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Nitric Oxide Reduction by CO on Cu/TiO$_2$ Catalysts

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Characterization by high-resolution transmission electron microscopy of differently pretreated Cu/TiO$_2$ samples and IR and mass spectroscopic studies of NO–CO interaction on them from room temperature to 473 K are presented. All samples are characterized by Cu particles well dispersed on TiO$_2$ surface. The adsorption of CO produces an absorption in the 2112–2130 cm^{-1} frequency range; the intensity and position of the band strongly depends on the sample pretreatment, and it is strongly affected by NO interaction. NO dosing on a sample reduced at low temperature (LTR) precovered with CO leads to the formation of some CO$_2$ but the reaction is not complete after heating at 473 K; on a sample reduced at high temperature (HTR) large amounts of N$_2$O and CO$_2$ are detected already after short contact times at room temperature. By heating at 473 K an almost complete conversion to CO$_2$ and N$_2$ is observed. On both LTR and HTR samples neither NO nor isocyanate-adsorbed species are detected. Reaction products are observed if the sample HTR is contacted, after outgassing of a previous interaction mixture without desorption of the oxygen atoms produced in the NO dissociation, with a 1:1 NO–CO mixture or with CO and then with NO. If NO is preadsorbed prior to CO dosing in a second run of the reaction, almost no N$_2$O and CO$_2$ are observed. The experimental data indicate that HTR Cu/TiO$_2$ is significantly more active than LTR Cu/TiO$_2$, the activity being related to an easy dissociation of the NO molecules, determined by an electron transfer from reduced titania to antibonding orbitals of the NO. Free reduced copper sites are needed for CO activation, the reaction being to some extent inhibited by NO oxidation of the copper.

1. INTRODUCTION

The reduction of NO by CO has been studied extensively in recent years because of its interest in the control of exhaust emissions (1) The most employed systems are based on Pt, Pd, and Rh, which are extremely expensive metals; recently it was shown that these metals, in particular Pt supported on reducible oxides, show the highest activity if reduced at high temperature (2). This behaviour can be explained by an easier NO dissociation after this treatment, caused by an electron transfer from the reduced surface to an antibonding orbital of the NO; an IR study of the CO–NO reaction on Pt/ZnO (3) and Ru/ZnO (4) samples confirmed this hypothesis.

Nevertheless, in spite of the progress made in the field of catalysts based on noble metals, the need for catalysts based on more widespread and more abundant elements is clear. Copper-based catalysts for NO decomposition and reduction have recently become objects of great interest; in particular NO decomposition and reduction over Cu/Al$_2$O$_3$ catalysts (5, 6) and over Cu-exchanged zeolites have been studied (7–9). The mechanism of the reaction is not clear: a cyclic redox mechanism, involving cuprous–curpric ion transformation (7) or cupric gem–dinitrosyl species (8) as relevant reaction steps, has been suggested and is the subject of an open debate. One of the main features supporting the redox mechanism is the IR spectrum of NO adsorbed on these samples (9), showing a doublet at 1827 and 1734 cm^{-1}, ascribed to a dinitrosyl species and decreasing with the contact time. This species is adsorbed on Cu$^+$ sites, since it is blocked out by CO, known to adsorb more strongly on cuprous ions than on cupric or metallic copper sites (10).

Recently we have studied by IR the CO adsorption on Cu/TiO$_2$ samples (11) submitted to reductive treatments at different temperatures: on all the samples a band of CO adsorbed on Cu surface sites, "blue-shifted" in comparison with the band usually observed on Cu° single-crystal surfaces and on Cu particles supported on different oxides, was observed. The blue shift, which is a maximum on the most strongly reduced samples, was interpreted as due to an electronic interaction of copper with reduced titania, leading to copper sites made partially positive and which are almost isolated.

In this paper we present high-resolution transmission electron microscopy (HRTEM) characterization and IR and quadrupole mass spectrometry results on the CO–NO interactions on differently pretreated Cu/TiO$_2$ samples.

2. EXPERIMENTAL

2.1. *Materials*

The titania used in this study as support is a P-25 (Degussa), with a BET surface area of ≈ 50 m^2/g; it is predominantly anatase (≈80%), the remainder being rutile.

The impregnated samples were prepared by an aqueous solution of Cu(NO$_3$)$_2$ of suitable concentration and vol-

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ume; after impregnation the samples were dried at 393 K for 2 h and finally calcined for 15 h at 773 K. The studied samples have a 1, 4, and 10 mol% Cu/(Cu + TiO_2) content. The HRTEM micrographs shown are relative to the 10% sample, and the spectroscopic data are relative to the 1% sample.

