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DRIFTS studies of the interaction of nitric oxide and carbon monoxide on Au–TiO_2

M.A. Debeila[a], N.J. Coville[a], M.S. Scurrell[a,*], G.R. Hearne[b]

[a] *Molecular Sciences Institute, School of Chemistry, Private Bag X3, University of the Witwatersrand, Johannesburg 2050, South Africa*
[b] *Mössbauer Laboratory, School of Physics, Private Bag X3, University of the Witwatersrand, Johannesburg 2050, South Africa*

Abstract

DRIFTS data were collected on the interaction of NO and CO over Au/TiO_2 prepared by a deposition–precipitation procedure. Reduction of Au/TiO_2 in hydrogen at 300 °C for 30 min did not completely reduce the catalyst and both ionic and metallic gold sites were found to be present. Adsorption of NO is dominated by the formation of dinitrosyl complexes. CO readily adsorbs on Au/TiO_2 leading to multi-bonded carbonyl species. These species readily react with gaseous O_2 to form carbonate 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 is rationalized in terms of the low tendency of NO to undergo dissociation on Au/TiO_2.

Keywords: Gold; Titania; NO; CO; $Au(NO)_2$; DRIFTS

1. Introduction

Nitric oxide and carbon monoxide are undesirable pollutants. These molecules are co-reacted over noble metals in automobile exhaust emission catalytic converters into CO_2 and N_2 [1]. The interaction of CO with gold surfaces has been the subject of much interest during the last decade [2]. CO adsorbs on gold sites to form both linear carbonyl (ν_{CO} = 2140–2100 cm^{-1}) [2–7] and bridge-bonded carbonyl (ν_{CO} = 1992–1940 cm^{-1}) [10,11] that are readily identified via infrared spectroscopy. However, the interaction of NO with gold sites and the molecular nature of adsorbed NO is less well understood. NO adsorbs molecularly on gold ions, and several nitrosyl species have been identified and characterized by bands at 1900–1907 cm^{-1} (due to Au(I)(NO$^{(+)}$) species) and 1820 cm^{-1} (due to NO$^{(-)}$ species) [12]. Extensive studies have been carried out on the interactions of NO and CO with catalyst surfaces [13,14] and the kinetics of the reaction have been well documented [15]. The interaction of CO with NO over gold catalysts supported on ZSM-5 resulting in the formation of N_2O and CO_2 has been reported [10,16]. The formation of N_2O and CO_2 is described by the following set of reactions:

$$NO_{ad} \rightarrow N_{ad} + O_{ad} \quad (1)$$

$$NO_{ad} + N_{ad} \rightarrow N_2O_{ad} \quad (2)$$

$$CO_{ad} + O_{ad} \rightarrow CO_{2ad} \quad (3)$$

Vibrational spectroscopic studies of the NO + CO reaction over supported-gold catalysts have revealed the formation of NCO (bands at 2280 cm^{-1}) but only when hydrogen is included in the reactant mixture, i.e. CO/NO/H_2 at 423 K [17]. Spectroscopic evidence for NCO formation on oxide supports has been obtained for Al_2O_3 supported surfaces [18,19]

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[*] Corresponding author.
E-mail address: scurrell@aurum.chem.wits.ac.za (M.S. Scurrell).

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and SiO_2-supported Rh [20]. In this work, an investigation of the adsorption characteristics of CO and NO on Au/TiO_2 to study the NO + CO reaction over supported-gold catalysts has been carried out. To the best of our knowledge, this is one of the first reports to show, by means of IR spectroscopy, the formation of various NO species on Au/TiO_2.

2. Experimental

Degussa TiO_2 (P-25) (80% anatase and 20% rutile) was used as the support and $HAuCl_4$ (supplied by Next Chemica) was used as the Au source. Au–TiO_2 samples (Au loading of 5 wt.%) were prepared by standard deposition–precipitation procedures as described elsewhere [21]. A solution of $HAuCl_4$, dissolved in de-ionized water, was adjusted to the required pH (pH 3.5–4) with vigorous stirring using a solution of ammonium hydroxide at room temperature (RT). Once the required pH was obtained, the TiO_2 support was added to the solution. The resulting mixture was stirred for a further 30 min and then aged for 24 h. The water was removed by centrifuge and the solid sample dried in an oven at 150 °C for 16 h.

