Characterization and catalytic tests of Au/MFI prepared by sublimation of $AuCl_3$ onto HMFI

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Au/MFI was prepared by sublimation of $AuCl_3$ onto HMFI. The oxidation state of the gold in the as-synthesized sample is Au^{3+}. Upon heating in He or O_2, it transforms into gold metal and electron-deficient gold particles which agglomerate to larger Au particles. Reduction of Au^{3+} with CO to Au^+ is accompanied by formation of an $Au^+(CO)$ complex. The carbonyl ligand has a remarkable stabilization effect on Au^+ ions in zeolite cages. Strong IR bands show the CO vibration, and also the strong perturbation of the T–O–T vibrations of the zeolite lattice. $[Au^+(CO)]$/MFI has a characteristic XRD pattern and is stable up to 200 °C. Au/MFI catalyzes the decomposition of N_2O to N_2 even in the presence of 3% O_2. With hydrocarbons or NH_3 as the reductant, it has some NO_x reduction activity, but these catalysts deactivate at higher temperature even in inert gas atmosphere.

KEY WORDS: Au/MFI; sublimation method; gold carbonyl; NO reduction; N_2O and NO decomposition

1. Introduction

Gold has long been regarded as a very poor catalyst, but recent results show that certain forms of supported gold may have potential in heterogeneous catalysis. Haruta [1] and Bond and Thompson [2] have shown that highly dispersed gold catalyzes reactions such as CO oxidation and NO reduction. As a consequence of the low melting point and high surface mobility of gold, interest focuses on preparation methods which minimize gold agglomeration [3]. To prepare gold of high dispersion, Guillemot et al., Kang et al. and Ichikawa et al. have used zeolites Y [4–10] or MFI (ZSM-5) [11,12]. The catalysts were probed for the decomposition and reduction of nitric oxide and the oxidation of carbon monoxide.

In the present work Au/MFI catalysts have been prepared by a sublimation technique that was developed in this laboratory for the preparation of zeolite-supported gallium, palladium, iron and cobalt [13–16]. This technique yields catalysts with a high metal loading while positioning the metal ions in cation exchange sites. Even with multi-valent metal ions a loading of one metal ion per zeolite Al is achieved, as the excess positive charge is compensated by extra-lattice anions. Fe/MFI and Co/MFI catalysts prepared in this way are highly active in reducing NO_x in the presence of a large excess of O_2 and H_2O vapor [17].

The prepared Au/MFI catalyst was characterized and probed for NO_x reduction with ammonia or a hydrocarbon and for the decomposition of NO and N_2O.

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2. Experimental

Au/MFI was prepared by subliming $AuCl_3$ (Aldrich, >99.995%) vapor onto H-MFI. The procedure is similar to that reported for Fe/MFI and Co/MFI [15,16], but for Au/MFI 10% (volume) of Cl_2 gas (99.9%) was added to the flow, in order to minimize the decomposition of $AuCl_3$ vapor. The H-MFI zeolite was prepared by ion exchange of NaMFI, provided by UOP (Si/Al = 19, lot #99499506001), with a dilute ammonium nitrate solution at ambient temperature, followed by calcination at 550 °C. Ion exchange was repeated three times to ensure that all Na^+ ions were replaced by NH_4^+. Only the data leading to a reasonably stable catalyst will be reported here. The Au/Al ratios were calculated from the chemical compositions that were determined by ICP analyses.

FTIR, XRD, HRAEM (high-resolution analytical electron micrscopy), CO-TPR, H_2-TPR and He-TPD were used to characterize the samples. Details of these techniques have been described in previous work of this laboratory [15,16].

The catalysts were probed in a microflow reactor at atmospheric pressure. For the reduction of NO_x with a hydrocarbon or with ammonia, the same procedure was used as described for Fe/MFI and Co/MFI [15,18]. Ammonia was monitored by an ammonia analyzer. The decomposition of NO or N_2O was studied in the same reactor; the gas effluents were analyzed by mass spectrometry.