2.2. *Sample Pretreatments*

The adsorption experiments were carried out on samples submitted preliminarily to the following thermal and chemical treatments: (i) reduced and outgassed at 573 K; (ii) reduced and outgassed at 673 K; (iii) reduced and outgassed at 773 K. In the following, the differently prepared and pretreated samples are labeled by a letter, namely R for reduced samples, followed by a number corresponding to the temperature of the reductive treatment.

2.3. *Methods*

X-ray powder diffraction measurements were taken using a Phylips PW 1830 refractometer, κ_α = Co. The micrographs were taken with a Jeol 2000 EX electron micro-

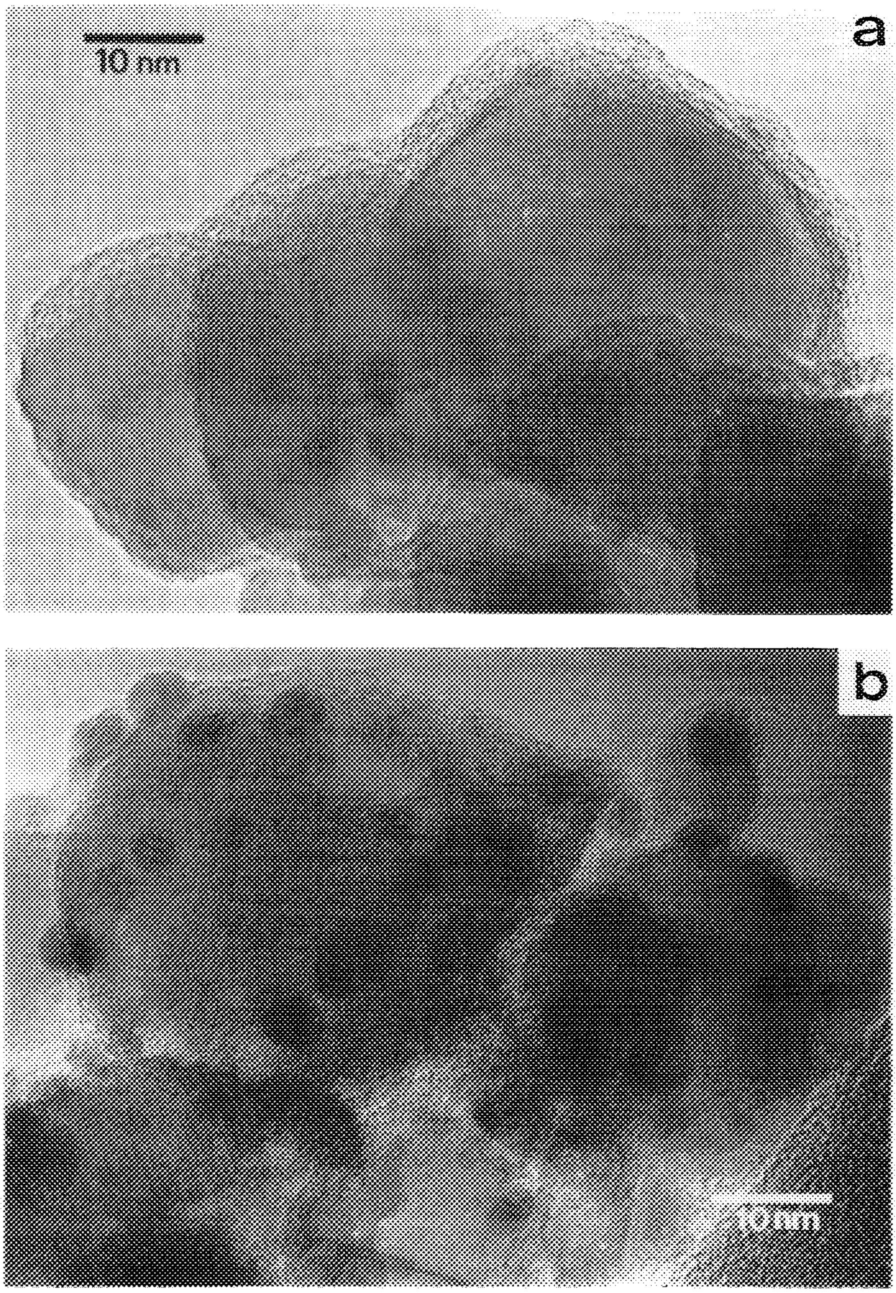

FIG. 1. Photomicrographs of differently pretreated 10% Cu/TiO_2 samples: (a) sample calcined at 773 K; (b) sample reduced in H_2 at 573 K; (c), sample reduced in H_2 at 773 K; inset in (c): HRTEM view of a metallic particle, original magnification 1 × 10^6, lattice fringe spacing = 2.26 Å.

