stand under vacuum at 338 K for 72 h, during which time crystals of AuCl<sub>3</sub> were slowly vaporized and migrated to interact with water molecules in the zeolite pores. By this process, the XRD, FTIR, UV–VIS, XPS, TPD and EXAFS/ XANES analyses produced evidence for the partial reduction of AuCl<sub>3</sub> and for a uniform distribution of gold(1) chloride species inside the zeolite cages and channel.<sup>9,10</sup>

#### **Reaction Study**

The activity measurements studies were made in a steady-state flow mode. The reactant gases were made up from three streams: premixed NO in He, H<sub>2</sub> and CO, and were blended in a mixture chamber with the use of independent mass-flow controllers (STEC-400) to obtain a feed-gas mixture of 4810 ppm NO, 1% CO and 1% H<sub>2</sub> diluted with He. The analysis of the effluent products from the reactor were periodically performed by use of an on-line gas chromatograph (Okhura GC-103) equipped with a thermal conductivity detector (TCD) set at 363 K to monitor catalytic activity. Two separation columns were employed at 353 K: the first column packed with Porapak-Q (4 m long, id = 4 mm) for CO<sub>2</sub>, N<sub>2</sub>O and NH<sub>3</sub> separation and the other with 5 Å molecular sieves (2 m long, id = 4 mm) for N<sub>2</sub>, NO and CO separation. All experiments were carried out with a tubular quartz fixed-bed.

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% NO conversion to 
$$N_2 = \frac{2N_2}{NO_{inlet}} \times 100$$
 (1)

% CO conversion to 
$$CO_2 = \frac{CO_2}{CO_{inlet}} \times 100$$
 (2)

## In situ FTIR study

The in situ FTIR absorption spectra were recorded in the temperature range 295-573 K on a Shimadzu FTIR-4100 doublebeam spectrometer with 20 scans at a resolution of 2 cm<sup>-1</sup>. A quartz IR cell equipped with NaCl windows and grease-free Teflon vacuum stopcocks was used in conjunction with a conventional vacuum and gas-handling system capable of evacuation to  $10^{-6}$  Torr. The sample was pressed into self-supporting wafers (15-20 mg), and mounted between the windows of the cell. Applying electric heating of the wafer could be maintained at any desired temperature. The temperature was measured with a chromel-alumel thermocouple in contact with the wafer. Temperature fluctuations were within  $\pm 1$  K. Before each experiment was initiated the following procedure was used: (a) evacuation while the sample was heated to 423 K; (b) treament with 50 Torr of hydrogen for 1 h at 423 K; (c) evacuation at 423 K for 30 min. Following this, the system was filled with the gas mixture NO-CO- $H_2$ (0.5:1:1) at a total pressure of 63 Torr with the temperature adjusted to the desired value.

#### **Results and Discussion**

## In situ FTIR study

Fig. 1(a) and (b) depict the IR spectra in two wavenumber regions obtained when an Au/NaY catalyst was treated with a NO-CO (0.5:1) gas mixture (bottom spectrum) and after the admission of hydrogen [NO-CO-H<sub>2</sub> (0.5:1:1)] at 473 K. The intensity of the bands at 2186 and 2120 cm<sup>-1</sup> did not change after 1 h of the NO-CO reaction over Au/NaY. The overall band at ca. 2186 cm<sup>-1</sup> is characterized by both CO coordinated to cationic Au<sup>I</sup> and gas phase CO in the cages of NaY zeolite (which is readily eliminated by evacuation).<sup>9</sup> The band at 2120 cm<sup>-1</sup> is due to CO species adsorbed on Au metal.9 It is also observed that no other bands for NCO complexes or products species were produced [bottom spectrum in Fig. 1(b)]. On the other hand, when H<sub>2</sub> was blended by mixing with NO-CO (remaining spectrum), a rapid appearance of isocyanate -NCO bands at 2280-2240 cm<sup>-1</sup> was observed. This result undoubtedly shows the dependence of the formation of isocyanate complexes on the presence of hydrogen in the NO-CO gas mixture. Additionally, IR bands of tentative product species at 2356, 2336 (CO<sub>2</sub>), 1680 (OC=O), 1646 (H<sub>2</sub>O), 1619 (=C=N-) and 1446 cm<sup>-1</sup>  $(NH_4^+, CO_3^{2-})$  were also observed (further insight into the assignments of the bands is given below). The formation of NCO complexes, together with product species, was followed as a function of time at 473 K. The intensity of the IR bands increased linearly with time following the introduction of hydrogen. The data in Fig. 1 did not show hydrogenation of NCO to NH<sub>3</sub> which must pass through the formation of



