Remarkable oxygen promotion of the selective reduction of nitric oxide by hydrogen over Au/NaY and Au/ZSM-5 zeolite catalysts

Tarek M. Salama,† Ryuichiro Ohnishi and Masaru Ichikawa*

Catalysis Research Center, Hokkaido University, Sapporo 060, Japan

A significant enhancement of the selective reduction of nitrogen oxide by H_2 is produced in the presence of oxygen over Au/NaY and Au/ZSM-5 catalysts by forming NO_2 and N_2O_4 intermediates, which are eventually reduced to N_2.

More efficient engine performance would be desirable by using higher air–fuel ratios than those permitted by the 'window' required for conventional three-way catalysts.[1] Thus, there is much interest in the O_2-assisted reduction of nitric oxide by hydrocarbons such as methane and propane on Cu/ZSM-5[2] and Pt, Co, Ni and Fe exchanged ZSM-5;[3] however, synergism effected by added oxygen in NO decomposition and reduction with hydrocarbons has not been observed. Although gold has been recognized to be poorly active as a catalyst, Haruta *et al.*[4] have recently found that highly dispersed Au particles on α-Fe_2O_3 and Co_3O_4 exhibit high activity for CO and H_2 oxidation at low temperatures. Recently, we reported the catalytic reduction of NO by CO[5] and H_2[6] over Au/NaY. Interestingly, the NO + CO reaction did proceed marginally at lower temperatures, *e.g.* 473–623 K, while adding H_2 significantly promoted the reaction on Au/NaY, where it assisted N–O dissociation with the formation of the intermediate NCO (with characteristic IR bands at 2280–2240 cm^{-1}).[5] The intermediate was converted into N_2 and CO_2 by interactions with NO in the gas phase. Here, we describe for the first time the remarkable enhancement of the selective reduction of NO by H_2 in the presence of oxygen over Au/NaY and Au/ZSM-5. The possible mechanism of O_2-assisted NO reduction by H_2 was also studied by means of *in situ* FTIR in order to identify the intermediates formed.

Au/NaY (Si/Al = 5.6; Linde, LZY-52, surface area 900 $m^2\ g^{-1}$) and Au/ZSM-5 (Si/Al = 23.8; Tosoh Co. Ltd, surface area 1000 $m^2\ g^{-1}$) samples were prepared by vaporization of $AuCl_3$ (Strem Chemical, 99% purity) into each zeolite, according to the monolayer dispersion technique.[7] The resulting $AuCl_3$ encapsulated in NaY or ZSM-5 was evidently reduced to AuCl by the extraframework hydroxy groups in the zeolites upon thermal treatment in vacuum at 338 K for 24 h. The catalysts contained 5% *m*/*m* Au, according to ICP analysis, and were characterized by EXAFS, XPS and XRD techniques.[7,8]

The catalytic performances in the reduction of nitric oxide by hydrogen in the presence and absence of oxygen were studied at atmospheric pressure in the steady-state flow mode. Four streams of NO–He, H_2, O_2 and He were supplied by mixing in a chamber using mass flow controller units to obtain a feed-gas mixture of 1375 ppm NO, 1.5% H_2 and 0.09–0.7% O_2 balanced with He at a total flow rate of 28 ml min^{-1}. Each catalyst (100 mg) was charged in a Pyrex glass tubular reactor. The stoichiometry of the feed stream was defined by $S = ([NO] + 2[O_2])/[H_2]$ at zero time. The reactor effluent gas was sampled and analysed by on-line gas chromatography equipped with a thermal conductivity detector, using molecular sieve 5A and porapak-Q columns. Prior to the NO– H_2–O_2 reaction, the catalyst was reduced in a flowing gas mixture of 10% H_2 in He at 623 K. The catalytic activity was expressed in terms of percentage conversion of NO to N_2 as a function of the reaction time and *S*.