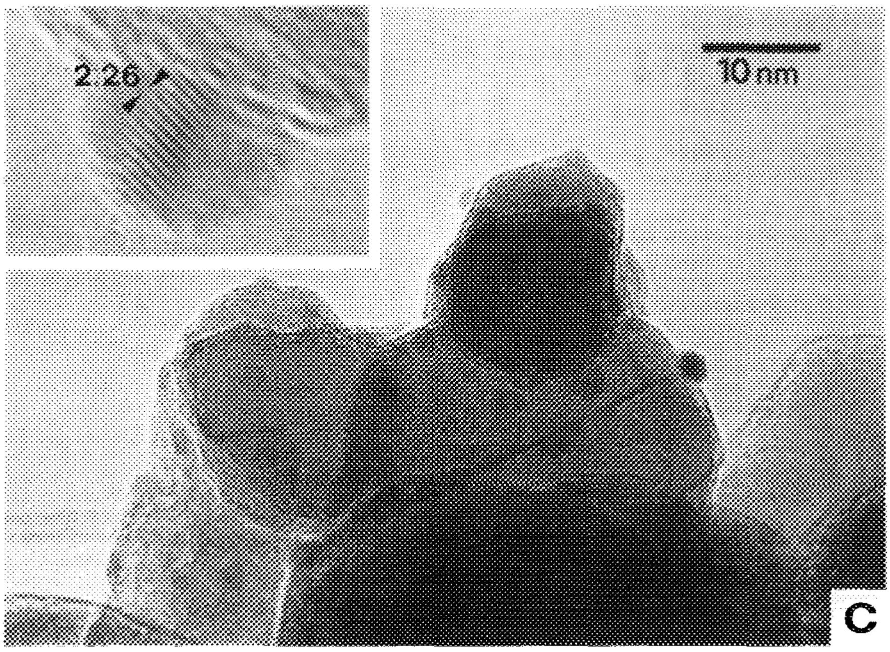

FIG. 1—*Continued*

scope, equipped with a top entry stage. The powder was ultrasonically dispersed in isopropyl alcohol, and the suspension was deposited on a copper grid coated with a holey carbon film.

The IR spectra were recorded at room temperature (RT) in an infrared cell designed to treat the samples *in situ*, using a Perkin–Elmer FTIR 1760 spectrometer, at a resolution of 2 cm^{-1}; the number of scans (100–200) was varied according to the transmission of the sample, with the aim to obtain similar levels of noise.

The mass spectra were taken by connecting the IR cell through a needle valve to a VG Micromass 100 instrument. Gases O_2, H_2, and CO from Matheson were used without purification, but NO was freshly distilled before use.

3. RESULTS AND DISCUSSION

3.1. XRD and Electron Microscopy Characterization

XRD patterns of the samples calcined in O_2 show the presence of the lines due to anatase and rutile phases; in the diffraction patterns of samples reduced at 573 K, additional lines at d = 2.09 and 1.81 Å, due to Cu° phase, are observed; as for the samples reduced at 773 K the lines of the Cu° phase are no longer present, and a new line at 2.30 Å is detected.

Figure 1a shows electron micrographs of a calcined Cu/TiO$_2$ sample, and Figs. 1b and 1c show those for the sample reduced at 573 and 773 K, respectively. The microcrystals of TiO$_2$ in the calcined sample are almost completely covered by a layer 2–3 nm thick, on which lattice fringes are not detected. The samples reduced at 573 and 773 K do not show the amorphous layer on top of the TiO$_2$ microcrystals; on the sample reduced at 573 K quite homogeneously dispersed particles of mean diameter 4.5 nm are observed, whilst on the sample reduced at 773 K the mean particle size decreases to 2.5 nm.

The layer covering the TiO$_2$ microcrystals in the calcined sample is a CuO surface phase formed by decomposition of the Cu(NO$_3$)$_2$; the absence of this layer on the reduced samples and its stability on the calcined samples under the electron beam are an indication that in the experimental conditions adopted there are no effects of support damage or contamination. Sanati *et al.* (12) showed in very precise HRTEM work on V_2O_5/TiO_2 the presence of an amorphous and continuous layer of vanadia on anatase, approximately 2.5 nm thick. The formation of amorphous overlayers in the oxide supported on oxides is related to the propensity of the oxides to wet other oxides.