DRIFTS spectra were recorded on a Nicolet Impact 420 IR spectrometer, equipped with a DTGS KBr detector at a spectral resolution of 4 cm^{-1}. The fine powdered samples were loaded in a sample cell (Harrick Scientific) equipped with a ZnS window which allowed the treatment of samples in various controlled atmospheres. Gases were supplied by Afrox Ltd. After loading the sample into the DRIFTS cell, H_2 gas was introduced at a flow rate of 30 ml min^{-1}. The temperature of the system was raised at a ramping rate of 10 °C min^{-1} to 300 °C. The sample was reduced at this temperature for 30 min. H_2 gas was then replaced by He and the system was cooled to room temperature. The background spectrum of the reduced sample was collected before introducing the probe gas. The pressures quoted in this study are gauge pressures unless otherwise indicated.

3. Results

3.1. Adsorption of nitric oxide (NO)

Introduction of NO (0.3 bar total gas pressure) at room temperature gave absorption on Au/TiO_2 spectra as depicted in Fig. 1. The figure shows the evolution of the spectra of nitric oxide as a function of time (curves a–f), gas pressure (curves f–h) and temperature (curves h and i). The spectra are initially characterized by an intense and broad band around 1657 cm^{-1} which decreased in intensity in the later stages of NO adsorption. At the commencement of the adsorption, there are virtually no bands in the nitrosyl stretching region (2100–1700 cm^{-1}). The intense band at 1657 cm^{-1} could be assigned to $\nu_{asym}(NO_2)$ of NO_2 species and the corresponding $\nu_{sym}(NO_2)$ is found within the band at 1301 cm^{-1} [16]. However, this band (1657 cm^{-1}) is broad and overlaps with a band due to the bending mode of water δ(HOH) by analogy with the band observed at 1650 cm^{-1} seen after reaction of NO with H_2 on Au(I)/NaY zeolites [17]. The bands at 1358 and 1225 cm^{-1} may be assigned to $\nu_{asym}(NO_2)$ and $\nu_{sym}(NO_2)$ of nitrito surface species in a chelated state [22]. The shoulder at 1581 cm^{-1} is close in wavenumber to values previously assigned to $\nu_{asym}(NO_2)$ of asym-N_2O_3 possibly located on Au(I) ions [12]. A band at 1472 cm^{-1} is assigned to (N=O) of nitrito species in a unidentate state [22].

In the early stages of NO adsorption (curves a–d), the spectra show the development of a band at ∼1796 cm^{-1} which grew in intensity with time. The band exhibited a blue shift to higher wavenumbers with time (1796–1810 cm^{-1}) and at 50 °C the absorption maximum shifted to ∼1825 cm^{-1}. After ∼75 min, a second band at 1740 cm^{-1} was observed and the two bands (1810 and 1740 cm^{-1}) grew together in intensity with time. The two bands (1810 and 1740 cm^{-1}) decreased with increase in temperature (50–100 °C) (data at 100 °C is omitted) while the band at 1740 cm^{-1} disappeared. The band at 1796–1810 cm^{-1} is very close to that previously assigned to NO^- species (Au–NO^-) [17]. The bands for Au–nitrosyl species in this region (1880–1800 cm^{-1}) have previously been observed only when NO was introduced to Au^0/NaY [17]. On the basis of this previous experience, the band at 1796–1810 cm^{-1} suggests the presence of Au metallic sites in our sample. This gradual blue shift of the band (1796 to 1810 to 1825 cm^{-1} at 50 °C) suggest changes in the electronic states of the underlying metal. It is reported that the average work function of Au (4.83 eV) is lower than that of TiO_2 (5.3 eV) and hence for

