Infrared study of the NO + CO interaction over Au/TiO_2 catalyst

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It was demonstrated that, in contrast to previous results, an NCO surface complex does form on Au/TiO_2 catalysts in the high-temperature reaction of NO + CO. By means of Fourier transform infrared spectroscopy two new absorption bands at 2180–2190 and 2205–2210 cm^{-1}, not observed in separate adsorption of reacting gases, were detected during the catalytic reaction. The former is attributed to Au–NCO and the latter to Ti–NCO species. It was assumed that, similar to the case of supported Pt metals, NCO is primarily formed on Au crystallites and then spills over onto titania. This idea was strengthened by the results obtained following the adsorption of HNCO on the catalyst and on the support.

KEY WORDS: Au catalyst; TiO_2 support; NO adsorption; NO + CO reaction on Au; NCO formation on Au; HNCO adsorption on Au/TiO_2.

1. Introduction

Considerable interest has been devoted in the past decade to the catalytic properties of supported Au [1–12]. One of the reasons is that Au catalyzes the oxidation of CO at such a low temperature at which H_2 remains practically intact. The adsorptive and catalytic behavior of Au has been also tested in the NO + CO reaction [13–17]. As regards the NO adsorption, quite different results were obtained. Lee and Schwank [13] found that NO by itself does not give rise to a band attributable to NO adsorbed on Au/SiO_2 or Au/MgO; however, exposure of supported Au to NO renders the catalyst unable to adsorb CO. Pre-adsorbed CO, on the other hand, is displaced from the Au catalysts by NO. Other authors identified several nitrosyl species at 1800–1900 cm^{-1} by means of FTIR spectroscopy [14]. The interaction and reaction of NO + CO have been also the subject of extensive studies. Since supported Au is not considered to be an effective activator for NO compared to Rh, it was not expected to exhibit a high catalytic activity in the NO + CO reaction. Recent results, however, showed that supported Au catalysts are superior in their low-temperature activity to Rh-, Pt- and Pd-modified catalysts for the NO + CO reaction [15]. It appears now clear that the catalytic properties of Au are much more sensitive to the preparation methods, in other words to the state of Au compared to precious metals. In spite of the high activity of supported Au in the NO + CO reaction, attempts to detect the formation of NCO intermediates have so far been unsuccessful [13–17]. This is quite surprising as NCO species are formed readily on other supported metals effective for the NO + CO reaction [18–33]. Recently, Debeila *et al.* [11] studied the interaction of NO and CO over Au/TiO_2. They found that adsorption of NO is dominated by the formation of dinitrosyl complexes at room temperature. CO readily adsorbs on Au/TiO_2 leading to multi-bonded carbonyl species. Displacement of adsorbed CO by gaseous NO showed no interaction between the two adsorbates and there is no experimental evidence for the formation of isocyanate species. This was rationalized in terms of the low tendency of NO to undergo dissociation on Au/TiO_2.

The primary aim of this work is to investigate more thoroughly the NO + CO interaction over Au/TiO_2 catalyst by means of FTIR spectroscopy with particular attention paid to the formation of NCO surface complex.

2. Experimental

2.1. Methods

Infrared spectra were recorded with a Biorad (Digilab. Div. FTS 155) instrument with a wavenumber accuracy of ±4 cm^{-1}. Typically 128 scans were collected. All the spectra presented in this study are difference spectra. Spectra of pretreated catalysts and the adsorbing gases were subtracted from the actual spectra. All subtractions were taken without the use of a scaling factor ($f = 1.0$).

2.2. Materials

The gases used were of commercial purity (Linde). The preparation of HNCO was as described before [23]. Au/TiO_2 catalyst with an Au loading of 1 and

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5 wt% was prepared by a deposition–precipitation method. Chloroauric acid ($HAuCl_4$·aq p.a. 49% Au, Fluka AG) was first dissolved in triply distilled water. After the pH of the $HAuCl_4$ aqueous solution was adjusted to 7.5 by adding 1 M NaOH solution, TiO_2 powder (Degussa P25) was suspended and kept at 343 K for 1 h with continuous stirring. The suspension was aged for 24 h at room temperature, washed with distilled water repeatedly, dried at 353 K and then calcined in air at 573 K for 4 h. Afterwards, the powder of the sample was pressed into self-supporting wafers (30×10 mm, $\sim$10 mg/cm^2), and reduced in 100 torr of H_2 in the IR cell at 673 K for 60 min. This was followed by degassing for 15 min at the same temperature and by cooling of the wafer to the temperature of the experiment. The average particle size of Au in the case of 5% Au/TiO_2 as determined by transmission electron microscopy was 6.5 nm.