3. Results

The MFI zeolite described in this work became yellow after sublimation of $AuCl_3$ onto it. The Au/Al ratio was 1.63 after sublimation, but fell to 0.95 after washing with DDI

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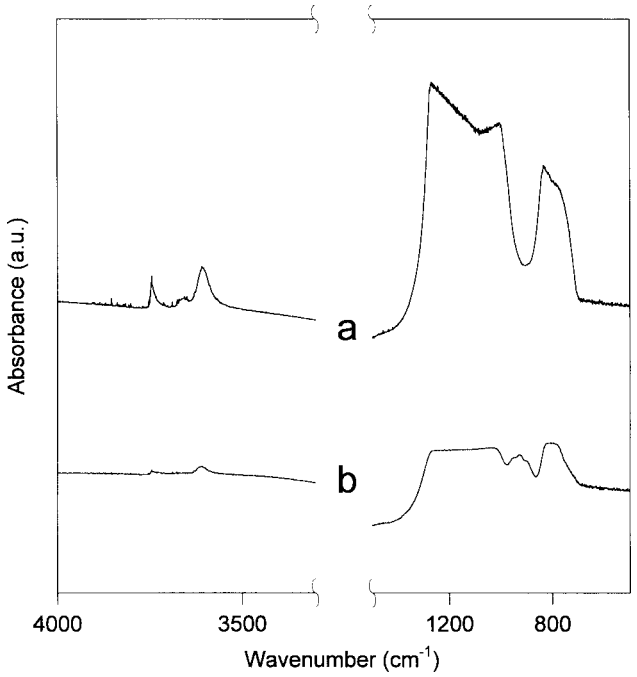

Figure 1. FTIR spectra of MFI before and after sublimation. Spectra were registered at RT after treatment in O_2/He at 400 °C for HMFI (a) or at 240 °C for Au/MFI (b).

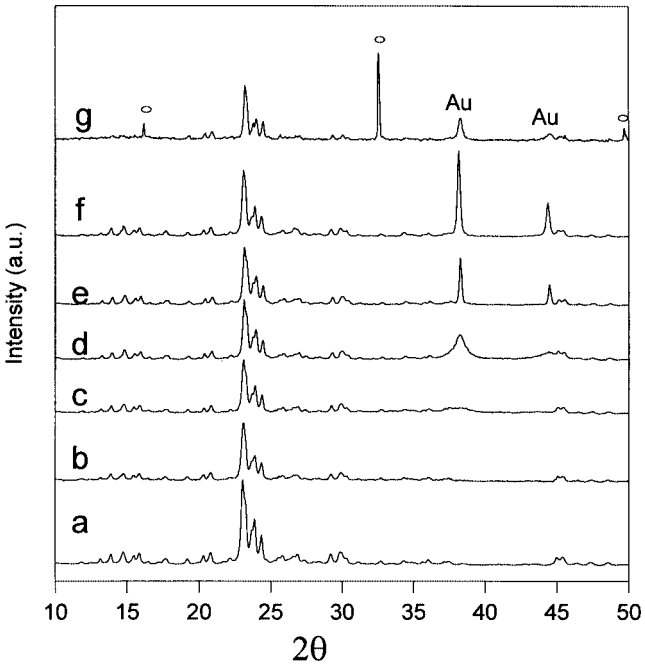

Figure 2. XRD patterns of MFI zeolite based catalysts: (a) HMFI, (b) Au/MFI, (c) Au/MFI treated in O_2 at 180 °C, (d) Au/MFI treated in O_2 at 240 °C, (e) Au/MFI treated in O_2 at 500 °C, (f) Au/MFI after DeNOx reaction and (g) Au(CO)/MFI.