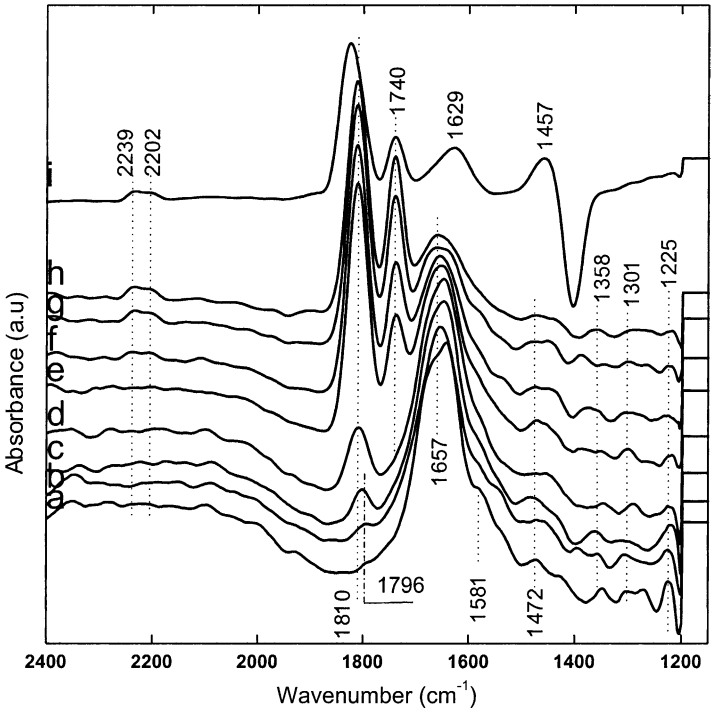

Fig. 1. IR spectra (room temperature) after adsorption of NO at: (a) 0.3 bar total pressure, 15 min; (b) 0.3 bar total pressure, 30 min; (c) 0.3 bar total pressure, 45 min; (d) 0.3 bar total pressure, 60 min; (e) 0.3 bar total pressure, 75 min; (f) 0.3 bar total pressure, 90 min; (g) 1 bar total pressure, 105 min; (h) 2 bar total pressure, 120 °C; (i) 2 bar total pressure, 50 °C.

an ideal Au–TiO_2 junction, electrons are expected to flow from the Au metal to TiO_2 [23]. This will cause electron redistribution and thus a change in NO bond order in chemisorbed NO molecules. This assignment is partially supported by the fact that a band at 1820 cm^{-1} (for NO on Au(I)/NaY) has previously been assigned to Au(I)–NO$^{\delta-}$ species [12]. If this is true, this process must be an activated one since the band shift to 1825 cm^{-1} could only be observed at temperatures above 25 °C.

The band at 1810 cm^{-1} is broad and might involve an overlap with bands associated with other species. Analysis of this band centered at 1810 cm^{-1} shows that it can be approximated to a Lorentzian shape and appears to be made up of the superposition of approximately three bands which reflect the adsorption of NO on different sites and/or the formation of different species [24]. Valyon and Hall [25] observed IR bands at 1824 and 1730 cm^{-1} on Cu sites which they assigned to dinitrosyl species. The band at 1824 cm^{-1} was shown to be made up of two overlapping bands at 1824 and 1810 cm^{-1} and could only be resolved by raising the temperature of the system. This latter band (1810 cm^{-1}) was assigned to monomeric NO$^{\delta-}$ species. It is not unreasonable to assume that similar overlapping bands are observed in this study. Indeed the two bands (1810 and 1740 cm^{-1}) seem to grow or decrease in intensity together and thus behave by analogy with $Au(NO)_2$ previously observed on a Au(I)ZSM-5 catalyst (1837 and 1741 cm^{-1}) [16]. Therefore, a conversion from mono- to di-nitrosyl complexes is a likely explanation. However at 100 °C, mononitrosyl species prevail when $Au(NO)_2$ species disappear. Other low intensity bands are observed at 2239 and 2202 cm^{-1} which grew slowly with increased pressure. By comparison with previous data, the bands at 2239 and 2202 cm^{-1} are assigned to nitrous oxide (N_2O) [10–12,16,17,30].

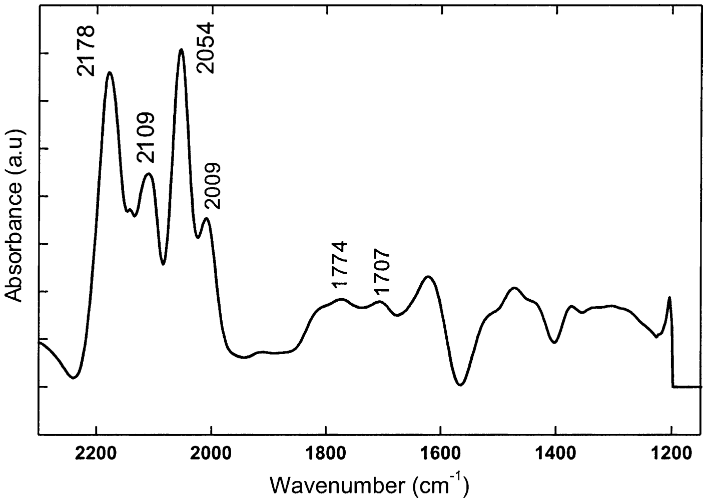

Fig. 2. IR spectrum of CO adsorbed at room temperature at 2 bar total pressure.