The selective reduction of NO by H_2 into N_2 proceeded in the temperature range 373–673 K over Au/NaY and Au/ZSM- 5. As shown in Fig. 1, the NO conversion to N_2 was markedly enhanced by 5–10 times by the addition of oxygen (0.2 % *v*/*v*) in the feed stream. Therefore, oxygen in the reaction gas stream plays a synergetic role in the NO–H_2 reaction. All the runs showed almost analogous trends of promotion by adding oxygen. The effect is greater on Au/NaY (*a*) than for Au/ZSM-5 (*b*) at the same oxygen level. The data militate against the claim that Cu/ZSM-5 is better than Cu/NaY for the oxygen promotion in NO reduction by hydrocarbons.[9] Control transient response experiments with pulse addition of O_2 into an NO–H_2 stream revealed that the differences in NO conversions obtained are related to competing reactions of NO and H_2 with O_2 over the gold catalysts. The oxygen promotion was linearly proportional to the oxygen concentration (0.09–0.21 %). After 2 h reaction time, the oxygen supply was turned off which resulted in a dramatic loss of the NO conversion (Fig. 1).

In the presence of O_2, NO reduction by hydrogen selectively goes to N_2 formation and neither NH_3 nor N_2O were detected over Au/NaY and Au/ZSM-5 catalysts in the effluent stream at the outlet. By contrast, Hastvan *et al.*,[10] have reported for the same reaction over Pd-MoO_3/γ-Al_2O_3 catalysts that NH_3 and N_2O are the major products. It has also been observed[11] that a better N_2 selectivity in the NO reduction by hydrogen is achieved by combining precious metals (Pt, Pd and Rh) and transition-metal oxides on Al_2O_3.

To gain insight into the mechanism of oxygen promotion in the selective NO redution by hydrogen, *in situ* FTIR studies were performed over Au/NaY and Au/ZSM-5 samples. *In situ* IR absorption spectra were recorded over the temperature range 474–573 K. A self-supporting wafer was placed in an IR cell

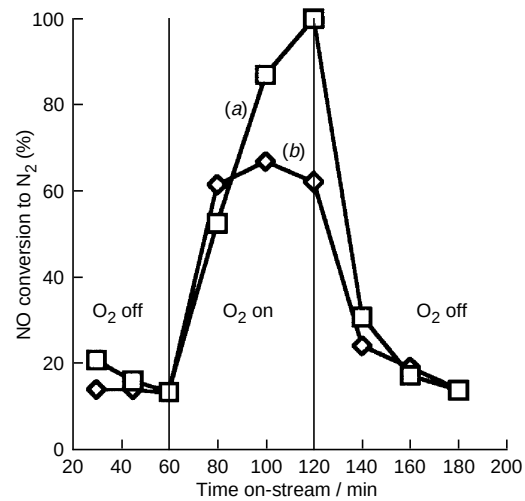

Fig. 1 NO conversion (mol%) to N_2 as a function of time and O_2 (0.2% *v*/*v*) switch on–off in the NO (0.14% *v*/*v*)–H_2(1.5% *v*/*v*) flow mode reaction (flow rate = 28 ml min^{-1}) over Au/NaY (5% mass Au loading) (*a*) and Au/ZSM-5 (5% mass Au loading) (*b*) at 523 K, respectively

equipped with NaCl windows. The sample was reduced in circulating hydrogen (50 Torr) at 473 K before conducting the $NO–H_2–O_2$ reaction at the desired temperature. IR spectra were recorded with a Shimadzu 4100 FT IR double- beam spectrometer with a resolution of 2 cm^{-1}.