**Fig. 1** In situ FTIR spectral changes in the regions 2400–1700 cm<sup>-1</sup> (a) and 1800–1300 cm<sup>-1</sup> (b) obtained on Au/NaY at 473 K: the bottom spectra were produced from reaction between NO and CO (NO: CO = 0.5:1) for 1 h. The second to bottom spectra were obtained at the very beginning (3 min) of the introduction of H<sub>2</sub> to the gas mixture (NO: CO: H<sub>2</sub> = 0.5:1:1). Following spectra were collected simultaneously with increasing reaction time (up to 5 h).

HNCO complexes, which would give rise to bands at higher wavenumbers than that of NCO species. No band for HNCO was observed under our experimental conditions.

It should be noted that the bands at 2280 cm<sup>-1</sup> [covalently bonded isocyanate (-NCO)] and 2240 cm<sup>-1</sup> [anionic iso-cyanate, (-NCO)<sup>-</sup>]<sup>3,4</sup> were superimposed on each other at a shorter contact time after the H<sub>2</sub> admittance. The intensity of the band at 2240 cm<sup>-1</sup> did not change with time, whereas the bands of the covalently bonded species at 2280 cm<sup>-1</sup> progressively decreased in intensity. Most frequently a more weakly bound [-NCO] took a part as an intermediate in the NO-CO- $H_2$  reaction over the gold catalyst. However, the decrease in the -NCO concentration appears to correspond to a relative increase in the concentrations of product species. A satisfactory explanation for the coexistence of NCO and  $(-NCO)^{-}$  species at 473 K must be presented in terms of the presence of hydrogen in the gas reaction mixture. In a study by Solymosi *et al.*,<sup>4</sup> – NCO bands produced from the NO-CO reaction did not appear until the temperature of a 5% Pt/Al<sub>2</sub>O<sub>3</sub> catalyst was raised to 573 K, whereas the -NCO)<sup>-</sup> band first appears at 673 K. In our system (Au/ NaY), the (-NCO)<sup>-</sup> band hardly appeared at 473 K by contrast with the dominant band of -NCO, which appeared at this temperature or below.

The formation of -NCO complexes must involve the rupture of an N-O bond with active involvement of added hydrogen. The H-assisted dissociation of NO may take place via two different routes<sup>11</sup> [eqn. (3) and (4)].

$$NO_s + H_s \rightarrow N_s + OH_s,$$
 (3)

$$NO_s + H_s \rightarrow NH_s + O_s$$
 (4)

From the calculated activation barriers of the above reactions on Pt, the presence of  $H_s$  decreases the activation barrier for cleavage of the N—O bond to form N<sub>s</sub>, compared with direct NO<sub>s</sub> dissociation to N<sub>s</sub> and O<sub>s</sub> ( $\Delta E_{NO}^* = 13$  kcal mol<sup>-1</sup>).<sup>11</sup> Corresponding values of  $\Delta E_{NO}^*$  for reactions (3) and

(4) are 6 and 23 kcal mol<sup>-1</sup>, respectively.<sup>11</sup> The lower energy barrier for NO dissociation by  $H_s$  according to eqn. (3) may explain the preferable formation of NCO intermediates over HNCO intermediates on the gold catalyst according to eqn. (5).

$$N_s + CO_s \to NCO_s \tag{5}$$

The NCO<sub>s</sub> ligand can bind through either the nitrogen or oxygen atom, but with gold only the N-bonded form is found in isocyanatogold(I) complexes.<sup>12</sup>