3.2. Adsorption of carbon monoxide

After reduction of Au/TiO$_2$ (see above), CO was introduced (2 bar total gas pressure) at room temperature for 15 min, during which the DRIFTS spectrum of the surface was recorded (Fig. 2). The spectrum is characterized by bands at 2178, 2109, 2054 and 2009 cm^{-1}. Other low intensity and broad band are visible between ∼1820 and 1700 cm^{-1} with maxima at 1774 and 1707 cm^{-1}. A band at 2178 cm^{-1} is close to previous reports of CO adsorbed on partially reduced gold sites (2175 cm^{-1} [10]). A similar band (2170 cm^{-1}) was previously assigned to monodentate carbonyl bound to Au(I) sites [16]. However, other assignments are possible, e.g. Ti^{4+}–CO [26]. The band at 2109 cm^{-1} is close to that observed on Au/TiO$_2$ and assigned to a CO molecule adsorbed on a metallic gold site [7–9], in agreement with NO adsorption studies (see above). The band at 2054 cm^{-1} is close to that observed on Au/SiO$_2$ [10] (2060 cm^{-1}) and a band at 2009 cm^{-1} was previously reported on Au/ZnO (2002 cm^{-1}) [4].

DRIFTS spectra obtained after flushing with He as a function of time are shown in Fig. 3. The two bands at 2009 and 2054 cm^{-1} were easily removed by flushing with He for 15 min at room temperature indicating that they are due to weakly adsorbed species. However, the bands at 2179 and 2109 cm^{-1} were relatively stable and could be removed only after ∼105 min of flushing with He at room temperature (Fig. 3, curve f). During this time, a broad band in the region 1820–1700 cm^{-1} was also removed by 15 min flushing, except for a shoulder which appeared on the higher wavenumber side at 1820 cm^{-1}, and which grew to become an intense band in the spectrum. The band blue shifted to 1824 cm^{-1} with continuous flushing at room temperature. Lee and Schwank [10] observed a broad band at around 2040 cm^{-1}, with a shoulder in the region below 2000 cm^{-1} at CO pressures of >15 Torr. On reducing the CO pressure to <1 Torr, the authors observed that the low frequency shoulder (below 2000 cm^{-1}) developed into a doublet at 1970 and 1940 cm^{-1}. It seems that the band observed in this study (1820–1824 cm^{-1}) is also similarly formed under low CO pressures. Absorptions due to bridge-bonded CO species were previously reported at 1992 cm^{-1} (on Au/ZrO$_2$) [11] and at 1970 and 1940 cm^{-1} (on Au/SiO$_2$) [10]. The position of the band observed in this study is much lower than that associated with bridge-bonded CO on gold reported to date. As reported for Pt catalysts [27–29], there are several overlapping IR bands for carbonyl species in this region, e.g. a broad band with maxima at 1878, 1835 and 1824 cm^{-1} was observed on Pt/Al$_2$O$_3$ and was assigned to multi-bonded CO adsorbed on different Pt sites. The band observed in