$^{15}NO_2$ and $^{15}N_2O_4$ were produced by the addition of O_2 to ^{15}NO (1 : 1 *v*/*v*) at 474 K on Au/ZSM-5. As shown in Fig. 2, after the $NO–O_2$ system reached a steady state [Fig. 2(*a*)], a pair of bands with an intensity ratio of *ca.* 1 : 1 developed at 1780 and 1760 cm^{-1} arising from the stretching mode of monomeric $^{15}N–O$ on Au^I and Au^IO, respectively. These bands were similarly assigned by Valyon and Hall[9] in NO chemisorption on Cu/ZSM-5. We did not observe such terminal NO species in the absence of oxygen on the Au/NaY and Au/ZSM-5 samples at identical NO chemisorption conditions. This implies that oxygen acts as a promoter for NO chemisorption on Au. The respective shift to lower wavenumbers (*ca.* 30 cm^{-1}) compared to those for ^{14}NO at 1811 and 1792 cm^{-1} indicates that they are mononitrosyl species.

After heating the samples to 573 K, the ill resolved doublet bonds assigned to $^{15}N_2O_4$ completely vanished and were replaced by species at 1780 and 1760 cm^{-1} [Fig. 2(*b*)]. The $^{15}NO_2$ bands were also decreased in intensity but to a lesser extent. This leads us to conclude that $^{15}N_2O_4$ together with $^{15}NO_2$ species dissociated back to monomeric NO and NO(O) at higher temperatures. It was previously reported that NO_2 dissociates on Au to form coadsorbed $NO_{(a)}$ and $O_{(a)}$ with a kinetic-energy barrier of $E_d \geqslant 17$ kcal mol[12] (1 cal = 4.184 J). The assignments of the observed IR bands associated with nitrogen oxides are summarized in Table 1.

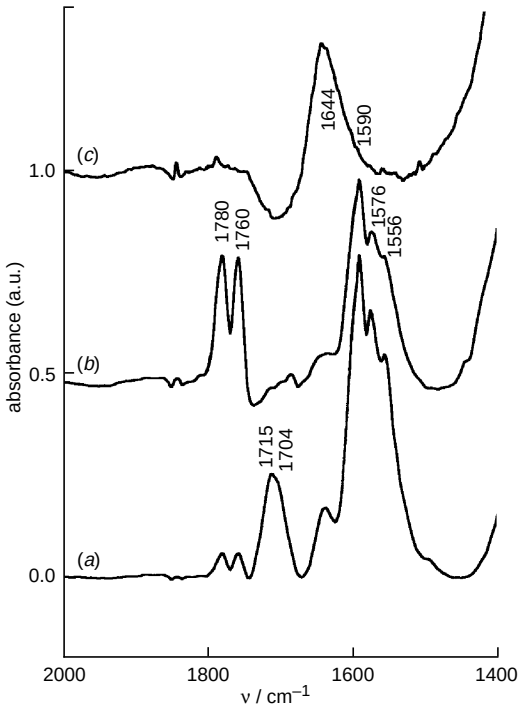

Fig. 2 *In situ* IR spectra obtained on Au/ZSM-5 (5% Au loading) from (*a*) ^{15}NO (40 Torr)–O_2 (40 Torr) reaction at 474 K, (*b*) obtained upon increasing the reaction temperature to 573 K for 10 min, and (*c*) after admission of H_2 (100 Torr) at 573 K for 20 min

Table 1 IR bands from the $NO–H_2–O_2$ reaction on Au/ZSM-5 and their assignment

ν/cm^{-1}				
$^{14}NO^a$	$^{15}NO^a$	Calc.^{b}	Assignment	Ref.
1811	1780	1781	NO accessible to Au^I	This work
1792	1760	1762	NO on Au^I carrying extralattice oxygen	This work
1755	1715	1714	Solid-state N_2O_4	13
1744	1704	1702	Gas-phase N_2O_4	13
1630	1590	1591	NO_2 and NO_2^-	14
1612	1576	1574		14
1597	1556	1557		14

^{a} NO stretching vibration. ^{b} Calculated using $\nu_{15} = \nu_{14}(\mu_{14}/\mu_{15})$ where μ_{14} is the reduced mass for ^{14}NO and ^{16}O and μ_{15} the reduced mass for ^{15}NO and ^{16}O.