H_2O. The FTIR spectra in the hydroxyl stretching region and perturbation region of the parent MFI before and after sublimation are shown in figure 1. The bands at 3750 and 3610 cm^{-1} have been assigned to silanol groups and acidic bridging hydroxyl groups, respectively [19]. Their intensities are lowered by depositing $AuCl_3$, indicating reaction with acidic protons to form HCl and $[AuCl_2]^+$ ions. A very weak band at 3665 cm^{-1} is assigned to hydroxyl groups attached to extra-framework alumina [20]. These results indicate that gold initially occupies mainly cation exchange sites. Upon treatment at higher temperature, the intensities of the O–H bands increase to the values of the parent HMFI, because the deposited gold complexes and gold agglomerates.

Gold ions in exchange sites induce a local deformation of the T–O–T bonds of the zeolite framework; this produces IR bands centered at about 920 cm^{-1}. Similar bands of perturbed T–O–T vibrations have been reported for Ga [14], Cu [21], Fe [22] and Co [23] cations ligated to zeolite oxygen.

HRAEM results (not shown) display interference fringes of the MFI crystal structure and rather evenly spaced small particles on the surface of the freshly prepared sample. EDX identifies them as Cl-free Au particles. Their size grows from 3–4 nm in the fresh sample to 40–30 nm upon heating in O_2 to 180 °C.

XRD of Au/MFI and HMFI shows that interaction of the zeolite with $AuCl_3$ does not damage its structure or dealuminate it (see figure 2 (a)–(e)). No $AuCl_3$ phase is detected. The average Au particle size; derived from Scherrer's equation, increases with temperature from 10 nm at 240 °C to 34 nm at 500 °C. After use as a catalyst for the reduction of NO (figure 2(f)), the calculated particle size was >40 nm, and the color had changed from yellow to reddish brown.

Programmed heating in a He flow shows an irreversible color change from bright yellow to dark brown. Simultaneous gas analysis by mass spectrometry reveals release of H_2O ($m/e = 18$), Cl_2 ($m/e = 70$) and HCl ($m/e = 36$). The evolution of these gases reaches maxima at 130, 190–200 and 260 °C. After washing with DDI H_2O, the He-TPD profile shows only traces of HCl, indicating overwhelming replacement of Cl by OH groups. In a control experiment with HMFI that had been exposed to Cl_2 for 3 min, the TPD profile shows only H_2O and HCl but no Cl_2.

Some remarkable results were observed when the deposited gold complexes interacted with carbon monoxide. CO-TPR of Au/MFI showed two peaks, a major feature at 90 °C and a very small one at 145 °C. No such peaks were detected with HMFI. The peaks for CO consumption and CO_2 formation occurred at the same temperature. For Au/MFI that had been treated with DDI H_2O, the main peak is located at 140 °C with smaller shoulders at 110 and 240 °C.

The amounts of consumed CO and produced CO_2 are not equal. After calibrating the instrument sensitivity for both gases by means of CO-TPR with CuO, the peak areas were integrated for quantitative evaluation. As shown in figure 3, only 0.83 CO_2 molecules were formed per Au atom, while 1.93 molecules of CO were consumed. It follows that only 50% of the CO was oxidized to CO_2 (by reaction with gold-associated OH groups or oxide groups), the other 50% is retained by the catalyst. After this treatment the color of the sample is white.