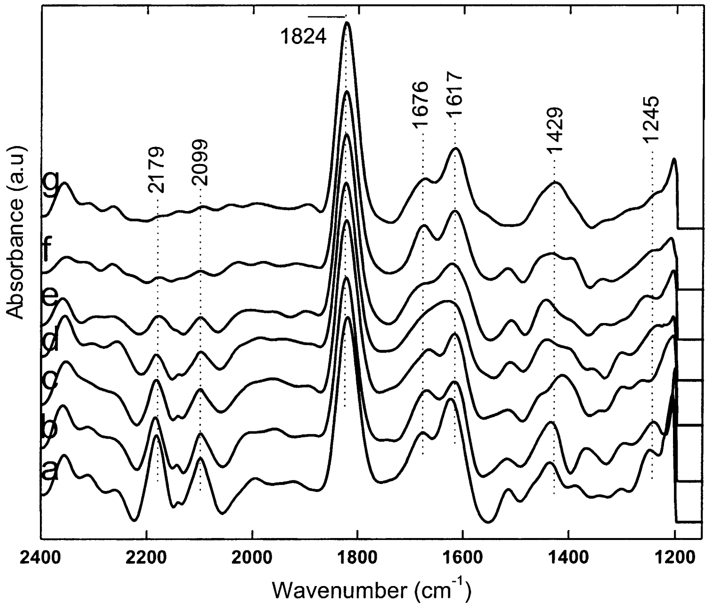

Fig. 3. IR spectra observed (room temperature) during purging of adsorbed CO with He as a function of time (15 min intervals).

this study is very broad and might consist of overlapping bands associated with the adsorption of CO on different gold sites. We are unable to unambiguously assign this band to specific sites on this sample and/or to state how many gold atoms are associated with one CO molecule.

Bands in the lower wavenumber region also grew in intensity with time. Bidentate carbonate species are associated with bands observed at 1676 and 1245 cm^{-1} [11] and monodentate carbonate species give rise to the band at 1429 cm^{-1} [11]. The band at 1617 cm^{-1} is close to ν(C=O) of a bridging carbonate species. This assignment requires the presence of an antisymmetric stretching frequency at 1270–1250 cm^{-1} [31] and this band might be contained within that seen at 1245 cm^{-1}.

He gas was replaced by O_2 gas and evolution of the spectra was followed as a function of time (Fig. 4):

- The intense band at 1824 cm^{-1} decreased in intensity to give a low intensity band observed at 1839 cm^{-1}.
- Bands at 1676, 1615 and 1425–1437 cm^{-1} associated with carboxylate species grew in intensity at the expense of the 1824 cm^{-1} band.
- Low intensity bands in the CO stretching region were observed at 1896, 1965, 2149 and 2264 cm^{-1}.

3.3. Adsorption of NO on a preadsorbed CO surface

After reduction, the catalyst was initially exposed to CO at 2 bar (total gas pressure) and room temperature for 15 min, as before; and the spectrum was found to be identical to that shown in Fig. 2. NO was then introduced into the system and spectra were recorded as a function of time (Fig. 5). On introducing NO, the low intensity CO bands observed at ~1817–1707 cm^{-1} were immediately replaced by two NO bands at 1819 cm^{-1} (strong) and 1741 cm^{-1} (medium); the two bands increased in intensity with time. The replacement of the CO band by two NO bands in this region suggest that CO and NO are competing and/or share the same sites. Raising the temperature of the system to 50 and 100 °C decreased the intensity of both bands; the band at 1742 cm^{-1} disappeared at 100 °C. These bands are assigned to Au–NO and $Au(NO)_2$ complexes. This spectral change is similar to those obtained when NO was absorbed on Au/TiO_2 (Fig. 1) except that the development of these

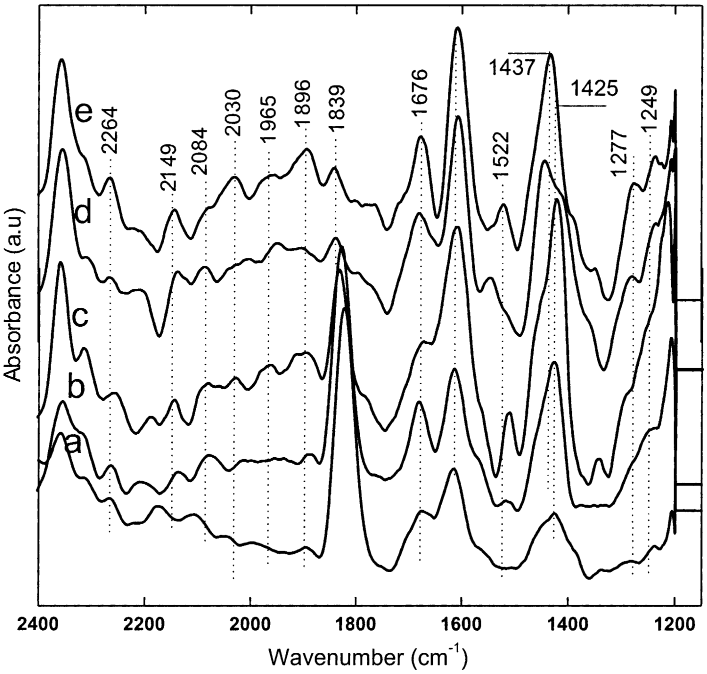

Fig. 4. IR spectra observed (room temperature) during purging of adsorbed CO with gaseous O_2 as a function of time (15 min intervals). In spectrum (a), He was used at 2 bar, in spectra (b)–(e), O_2 was used at 2 bar.