Subsequently, H_2 (100 Torr) was admitted to the reacting system [Fig. 2(*c*)], resulting in the complete disappearance of NO_2 and N_2O_4 species on Au/ZSM-5 with substantial formation of N_2 (*m*/*z* 28) and H_2O (band at 1644 cm^{-1}). Oxygen promotion in the selective reduction of NO by H_2 on Au/NaY and Au/ZSM-5 is proposed to proceed as follows:

$$2NO + 2O_{ads} \xrightarrow[O_2]{\text{very fast}} [2NO_2 \rightleftharpoons N_2O_4]_{ads}$$

$$N_2O_4(NO_2) + 2H_2 \rightarrow N_2 + 2H_2O$$

$$2NO + 2H_2 \rightarrow N_2 + 2H_2O$$

Bands assignable to N_2O and NH_3 were not detected by an *in situ* IR experiment in the presence of oxygen even when the reaction took place over a wide range of temperature. Nevertheless, we have previously reported that N_2O and adsorbed NH_4^+ were partially detected as by-products due to NO dissociation in the $NO–H_2$ reaction over Au/NaY.[5] Accordingly, the results suggest that oxygen surpresses the dissociation of NO on Au/NaY, while promoting the formation of oxygenated intermediates such as NO_2 and N_2O_4, which are readily reduced by hydrogen selectively to N_2. Moreover, it is noteworthy that the synergism effected in the presence of excess oxygen is produced by inhibiting the sintering of Au due to a facile redox process between Au^I and Au^0 in NaY and ZSM-5 even under the reductive $NO–H_2$ atmosphere.

Footnote

† On leave from the Chemistry Department, Faculty of Science, Al-Azhar University, Cairo, Egypt.

References

1 T. J. Truex, R. A. Searle and D. C. Sun, *Platinum Met. Rev.*, 1992, **36**, 1.
2 J. O. Petunchi, G. Still and H. K. Hall, *Appl. Catal. B: Environ.*, 1993, **2**, 303.
3 T. Li and J. N. Armer, *US Pat.* 5 149 512,1992, to Air Products and Chemicals, Inc.
4 M. Haruta, N. Yamada, T. Kobayashi and S. Iijima, *J. Catal.*, 1989, **115**, 301.
5 T. M. Salama, Y. Ohnishi and M. Ichikawa, *J. Chem. Soc., Faraday Trans,*. 1996, **92**, 301.
6 T. M. Salama, Y. Ohnishi, T. Shido and M. Ichikawa, *J. Catal.*, 1996, **162**, 169.
7 T. M. Salama, T. Shido, H. Minagawa and M. Ichikawa, *J. Catal.*, 1995, **152**, 322; S. L. Qiu, R. Ohnishi and M. Ichikawa, *J. Chem. Soc., Chem. Commun.*, 1992, 1425.
8 T. M. Salama, T. Shido, Y. Ohnishi and M. Ichikawa, *J. Phys. Chem.*, 1996, **100**, 3688.
9 J. Valyon and W. K. Hall, *J. Phys. Chem.*, 1993, **97**, 1204.
10 I. Halasz, A. Brenner and M. Shelef, *Catal. Lett.*, 1993, **18**, 289.
11 Y. J. Mergler, A. van Aals and B. E. Nieuwenhuys, *207th National Meeting*, American Chemical Society, 1994, vol. 39, p. 161.
12 D. T. Wickham, B. A. Banse and B. E. Koel, *Catal. Lett.*, 1996, **6**, 163.
13 U. Schwalke, J. E. Parmeter and W. H. Weinberg, *J. Chem. Phys.*, 1986, **84**, 4036.
14 J. W. London and A. T. Bell, *J. Catal.*,1973, **31**, 32.
15 K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds*, Wiley, New York, 1978, 3rd edn., p 9.

Received, 2nd October 1996; Com. 6/06761A