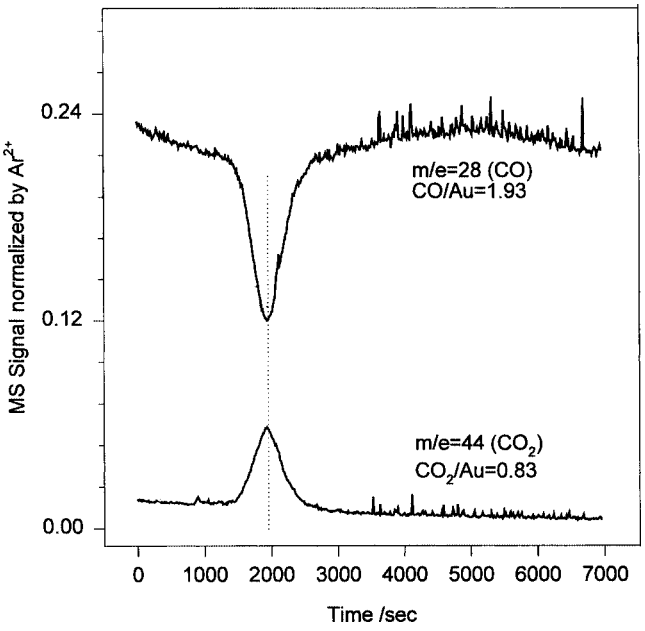

Figure 3. CO-TPR profile of Au/MFI up to 100 °C.

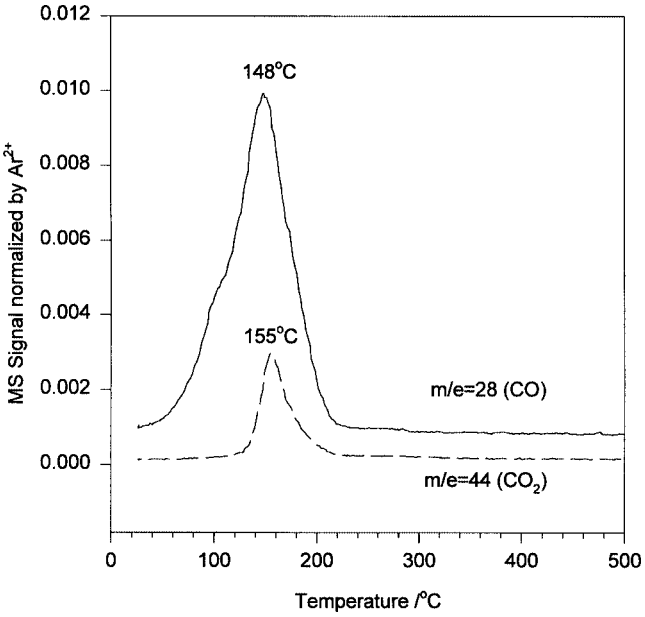

Figure 4. He-TPD profile of Au(CO)/MFI.

Calcination of Au/MFI in oxygen at various temperatures showed that CO_2 formation decreases with increasing calcination temperature. This indicates increasing formation of elementary gold in agreement with the XRD data.

The white sample which was reduced with CO/Ar up to 100 °C and which had retained 1.1 mol of CO per Au was studied after cooling to RT, by He-TPD and XRD. The TPD results in figure 4 show that CO and CO_2 are released in a ratio of $CO/CO_2 = 9$. The white Au(CO)/MFI sample shows characteristic XRD lines; the pattern is different from that of the solid compound Au(CO)Cl ($2\theta = 10.8°$, 28.1° and 32.1°). Diffraction lines between $2\theta = 23°$ and 25° in figure 2(g) are attributed to the MFI lattice, the lines