It is known, at least for Pt<sup>4</sup> and Ru,<sup>13</sup> that NCO intermediates are more strongly bound on partially oxidized surfaces. This was observed in the present study when the sample at the end of the previous experiment was cooled to lower temperatures after the reacting gases were pumped off for 5 or 10 s at 473 K (Fig. 2). Evacuation at 473 K brings about the preferential removal of NO (1876 cm<sup>-1</sup>), entrapped CO gas and CO attached to metallic Au. The strong and sharp distinct carbonyl band at 2188 cm<sup>-1</sup> which became more prominent upon lowering the pellet temperature is very characteristic of a CO vibration in an Au<sup>1</sup> CO moiety,<sup>14</sup> this species being less stable at higher temperatures.<sup>15</sup> The simultaneous increase in intensity of the bands at 2188  $\rm cm^{-1}$ appears to parallel the slight decrease in band intensity at 2280 cm<sup>-1</sup>. It is conceivable that  $-(NCO)^{-}$  species undergo configurational rearrangement in the absence of NO, CO and  $H_2$  in such a way that the carbonyl groups became more accessible to Au<sup>1</sup> sites upon lowering the temperature. This conclusion was supported by the switch from  $Au^+ - NCO^$ structures at 2240 cm<sup>-1</sup> (upper spectrum in Fig. 1) to Au-NCO structures at 2280 cm<sup>-1</sup> (Fig. 2) after gas evacuation for a short time and decreasing the temperature.

Further evidence for the significant role of NCO intermediates was obtained by carrying out the NO-CO-H<sub>2</sub> reaction over Au/NaY at increasing temperatures (423-573 K, Fig. 3). Here, the order of introducing the reductants was altered to study their respective roles in the production of NCO intermediates. After the NO-H<sub>2</sub> (0.5 : 1) reaction was conducted for 45 min at 423 K (not shown here<sup>6</sup>), NCO bands first appeared



**Fig. 2** In situ FTIR spectra in the carbonyl region on Au/NaY obtained following the NO-CO-H<sub>2</sub> (0.5:1:1) reaction at 473 K for 5 h: (a) after degassing at 473 K for 5 s; (b) upon further degassing for 10 s at the same temperature; and upon cooling the sample to 413 (c), 380 (d), 358 (e), 341 (f), 323 (g), 313 h and 303 K (i)



Fig. 3 In situ FTIR spectra obtained from the NO- $H_2$ -CO reaction over Au/NaY after the system had equilibrated for 2 h at (a) 423 K and at increasing temperatures: 488 (b), 496 (c), 508 (d), 518 (e), 529 (f), 533 (g), 548 (h) and 573 K (i)

when CO was introduced into the system at the same temperature. This result is not surprising according to the foregoing discussion on the decisive role of hydrogen in the generation of NCO groups. Thus, the sequence of the introduction of CO or  $H_2$  gas to the preliminarily existing gas mixture is not important. This led us to assume that neither N atoms nor CO molecules were strongly bound to the gold sites, although the NCO species is relatively stable under these experimental conditions.

After the system had equilibrated at 423 K for 2 h to give the spectrum of Fig. 3a, the spectra were collected at increasing temperatures [Fig. 3b-i]. The bands at 1646 cm<sup>-1</sup> (H<sub>2</sub>O) and 1446 cm<sup>-1</sup> (NH<sub>4</sub><sup>+</sup>) in Fig. 3a are the result of NO reduction by H<sub>2</sub> which starts at a lower temperature than NO reduction by CO according to eqn. (6) and (7).

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O \tag{6}$$

$$2NO + 5H_2 \rightarrow 2NH_3 + 2H_2O \tag{7}$$

Upon increasing the reaction temperature to 488 K (Fig. 3), bands at 1680 and 1619  $\text{cm}^{-1}$  began to appear while the intensity of the bands at 1646 and 1446 cm<sup>-1</sup> increased. The intensity of the bands at 1680 and 1619 cm<sup>-1</sup> continued to increase up to 508 K (Fig. 3d), and then decreased and eventually disappeared at higher temperatures, e.g. 573 K (Fig. 3i). In this temperature region the hydrogen plays a mechanistic role in the NO dissociation in the NO-CO-H<sub>2</sub> reaction over gold catalysts. We emphasize that the 1446  $cm^{-1}$  band is not only contributing a vibration mode to NH<sub>4</sub><sup>+</sup> species, but also to  $CO_3^{2-}$  species, since the incorporation of CO gas produces the latter species at temperatures above 423 K (Fig. 3b-f). However, the vibrations of both species were reported to be located in this wavenumber range.<sup>16</sup> The simultaneous development of O(C=O) species at 1680 cm<sup>-1</sup> from the NO-CO-H<sub>2</sub> reaction over Au/NaY with increasing temperature from 423 to 508 K, parallel to the increase of the 1446 cm<sup>-1</sup> band intensities, must confirm our conclusion. Further consideration of the nature and assignment of these species in the NO-H<sub>2</sub> and NO-CO-H<sub>2</sub> reactions is given below. Evidently, the fundamental band of gaseous NO at 1876 cm<sup>-1</sup> and the NCO bands at 2280-2240 cm<sup>-1</sup> were simultaneously diminished upon raising the catalyst temperature, giving rise to bands of product species. This indicates that a reaction between NCO and NO had occurred. At 573 K, bands of gas-phase CO<sub>2</sub> were produced while the band at 1740 cm<sup>-1</sup> may be assigned to an unstable carboxylato [C=O(OH)] species.<sup>17</sup> In somewhat simplistic terms, this reaction can be summarized by eqn. (8)