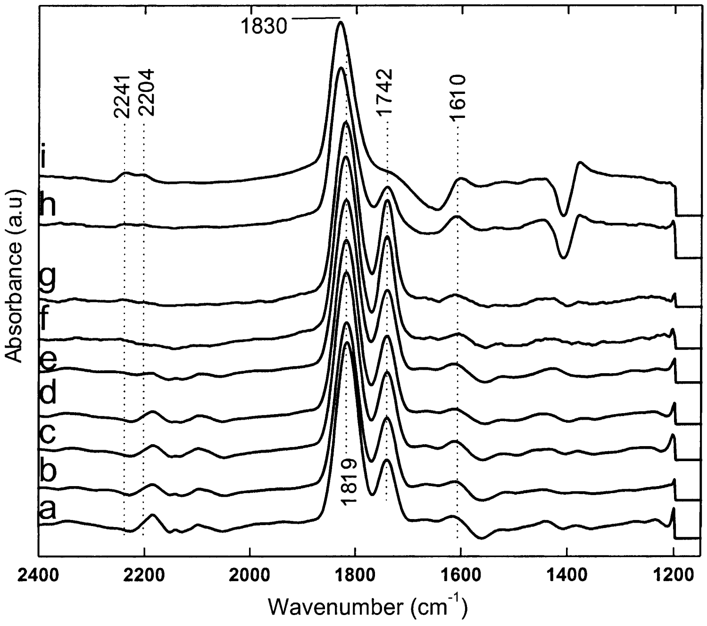

Fig. 5. IR spectra (room temperature) after purging adsorbed CO with NO at: (a) 1 bar total pressure, 15 min; (b) 1 bar total pressure, 30 min; (c) 1 bar total pressure, 45 min; (d) 1 bar total pressure, 60 min; (e) 2 bar total pressure, 75 min; (f) 2 bar total pressure, 90 min; (g) 2 bar total pressure, 105 min; (h) 2 bar total pressure, 50 °C; (i) 2 bar total pressure, 100 °C.

Table 1
Summary of the results concerning the state of gold and assignment of observed IR bands

Species	Wavenumber (cm^{-1})
$Au^{n+} \cdots CO$ and/or $Ti^{4+} \cdots CO$	2178
$Au^{0} \cdots CO$	2109, 2054
$(Au)_x(CO)_y$	1820–1824
Chelating carbonate	1677, 1256
Monodentate carbonate	1426
Bridging carbonate	1615
$Au–NO^-$	1810
$Au(NO)_2$	1820, 1740
N_2O	2239, 2202
NO_2 and/or δ(HOH)	1650, 1301
Chelating $NO_2{}^-$	1358, 1225
$Au^+(N_2O_3)$	1581
Unidentate nitrito	1472

bands seems to be enhanced in the presence of CO. Similar observations have been reported after interaction of CO and NO on Au(I)/ZSM-5 catalysts at room temperature [16]. The bands for N_2O, as observed at 2241 and 2202 cm^{-1} appeared to be slightly enhanced when the temperature was raised to 100 °C. The spectra in Fig. 5 are different from those discussed above:

- The broad band observed at 1651 cm^{-1} on the introduction of NO (Fig. 1) is replaced by a low intensity band at 1610 cm^{-1}.
- The carboxylate species observed when He and/or O_2 was used to displace CO are absent.

Table 1 gives a summary of the various states of gold and assignment of the observed bands obtained in this study.