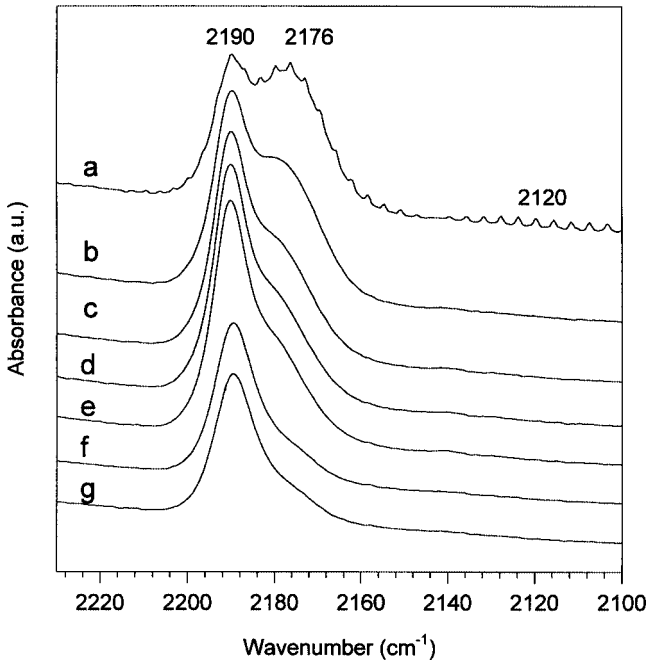

Figure 5. FTIR spectra in the carbonyl stretching region: (a) after exposure of Au/MFI to 0.5% CO/He for 12 min at RT; (b)–(e) same after He purge at RT for 45, 90, 120 and 150 min, respectively; (f) after He purge at 80 °C for 20 min and (g) after 35 min.

at $2\theta = 38.2°$ and 44.4° are assigned to Au^0. The lines at $2\theta = 16.3°$, 32.6° and 49.5° might be due to Au^+ carbonyl ligated to zeolite oxygen. This complex is, however, reduced by the X-rays, as indicated by the color change. It decomposes upon heating, and gold metal is formed.

H_2-TPR of fresh Au/MFI shows a peak at 180 °C. The reduced material cannot be re-oxidized even at 500 °C. The same holds for samples that were reduced with CO up to 500 °C.

The FTIR spectra after exposing Au/MFI to CO are shown in figure 5. At room temperature, exposure to 0.5% CO/He produces two intense FTIR bands at 2190 and 2176 cm^{-1}. On similar catalyst with a Si/Al ratio of 1600, Qiu et al. observed an intense band at 2170 cm^{-1} with a weak shoulder at 2160 cm^{-1}. They assigned the 2170 cm^{-1} band to a monodentate carbonyl bound to Au^+ highly dispersed in the MFI channels, and the 2160 cm^{-1} band to CO bound to Au^+ ions at the external surface of MFI [11]. The higher frequencies in the present work might be due to the smaller Si/Al ratio of 19. A He purge lowers the intensity of the band at 2176 cm^{-1}, while the 2190 cm^{-1} band increases. This band is rather stable at room temperature, but its intensity decreases upon heating to 80 °C. During the release of CO, gold is reduced to the metal. The adsorption of CO on Au^0 is weak, a small IR peak at 2140 cm^{-1} is presumably due to adsorption of CO on electron-deficient gold [5]. Water is weakly adsorbed on Au^+ ions; at room temperature it is slowly displaced by CO. Therefore, CO adsorption is faster on a dry sample that was heated in O_2 at 240 °C (saturation reached in 5 min) than on a wet sample (saturation after 120 min). The band position is the same in both cases