3. Results and discussion

3.1. CO adsorption

The adsorption of CO (4 torr) on reduced 1 wt% Au/TiO_2 at 95 K produced absorption bands at 2178 and 2036 cm^{-1}. On decreasing the pressure to 0.5 torr the intensity of both bands decreased significantly. After evacuation at 95 K for 10 min both bands disappeared. When 10 torr CO was introduced into the cell at 300 K two bands appeared at 2185 and 2030 cm^{-1}, which were eliminated by degassing. The same features were observed for 5% Au/TiO_2 with the difference that the bands were somewhat stronger.

3.2. NO adsorption

The adsorption of NO (10 torr) on reduced 5% Au/TiO_2 at 300 K for 15 min produced absorption bands at 1747, 1630, 1583, 1487, 1315 and 1241 cm^{-1}. Evacuation at 300 K caused only slight changes of the spectrum. From these spectral features only the bands at 1747 and 1583 cm^{-1} can be attributed to the vibration of NO bonded to Au, as all other bands have been detected on the TiO_2 support alone following the adsorption of NO. Heating the sample in 10 mbar NO from 300 to 673 K, and taking the spectra at 300 K, resulted in only slight spectral changes.

3.3. NO + CO adsorption

The coadsorption of NO + CO gas mixture on 5% Au/TiO_2 at 300 K produced the same absorption bands as observed following separate adsorption of the two gases. Heating the sample in the gas mixture to 573 K for several hours did not cause any appreciable spectral changes. Above 623 K, however, the bands due to adsorbed NO dramatically diminished after a certain time, which depended on the temperature. This is very likely caused by the occurrence of the NO + CO reaction, i.e. the consumption of NO, as indicated by the mass spectrometric analysis of the gas phase. New spectral features appeared only at and above 673 K, when two intense bands developed at 2190 and 2212 cm^{-1} after 5 min (figure 1). With the extension of the adsorption time an enhancement of these bands occurred. Evacuation at 300 K for 10 min caused a certain change only in the shape of the absorption bands, which underwent only a slight reduction in intensity. Repeating this measurement at 723 K produced the same new spectral features, but with higher intensities. These new bands were not observed on an oxidized surface up to 773 K. Note that treating the catalyst with 20 torr of CO at 673 or 723 K produced no absorption bands remaining in the spectrum after evacuation at 300 K (figure 1, spectrum (f)).

As the location of these bands is nearly the same as that attributed to NCO species attached to supported Pt catalyst [23–28], it is reasonable to assume that they are also attributable to the vibration of NCO surface complexes in this case.

To confirm this idea HNCO was adsorbed on 5% Au/TiO_2 at low temperature, where both the dissociation of HNCO on TiO_2

$$HNCO_{(a)} = H_{(a)} + NCO_{(a)}$$

and the spillover of NCO from the Au onto the titania were expected to be very limited. Note that no isocyanate

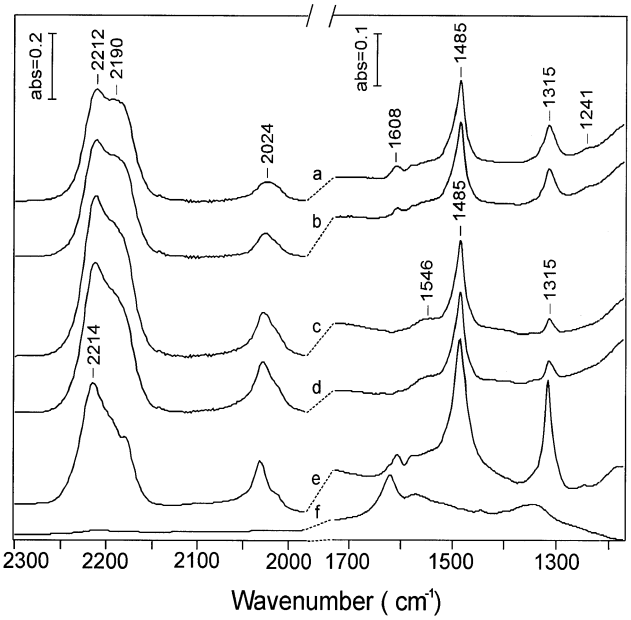

Figure 1. Infrared spectra of 5% Au/TiO_2 following the adsorption of 10 torr of NO + 20 torr of CO mixture at 673 K: (a) 5 min; (b) 30 min; (c) 120 min; (d) 180 min; (e) 360 min. Spectrum (f) was obtained after treating the catalyst with CO (20 torr) at 673 K for 360 min and then degassing the sample at 300 K.