4. Discussion

When NO is brought into contact with Au/TiO_2 (Fig. 1, curve a–c) a single low intensity band at 1796–1810 cm^{-1} is observed with no bands above this frequency attributable to nitrosyl species. Bands characteristic of N_2O species were also observed. The N_2O species may be formed through either (i) a dissociative mechanism (reactions (1) and (2)) and/or (ii) through the formation of dinitrosyl complexes [32,33]. This latter mechanism is expected to be dominant and the former is very limited on our sample under our experimental conditions. It is reported that NO dissociation took place on Au(I)/NaY zeolite at room temperature [30].

The interaction of NO and CO has been extensively investigated [1,13,14]. The products of the interaction of NO and CO are often CO_2 and NCO (isocyanate) species. The isocyanate species is characterized by bands for antisymmetric stretching vibrations in the region 2200–2150 cm^{-1} with the precise value depending on the coordinating surface [34]. In this study, there are no bands which could be attributed to isocyanate species. The formation of NCO requires prior dissociation of NO and subsequent reaction of N atoms with CO as in the reaction $M–N + CO \rightarrow M–NCO$ [13]. As discussed above, the dissociation of NO on Au/TiO_2 is limited and as a result no detectable amount of NCO was detected. It can be inferred that the majority of CO molecules are displaced from the catalyst surface and that little if any direct NO–CO interaction of a chemical nature occurs. The results of the present study are consistent with previous literature data. For example, no isocyanate species were detected in the reaction of preadsorbed CO with gaseous NO on Cr_2O_3/SiO_2 catalyst [13a] and on Au/SiO_2 and Au/MgO [10]. Similarly, introduction of CO on a NO covered surface of Au(I)/ZSM-5 catalyst at room temperature [16] led to the production of N_2O and CO_2. Further small amounts of N_2O and CO_2 were detected on Au/SiO_2 and Au/MgO after purging the adsorbed CO with NO [10]. NCO species were observed (2280 cm^{-1}) only after co-adsorption of $NO/CO/H_2$ at 423 K on Au(I)/NaY catalysts and no such species were observed during co-adsorption of CO/NO mixture [17]. It was suggested that H_2 enhanced the dissociation of NO. In this study, the sample was exposed to He at the reduction temperature and then immediately cooled down. Hence, the residual H atoms left on the surface (if any) could not effect the dissociation of NO.

The bands observed at 2241 and 2202 cm^{-1} characteristic of N_2O species were also present when only NO was introduced to the catalyst (Fig. 1) and therefore cannot be taken as evidence of the reaction between NO and CO. Rasko and Solymosi [13] suggested that $NO^{\delta-}$ species on the Cr_2O_3/SiO_2 surface is the most reactive NO species which dissociates to give nitrogen atoms and reaction with CO yields isocyanate species. The absence of isocyanate species on our sample (though NO^- species were detected at $1810\,cm^{-1}$) can be explained by the fact that no dissociation of NO^- species could take place under our experimental conditions. As stated above, the high NO pressures and low temperatures used in this study do not favor NO dissociation.

The interaction of CO and NO on Rh sites has been suggested to proceed via the formation of mixed species such as Rh(NO)(CO) [34]. Fig. 3 shows that carbonyl species, characterized by a band centered at $1824\,cm^{-1}$, are reactive towards gaseous oxygen at room temperature. In view of the reactivity of the carbonyl species on these sites and the competition between CO and NO for these sites, it might be expected that these sites act as centers for the $NO + CO$ reaction. However, there is no experimental evidence to suggest the formation of Au(NO)(CO) species on our sample or the reaction between CO and NO on these sites.

The present results do not allow us to arrive at a definitive conclusion with regards to the nature of the species responsible for the reduction of NO by CO and the corresponding reaction mechanism. The results obtained from Fig. 4 show that NO displaced CO from the Au/TiO_2 surface before reaction could take place. Similar observations have been reported previously [1,13,35,36].

5. Conclusions

Based on the data presented, the following conclusions may be drawn:

1. Treatment of Au/TiO_2 with hydrogen at 300 °C for 30 min appears to be sufficient for reduction of the gold surface.
2. Adsorption of NO on Au/TiO_2 is dominated by the formation of dinitrosyl species.

Adsorption of CO is dominated by the formation of multi-bonded carbonyl species which readily react with gaseous oxygen to form carbonate species.

Adsorption of NO on a CO covered surface enhances the formation of dinitrosyl species. NO displaced CO from the surface before reaction could occur. Hence, no isocyanate species were detected.

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