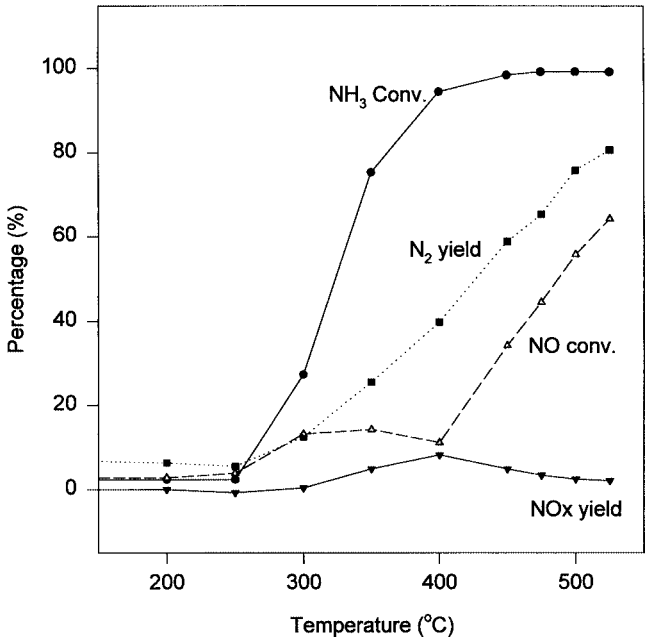

Figure 6. Results of catalytic NO reduction with NH_3 over Au/MFI catalyst. Feed: NO 0.1%, NH_3 0.1%, O_2 3% and He balance, GHSV 90000 h^{-1}.

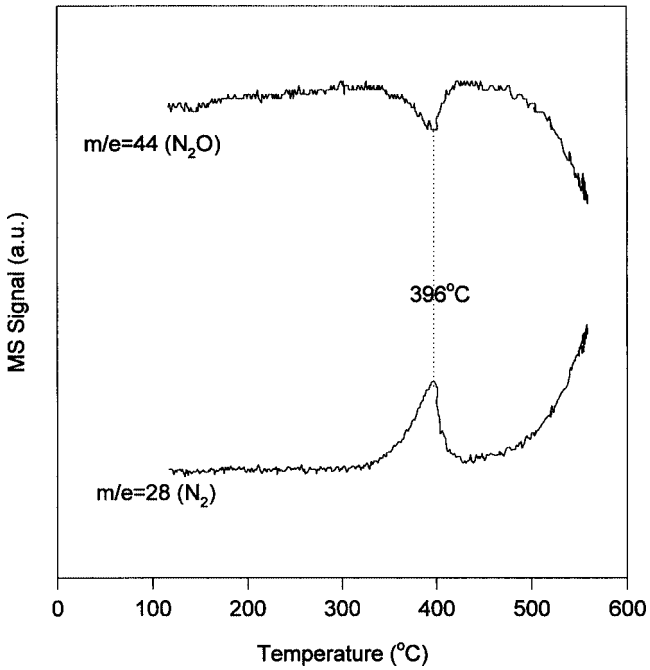

Figure 7. Temperature-programmed decomposition of N_2O over Au/MFI catalyst. Feed N_2O (0.2%) + O_2 (3%) + H_2O (1%) + He, GHSV = 42000 h^{-1}.

and also with Au/MFI washed by DDI H_2O. However, an additional feature at 2140 cm^{-1} indicates that some Au metal was formed during the washing process.

The band at 920 cm^{-1} which is visible in spectrum (b) of figure 1 and ascribed to the effect of Au ions on the T–O–T vibration, becomes even stronger after exposure of Au/MFI to CO at room temperature. This suggests that Au^+ ions which carry a carbonyl group are rather strongly attached to zeolite oxygens.

The results of NO reduction with NH_3 in the presence of excessive O_2 are shown in figure 6. Clearly, this catalyst is able to reduce NO to N_2 at $T \geqslant 250\,^{\circ}C$. Conversion of NH_3 reaches 100% at 425 °C. The effect of H_2O vapor on this catalysis was also studied. Below 350 °C, water vapor has little influence on the catalytic performance, but above 400 °C the conversion of NO is lowered by H_2O vapor, whereas the NH_3 conversion to N_2 remains unchanged.

During reduction of NO with isobutane, Au/MFI deactivates rapidly and irreversibly. At 325 °C, the conversion of NO to N_2 was 26% over Au/MFI. Under identical conditions it is 65–75% over Fe/MFI.

In the absence of a reductant, NO decomposed to N_2 + O_2 at 200 °C over fresh Au/MFI, but the catalyst deactivated in 30 min. Decomposition of N_2O over Au/MFI was investigated, while the temperature was increased from 25 to 550 °C. MS analysis of the exit gas showed that this decomposition of N_2O starts at 300 °C, reaches a maximum at 396 °C, then decreases. Above 450 °C, it increases again (figure 7). It is certain that this N_2O decomposition is catalyzed by the gold; no N_2O decomposition was detectable over a metal-free HMFI below 450 °C. With a feed containing 1% water vapor and 3% O_2, the gold-catalyzed decomposition of N_2O is 30% lower than with a dry feed. After use at high temperature the Au/MFI loses its activity for N_2O decomposition.