$$NCO + NO \rightarrow N_2 + CO_2 \tag{8}$$

The band of NCO species at  $2280 \text{ cm}^{-1}$  completely vanished at 573 K, leaving a small band due to NCO<sup>-</sup> species at  $2240 \text{ cm}^{-1}$  (Fig. 3i). Thus, NO interacts faster with adsorbed NCO species than with the corresponding NCO<sup>-</sup> species (Fig. 3), suggesting the presence of partially oxidized Au<sup>1</sup> sites in the gold catalyst at this temperature. It is a general observation for all metals that NCO concentration is at a maximum when NO is present in the reacting gases. The assumption seems reasonable since as long as NO is present in the gas phase, the metal surface is partially oxidized. Our data in Fig. 3 show that the remaining Au<sup>1</sup> sites in Au/NaY are stable even in the absence of NO in the gas phase.

Detailed measurements were carried out using <sup>13</sup>CO to derive information concerning the assignment of the various IR bands of product species (Fig. 4), under the experimental conditions as for the spectra measured in Fig. 1. The bands of species absorbing at 1680 and 1446 cm<sup>-1</sup> (Fig. 1) were shifted to 1657 and 1411 cm<sup>-1</sup> (Fig. 4), respectively, owing to the <sup>13</sup>CO isotope effect. Thus these species appear to contain carbon atoms but not nitrogen atoms and can be assigned to monodentate formate species, O(C=O), similar to those in  $Cd(HCO_2)_2$  ( $v_{C=O}$  1677–1700 cm<sup>-1</sup>)<sup>18,19</sup> and monodentate  $CO_3^{2-}$ , respectively.<sup>15</sup> Therefore, we confidently propose that in a consecutive NO-CO-H<sub>2</sub> reaction over Au/NaY, CO<sub>2</sub>  $(CO_3^{2-})$  and N<sub>2</sub> are produced. However, the NO + H<sub>2</sub> reaction over the same catalyst and under similar conditions produced N<sub>2</sub>, N<sub>2</sub>O and adsorbed NH<sub>4</sub><sup>+</sup> species.<sup>6</sup> The partial



Fig. 4 In situ FTIR spectra obtained from the reaction of NO:  $^{13}$ CO: H<sub>2</sub> (0.5:1:1) over Au/NaY at 473 K as a function of reaction time from 3 min to 2.25 h

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isotope shift of the band at 1619 cm<sup>-1</sup> to 1596 cm<sup>-1</sup> led to the assignment of this band as due not to a purely carboncontaining species but rather surface combination of carbon and nitrogen atoms. Imine, NH, or amine, NH<sub>2</sub>, are known to have wavenumber bands at *ca*. 1619 cm<sup>-1</sup>. However, the most probable assignment of this band is to species such as a substituted imine containing a carbon-nitrogen double bond; such structures are known to absorb in this wavenumber range.<sup>20</sup>

## Activity evaluation

Because hydrogen is essential for NO reduction by CO at temperatures < 623 K, the stoichiometry of this reaction can be effectively expressed by eqn. (9).

