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Low-temperature Catalytic Decomposition of NO over Excess-loading Gold(I) in NaY Zeolite

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The intrazeolite Au^I in NaY zeolite exhibits remarkable catalytic activities in the decomposition of NO to N_2 (N_2O) and O_2 at low temperatures; the NO decomposition reaction proceeds through the sequential formation of N_2O_3 and N_2O intermediates on Au^I/NaY at 300–673 K.

Catalysis can provide effective solutions for the control of the pollution of our environment by NO_x and CO. Since the initial review on the use of excess copper-containing catalysts, *e.g.* Cu^I/ZSM-5 for the decomposition of NO to N_2 and O_2 at high temperatures (623–873 K),[1–3] there has been considerable interest in this process. During NO decomposition on Cu/ZSM-5, the evolved oxygen remains on the surface and the catalyst loses its activity at lower temperatures. Despite the potential of copper as an active component in heterogeneous catalysis for NO reduction, few studies have been devoted to NO decomposition on other Group 1B elements, *i.e.* Ag and Au.[4] It has been reported that intrazeolite gold(I) was formed by the reductive carbonylation of monolayer-dispersed $AuCl_3$ in NaY and ZSM-5 zeolites.[5,6] The characterization of such catalysts by XPS, TPD (temperature programmed desorption), IR of CO chemisorption, and EXAFS has been reported.[7,8] Here, we report that Au^I/NaY exhibits remarkable catalytic activities in the decomposition of NO to N_2(N_2O) and O_2 at low temperatures, *e.g.* 300–673 K.

Excess-loaded Au^I/NaY (Au 13% *m*/*m*) was prepared at room temperature by the mechanical mixing of $AuCl_3$ (Strem Chemica, 99% purity) with partially dehydrated NaY zeolite (Si : Al = 5.6, surface area = 910 $m^2\ g^{-1}$) at 523 K, under a nitrogen atmosphere. The $AuCl_3$/NaY sample was brought under vacuum while the temperature was increased slowly (0.2 K min^{-1}) up to 338 K. The temperature was held constant for at least 72 h, by which time the $AuCl_3$ vapour had migrated to be hydrolysed by trace H_2O in the zeolite. As a consequence, HCl and newly developed OH groups were detected by TPD and IR, respectively.[8] The XPS and EXAFS studies had indicated that Au^{III} was partially reduced and Au^I was indeed the dominant oxidation state of gold.[7,8] The $AuCl_3$/H_2O–NaY reaction follows the equation:

$$AuCl_3 + 2\ H_2O\text{–}NaY \rightarrow AuCl/NaY + 2\ HCl + 2\ OH$$

In situ IR absorption spectra were recorded at room temperature. The sample was evacuated at 373 K prior to the introduction of NO (130 Torr) at 300 K. TPD experiments were conducted in a fixed-bed reactor using 50 mg of the sample. The 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 maintained. TPD started by increasing the temperature linearly with the rate of 5 K min^{-1} and scan time 10 s. The desorbed gases were analysed and gave the following elution traces: NO (M_r 30); N_2O (44); N_2 (28); and O_2 (32). The steady-state activity measurements were carried out in a flow mode. The reactant gas was a mixture of 4810 ppm NO in He. Product analysis was obtained using on-line gas chromatography with a thermal conductivity detector. Two separation columns were used. The first column was packed with porapak-N for NO and N_2O separation, while the other was packed with 5A molecular sieve for O_2 and N_2 separation.

The *in situ* IR spectra of NO chemisorption on Au^I/NaY at 300 K are shown in Fig. 1. Upon NO admittance, N_2O chemisorbtion onto Au^I began as evidenced by bands at 2400, 2000 and 1272 cm^{-1},[9] and remained unchanged by time. This result suggests that N_2O is not an intermediate product in NO decomposition on Au^I/NaY catalysts at 300 K. In contrast, the N_2O decayed with time on Au^0/SiO_2 and Au^0/MgO in the NO reduction with H_2.[10] The formation of N_2O was reported to be correlated to the existence of Cu^I on Cu/Al spinel catalyst.[11] The band at 1305 cm^{-1} grew very intense and appears to parallel with the bands at 1904 and 1571 cm^{-1}. This set of bands is attributed to adsorbed N_2O_3 species on Au^I/NaY (which is stable only at temperatures below 170 K), on NaY and Cu^I/NaY.[9] The doublet appearing at about 1400 cm^{-1} is shown growing in with the N_2O and N_2O_3 bands and was assigned to adsorbed NO_3 on Cu^I/NaY.[9] The formation of N_2O and NO_3 on Au^I/NaY may be depicted as follows:

$$Au^+(N_2O_3) + NO \rightleftarrows Au^+\ (NO_3) + N_2O$$

A TPD control experiment on NaY zeolite revealed that the zeolite does take up NO at 373 K, so any other NO desorption peaks must be associated with Au^I sites. NO desorbed from NaY zeolite almost without dissociation. From this, it is possible to conclude that the N–O bond is not significantly perturbed by adsorption and that the NaY–NO bond is weak.