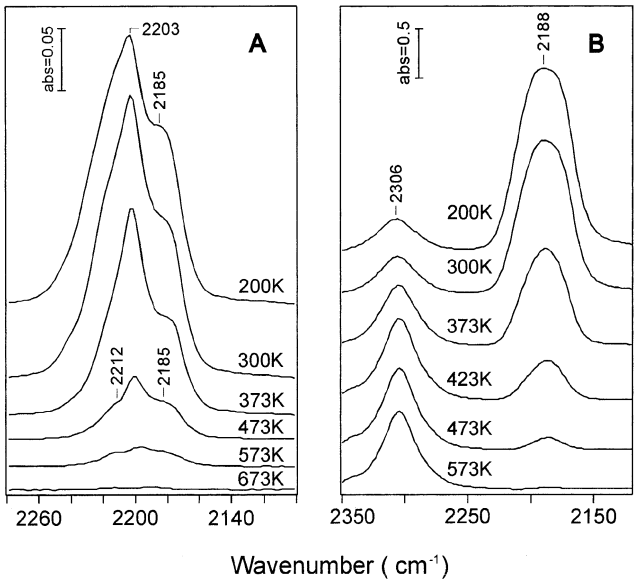

Figure 2. Infrared spectra of 5% Au/TiO_2 (a) and 1% Au/SiO_2 (b) following the adsorption of 0.02 torr HNCO at 200 K and after subsequent heating to higher temperatures under continuous evacuation.

complex can be produced on pure titana by the NO + CO reaction even at 773 K [25]. On exposing the reduced 5% Au/TiO_2 to 0.02 torr of HNCO at 200 K for 10 min and evacuating for 10 min, we obtained again two absorption bands, a broad one peaking at 2203 cm^{-1} and a shoulder at 2185 cm^{-1} (figure 2(a)). On heating the sample to higher temperature, the intensities of both bands decreased only at and above 300 K. At 473 K a new shoulder at 2212 cm^{-1} can be clearly distinguished on the high-frequency side of the 2203 cm^{-1} band. After annealing to 623 K a broad absorption in this frequency range can be still observed. Following the adsorption of HNCO on pure, metal-free TiO_2 we could distinguish two bands at 2203–2205 and 2210–2215 cm^{-1} attributed to the vibrations of NCO bonded to TiO_2 in different coordinations. Accordingly, the 2185 cm^{-1} band very likely corresponds to the vibration of NCO attached to the Au metal. From previous studies it appeared clear that while the position of the asymmetric stretch of NCO sensitively depends on the nature of the oxidic supports, it was practically independent of the metals: its location was always at 2180–2195 cm^{-1} [22–30].

Further evidence for the origin of the 2185 cm^{-1} band was obtained by adsorbing HNCO on 1% Au/SiO_2 at 200 K. In this case, initially one strong absorption appeared at 2188 cm^{-1} and a weak one at 2306 cm^{-1} (figure 2(b)). Raising the temperature under continuous degassing led to the attenuation of the 2188 cm^{-1} band with the gradual enhancement of the band at 2306 cm^{-1}, as a result of the spillover of NCO from the Au onto SiO_2. The 2188 cm^{-1} band disappeared at 573 K, whereas the 2306 cm^{-1} band was still very strong. This stable band is no doubt due to the vibration of Si–NCO species [23–28], while the less stable band at 2188 cm^{-1} can be assigned to Au–NCO species.

All these results suggest that, in contrast to previous results, NCO species do form on Au catalysts in the NO + CO reaction. It requires, however, a high temperature, in our case at least 673 K, when the dissociation of NO

$$Au–NO_{(a)} + Au = Au–N_{(a)} + Au–O_{(a)}$$

is more extensive. This step is followed by the reaction

$$Au–N_{(a)} + CO = Au–NCO_{(a)}.$$

We cannot exclude the possibility that NO formed a weak surface compound with CO, like Au(CO)(NO), as in the case of supported Rh [24], in which the dissociation of NO may proceed more easily. However, we have no spectroscopic evidence as yet for this complex in the present case.

Similar to supported Pt metals, the NCO species migrates from the Au onto TiO_2 surface where it is more stable. We can also assume the decomposition of Au–NCO at higher temperature

$$2Au–NCO = 2Au + N_2 + 2CO$$

or its reaction with NO

$$Au–NCO + NO = Au + CO_2 + N_2.$$

In order to see whether NCO bonded to Au and TiO_2 can react with gaseous NO, in subsequent measurements the Au/TiO_2 containing NCO species produced by HNCO in high concentrations was exposed to 10 torr of NO at 573–673 K. From the comparison of the declines in the intensity of NCO band with that measured in vacuum, we can say that the NCO band attenuated much more slowly than in the presence of NO. This suggests that NCO bonded to Au can react with gaseous NO

$$Au–NCO + NO = Au + CO_2 + N_2$$

to give N_2 and CO_2.

In summary we can conclude that as regards the elementary steps of the NO + CO reaction the behavior of supported Au is similar to that of Pt metals.

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