$$2NO + CO + H_2 \rightarrow N_2 + CO_2 + H_2O \tag{9}$$

The reaction of NO-CO-H<sub>2</sub> was carried out at 673 K on a freshly reduced Au/NaY catalyst to test the short-term stability of the catalyst (Fig. 5). The NO, CO and H<sub>2</sub> compositions in the feed were maintained at constant levels for all runs, i.e. 0.5, 1 and 1%, respectively. Therefore, the amounts of CO and H<sub>2</sub> in the feed were four times higher the stoichiometric amounts necessary for eqn. (9). During these series of experiments, the activity of the catalysts were reproducible and indeed slight increases were found to occur after prolonged exposure to the reacting gases. As shown in Fig. 5, a monotonic increase of conversion for both NO and CO to  $N_2$  and CO<sub>2</sub>, respectively, was obtained over 20 h of continuous reaction. Based on mass-balance calculations, CO conversion to  $CO_2$  was less than the expected value (0.5) relative to NO conversion to  $N_2$ . This may be due to accumulation of some  $CO_2$  as adsorbed  $CO_3^{2-}$  and O(C=O) species in the gold catalyst (Fig. 1). Since the water-gas shift reaction produces  $CO_2$  from  $H_2O$  and CO, this might also present difficulties in distinguishing between different sources of CO2. However, an in situ FTIR control experiment of the  $CO + H_2O$  reaction on Au/NaY showed that this reaction is unimportant in the temperature ranges employed, in agreement with expectation.<sup>3</sup> It is evident that N<sub>2</sub> and CO<sub>2</sub> are the only products over Au/NaY, in agreement with the foregoing in situ IR data; formation of N<sub>2</sub>O was not apparent. On the other hand, under similar experimental conditions for the same reaction over  $Pt/Al_2O_3$ , the major products were  $CO_2$  and (undesirable) NH<sub>3</sub>.

The slow increase in the NO and CO conversions over extended reaction times may arise from changes in the relative



Fig. 5 Conversions of NO and CO to N<sub>2</sub> and CO<sub>2</sub>, respectively, as a function of time-on-stream in the NO-CO-H<sub>2</sub> reaction over Au/NaY at 673 K. The inlet composition was [NO] = 4810 ppm, [CO] = [H<sub>2</sub>] = 1%.

electronic states in favour of partially charged Au species. It has been demonstrated in an earlier study that a dual  $Au^{I}-Au^{0}$  site is active for the NO + H<sub>2</sub> reaction,<sup>6</sup> and in particular Au<sup>I</sup> enhanced greatly the catalyst ability for CO chemisorption.9 Whether Au<sup>1</sup> sites are generated during the NO-CO- $H_2$  reaction on the gold catalyst with the presence of NO in the feed stream, or initially formed and stabilized by the framework of zeolite during the catalyst preparation, is an open question. EXAFS data for Au/MgO catalysts indicated the presence of highly dispersed gold carrying a formal charge of +1 in addition to metallic gold, which led to the activity of this catalyst for the NO +  $H_2$  reaction.<sup>21-23</sup> In addition, the stability of Au<sup>I</sup> is noted from the results of NO decomposition on an Au<sup>I</sup>/NaY catalyst where the liberation of  $N_2$  and  $N_2O$ was observed at high temperatures (ca. 600-700 K).<sup>7</sup> Regardless of this, we are still inclined to consider that Au<sup>I</sup> sites could also be formed under the net redox atmosphere used in the NO-CO-H<sub>2</sub> reaction and ESCA results illustrate the ability of surface Au atoms to change their oxidation state readily.<sup>9</sup> It should also be mentioned that NO conversion in the presence of by-product H<sub>2</sub>O is maintained overnight at the reaction temperature employed, i.e. 473-700 K. Therefore, water does not poison NO reduction on the gold catalyst.

Fig. 6 shows NO and CO conversions to  $N_2$  and  $CO_2$ , respectively, as a function of reaction temperature. The conversions systematically increase with temperature up to 673 K, followed by a sudden increase to ca. 78%  $N_2$  and 23%  $CO_2$ when the catalyst temperature increases to 723 K. Thus, no diminution of conversion was served, suggesting that no structural damage of the catalyst occurs even at this high temperature. Au has a low sublimation energy, and under conditions of thermal equilibrium it is expected that Au will be present on the surface as large metal particles. From the foregoing explanation and based on the combination of previous and current in situ FTIR and EXAFS experimental data,<sup>6</sup> the overall proposed structure is that of large gold particles with a large fraction of partially charged Au<sup>I</sup> sites. This may explain the unusually high activity of Au/NaY catalysts for this reaction.