On the other hand, the elution mass spectra after 5 min NO adsorption on Au^{n+}/NaY indicated that an appreciable amount of N_2 was evolved, while the amounts of N_2O and O_2 were detected to a lesser extent. The presence of product species prior to starting the temperature programme shows that the interaction between NO and the Au^I centres is strong

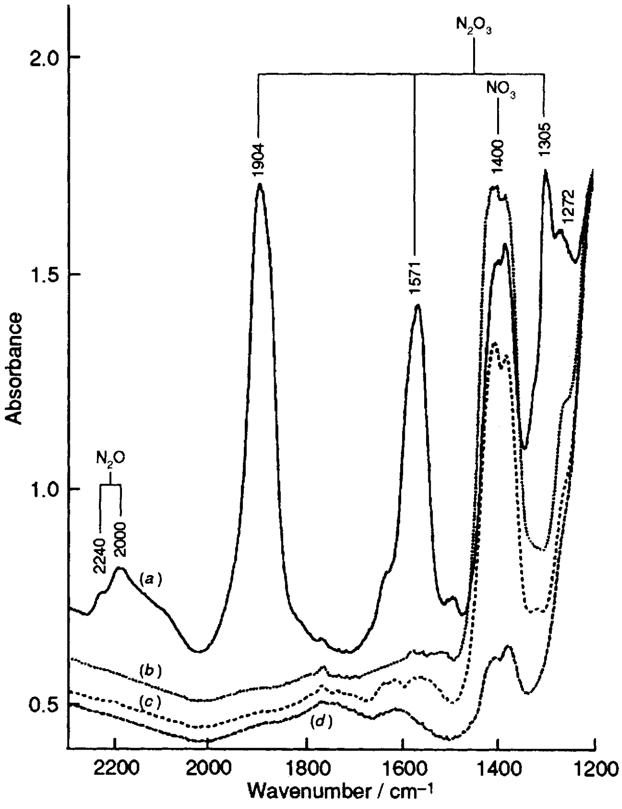

Fig. 1 FT-IR spectra obtained from NO (130 Torr) adsorbed on Au^I/NaY at 300 K. (*a*) NO at 303 K, (*b*) evacuation (EV) at 388 K, (*c*) EV at 483 K, (*d*) EV at 573 K.

and the decomposition of NO was promoted even at room temperature. Fig. 2(*a*) illustrates the NO–TPD spectra of the relevant species obtained on $AuCl_3$/NaY. Two NO desorption maxima were observed at 372 and 452 K, and the peak intensity decreased with increasing temperature. The former maximum is that of NO desorbed from bare zeolite. The latter peak coincided with the desorption peaks of N_2O and N_2. O_2 was evolved at a temperature lower than the liberation temperature of NO, N_2O and N_2 by 20 K, *i.e.* 432 K. It is quite likely that gold oxide was formed during NO adsorption at room temperature which has low thermal stability and decomposes at 423 K.[12] Once O_2 was released, N_2 and N_2O started to form. No evidence of NO_2 was apparent (M_r 46). The desorption capacities of N_2O and N_2 were almost the same at 573 K, while the desorption of O_2 ceased. This suggests a fast $N_2O \rightleftarrows N_2 + O$ equilibrium on the Au^I/NaY surface in this temperature region. On the higher temperature side, *ca.* 737 K, the N_2O evolution decayed with the simultaneous release of N_2 and O_2. This result implies that N_2O was dissociated according to the following equations:

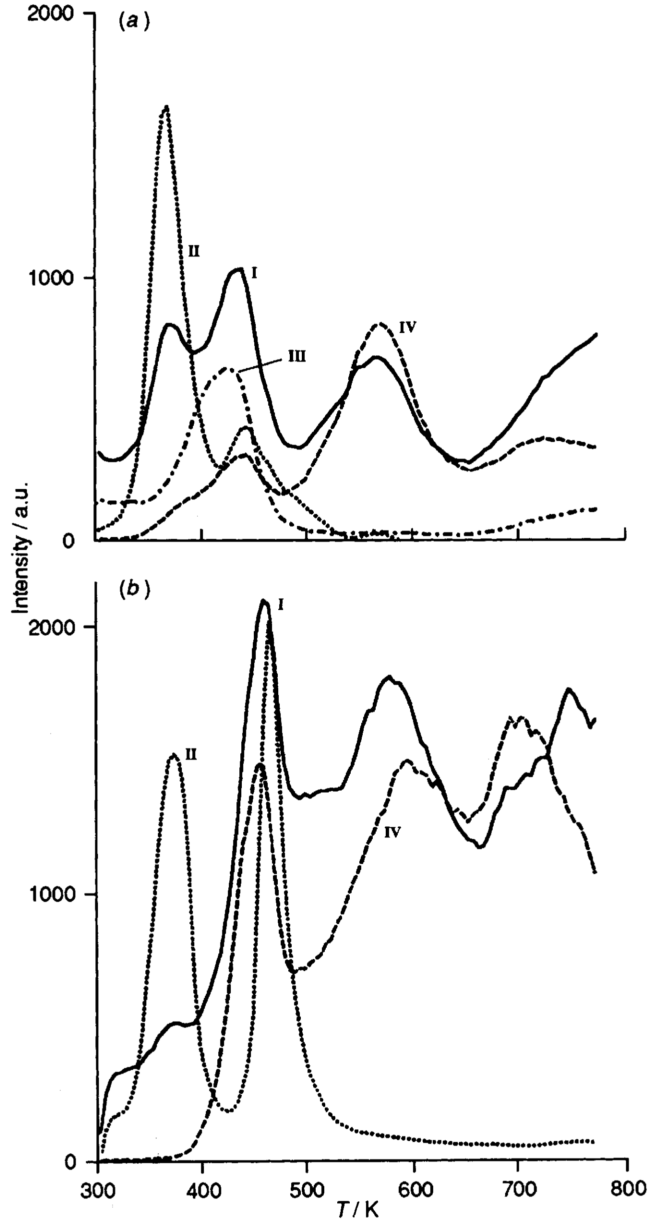

Fig. 2 TPD profiles of NO decomposition on (*a*) Au^{III}/NaY and (*b*) Au^I/NaY to form N_2 (**I**, M_r 28), NO (**II**, 30), O_2 (**III**, 32) and N_2O (**IV**, 44)

Table 1 Decomposition of NO over Au^I/NaY[a]

Drying[b] temp./K	Reaction temp./K	O_2/N_2	NO conversion to N_2 (%)[c]	NO conversion to N_2O (%)[c]
423	300	0.18	7.00	0.49
423	373	0.22	15.78	1.17
573	573	0.24	37.20	0.81
673	673	0.24	80.48	0.56
673[d]	673	0.02	4.42	0.64
737	737	0.25	32.19	0.43

[a] NO, 4810 ppm in He; contact time (*W*/*F*) = 0.48 g s cm^{-3}. [b] By He flushing with flow rate 30 cm^3 min^{-1}. [c] NO in the feed converted to N_2 or N_2O after 5 min. [d] Reduced in flowing H_2 at 473 K.

$$N_2O_{ads} \rightarrow N_{2,g} + O_{ads}$$

$$2\ O_{ads} \rightarrow O_{2,g}$$

The NO, N_2 and N_2O peaks at 455 K from Au^I/NaY [Fig. 2(*b*)] are substantially larger than the corresponding ones from Au^{III}/NaY. The N_2 and N_2O release did not cease when NO desorption was complete, since an additional two peaks at 594 and 704 K were observed. The high temperature liberation of N_2 and N_2O may be associated with the stability of Au^I in the pores of NaY zeolite. This suggests that these species were produced as a result of surface rearrangement involving the stable NO_3 species (Fig. 1). Table 1 shows that Au^I/NaY exhibited high catalytic activities in NO decomposition and the selectivity was directed mainly to N_2 and O_2 (O_2/N_2 = 0.18–0.24) in the temperature range 300–673 K. The initial activity to N_2 reached a maximum, *i.e.* 80% conversion at 673 K which relatively decreased above 673 K, probably due to sintering of gold metal exposed to external zeolite. It is of interest that O_2 was observed even at room temperature. Li and Armor[13] have reported that the onset temperature for steady NO decomposition on Cu/ZSM-5 is around 623 K, at which temperature O_2 begins to desorb from the catalyst. Table 1 also shows that when Au^I in NaY was reduced to Au^0, the activity decreased by 20 times at 673 K reaction temperature relative to that before the reduction. This result unequivocally shows that Au^I/NaY are effective catalysts for NO decomposition.

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