4. Discussion

The present work shows that gold can be incorporated in zeolite cavities by sublimation. The chemistry of this process can be summarized by

$$MCl_x(g) + H^+OZ^- \rightleftharpoons [MCl_{x-1}]^+\text{–}OZ^- + HCl(g) \quad (1)$$

$AuCl_3$, reacts with Brønsted sites of the zeolite in the same way as other volatile halides. Direct evidence that Au occupies the ion exchange sites is provided by the FTIR spectra in the OH stretching and the T–O–T perturbation regions. As expected, the 3610 cm^{-1} band diminishes, while a band at 920 cm^{-1} appears.

Immediately after sublimation, the Au/Al ratio is larger than unity, indicating that some $AuCl_3$ is deposited on the zeolite. After washing the Au/Al ratio approaches unity and Au^{3+} ions are mainly located in ion exchange positions. They are easily reduced to Au^0, which tends to agglomerate irreversibly.

A surprising development is that reduction with CO leads to an Au^+ state that is stabilized by formation of a gold carbonyl ion:

$$[Au^{3+}Cl_2]/MFI + 2CO + H_2O \rightleftharpoons [Au^+(CO)]/MFI + CO_2 + 2HCl \quad (2)$$

The IR data show that this complex displays characteristic C–O stretching bands at 2190 and 2176 cm^{-1}. The heat of adsorption of CO on Au^+ is much higher than that on Au^0,

resembling previous findings with CO on copper [24]. The band at about 2120–2150 cm^{-1}, which can be assigned to CO on Au^0 or electron-deficient gold, $Au^{\delta+}$, is very weak; it is detected when Au/MFI is reduced. The CO ligand stabilizes the Au^+ state which normally disproportionates to Au^0 and Au^{3+} in the absence of CO. As the original Cl^- ions are easily replaced by OH^- groups, the latter are a likely source of the oxygen in the CO_2 product, as described by equation (2).

In the absence of stabilization by CO no Au^+/MFI is obtained by heating $[Au^{3+}Cl_2]$/MFI in a He flow. Instead, all Au^{3+} ions are reduced to Au^0 upon heating to 500 °C. However, when thermal treatment in an O_2/He flow is interrupted at 240 °C, a subsequent CO-TPR run reveals formation of CO_2. The obtained ratio of $CO_2/Au = 0.7$ confirms that a significant amount of Au^{3+} has survived this thermal treatment.

Reduction of Au^{3+}/MFI leads to intermediate formation of Au^+/MFI, but at 500 °C the Au^+ ions are irreversibly transformed to Au^0. Ichikawa et al., who prepared Au/MFI by a different method, identified Au^+ ions by XPS. It is possible that in this case the Au^{3+} ions were reduced to Au^+ by X-rays inside the XPS chamber.

The XRD pattern of $[Au^+(CO)]$/MFI found in the present work is definitely different from that of the known compound $Au^+(CO)Cl$. The complex is thermally unstable and is reduced by X-rays at room temperature. We are unable to propose a structure based on the presently available data.

The present work confirms that highly dispersed gold on a zeolite is able to catalyze the reduction of nitrogen oxide, with hydrocarbon or ammonia as reductant. The initial catalytic activity is lower than that of Fe/MFI or Co/MFI prepared in a comparable way. The durability of the gold catalysts is low, as is to be expected on the basis of its easy and irreversible reducibility. Any catalytic application of Au/MFI prepared by sublimation will presumably remain confined to low-temperature processes such as the selective oxidation of CO or hydrocarbons.

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