A series of experiments were performed at 573, 623 and 723 K to study the effect of  $H_2$  added to the feed stream in the NO-CO- $H_2$  reaction on Au/NaY (Fig. 7-9). Fig. 7 shows the effect of adding  $H_2$  to an NO-CO gas mixture at 573 K. After steady-state activity was almost obtained after a reaction time of 4 h,  $H_2$  in the feed was turned off. This led to a substantial drop in conversions of both NO to  $N_2$  and of CO to CO<sub>2</sub>. The conversion fall off is a consequence of the significant contribution of  $H_2$  in this reaction at this temperature. When  $H_2$ 



Fig. 6 Conversions of NO to  $N_2$  (solid line) and CO to CO<sub>2</sub> (dotted line) as a function of reaction temperature in the NO-H<sub>2</sub>-CO reaction over Au/NaY



Fig. 7 Effect of  $H_2$  in the feed-stream on the conversions of NO and CO to  $N_2$  and CO<sub>2</sub>, respectively, at 573 K in the NO-CO-H<sub>2</sub> reaction over Au/NaY

was reintroduced, yields of  $N_2$  and  $CO_2$  were recovered. Switch off of the  $H_2$  feed led to a similar decline in conversions of both NO and CO but to a lesser extent when the catalyst temperature was increased to 623 K (Fig. 8). Thus, the



Fig. 8 Effect of  $H_2$  in the feed-stream on the conversions of NO and CO to  $N_2$  and CO<sub>2</sub>, respectively, at 623 K in the NO-CO-H<sub>2</sub> reaction over Au/NaY



Fig. 9 Effect of  $H_2$  in the feed-stream on the conversions of NO and CO to  $N_2$  and CO<sub>2</sub>, respectively, at 723 K in the NO-CO-H<sub>2</sub> reaction over Au/NaY

addition of hydrogen to the feed stream enhances the conversions of NO and CO only over a relatively low range of temperatures (573 K or below) with the role of  $H_2$  becoming less important at higher temperature (623 K). Further increase in the catalyst temperature to 723 K resulted in an entirely reversed behaviour where deleterious effects of  $H_2$  on the yields of CO<sub>2</sub> and N<sub>2</sub> are noted (Fig. 9). From the material balance at, or above, this temperature, the main competing reaction is expected to be that of eqn. (10).

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \tag{10}$$

The N—O bond cleavage is promoted on an Au/NaY catalyst at high temperatures (*ca.* 650–700 K) despite the assistant role of hydrogen as demonstrated by TPD results.<sup>6</sup> The parallel suppression in NO and CO conversions at 723 K should primarily involve the non-dissociative adsorption of NO caused by introduction of hydrogen. Thus, the decline of the catalyst activity at 723 K is plausibly caused by increased concentration of H-saturated catalyst atoms, thereby causing suppression in the NO dissociation. This is in accord with previous studies of the NO + H<sub>2</sub> reaction on Cu/ZSM-5 where a decrease in the NO conversion to N<sub>2</sub> + N<sub>2</sub>O at 723 K was observed upon increasing the concentration of H<sub>2</sub>.<sup>24</sup>

## Conclusions

(i) In the  $H_2$ -free mixture of NO–CO over Au/NaY, reaction did not proceed over an appreciable range of temperatures (473–623 K).

(*ii*) The NO + CO reaction in the presence of  $H_2$  over Au/NaY was promoted at 473–623 K. The catalyst becomes covered with NCO-adsorbed species which reacts relatively slowly with NO in the gas phase to form  $N_2$  and  $CO_2$ .

(*iii*) The NO interacted faster with covalently bonded NCO species than with anionic NCO<sup>-</sup> species, which are stabilized by Au<sup>1</sup> cations.

(iv) The NO-CO-H<sub>2</sub> reaction leads to the formation of  $N_2$  and CO<sub>2</sub> only independently of temperature.

(v) While  $H_2$  was indeed found to have promotional effects on the conversions of both NO and CO in the NO-CO- $H_2$ reaction on the Au/NaY catalysts over a wide range of temperatures (473-623 K), it has deleterious effects at higher temperatures.

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