On reduction the CuO layer disappears and small Cu particles are formed; by increasing the reduction temperature the mean particle size decreases (see Figs. 1b and 1c). The vast majority of the particles seen in a cross-sectional view show a quite large contact area with the support; those detected on the sample reduced at the highest temperature appear embedded in the support. Moreover, in spite of their very small size, the particles do not show any tendency to coalesce under the beam. These features indicate that a strong interaction, similar to that observed for Group VIII metals supported on titania, is acting also on this catalyst.

Only a few of the particles present lattice fringes, but one of them is shown in the inset to Fig. 1c. The lattice fringe spacing measured is 2.26 Å, significantly larger than the largest interplanar spacing of the Cu (d_{111} = 2.09 Å), quite close vice versa to the interplanar spacing of copper–titanium intermetallic compounds (d_{111} of $CuTi_3$ and d_{103} of $CuTi_2$ = 2.28 Å, JCPS 25-1144 and 15-717, respectively). This interplanar spacing is very close to the additional line at ≈2.30 Å observed in the XRD pattern of the same sample.

HRTEM inspection of samples reduced at 773 K and used in the CO–NO reaction does not show changes in the mean particle size of the metallic phase.

3.2. *NO Interaction on CO-Precovered Samples*

Figures 2–4 show the effects on the IR transmission spectra (sections a) and on the absorption bands of the adsorbed species (sections b) produced by interaction first of CO and then of NO on Cu/TiO_2 samples prereduced in H_2 at 573, 673, and 773 K. The spectra shown were run at room temperature after different contact times or after heating at different temperatures. The three differently pretreated samples (curves 1 in Figs. 2–4, section a) differ substantially as regards their IR transmission and the shape of their overall transmission profile; similar differences were observed also on Ru/TiO_2 pretreated in similar ways (13) and were related to the presence, in the most strongly reduced samples, of almost free electrons in reduced titania absorbing/reflecting the IR radiation. On all the samples the contact with CO does not produce changes in the IR transmission (curves 2 in Figs. 2–4) but different vibrational bands, more clearly visible in sections b of Figs. 2–4, curves 1. As already discussed in a previous paper (11) the two bands at high frequency, at 2186 and 2208 cm^{-1}, can be easily assigned to CO

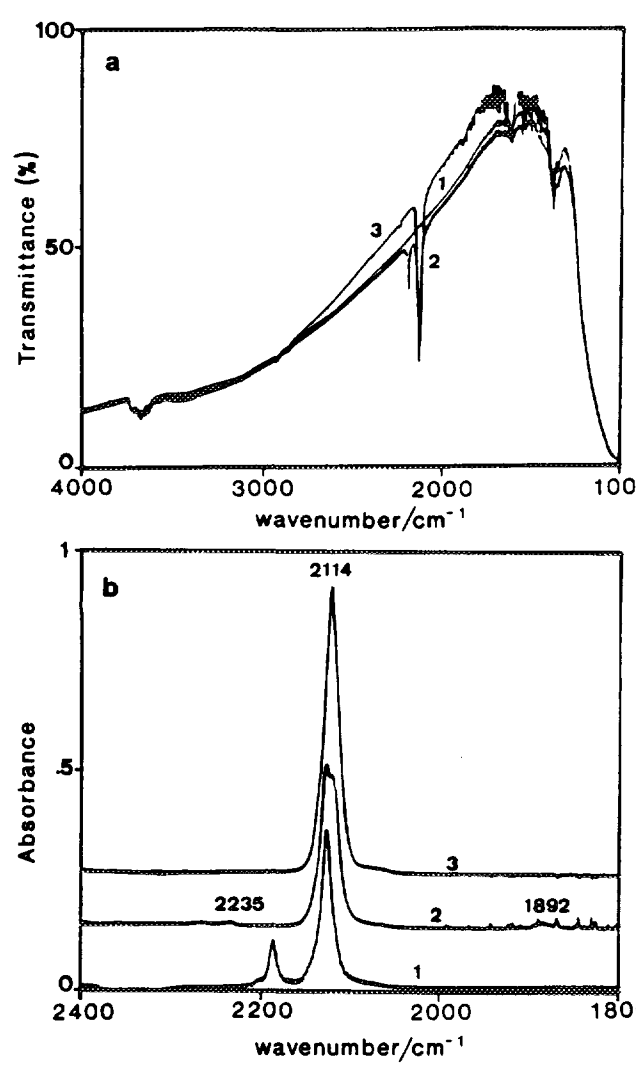

FIG. 2. IR spectra of NO interaction on R573 precovered with CO. (a) transmission spectra: 1, background; 2, 10 Torr of CO; 3, after inlet of 10 Torr of NO; (b) absorption spectra, run at RT: 1, 10 Torr of CO; 2, inlet of 10 Torr of NO; 3, after heating at 473 K.

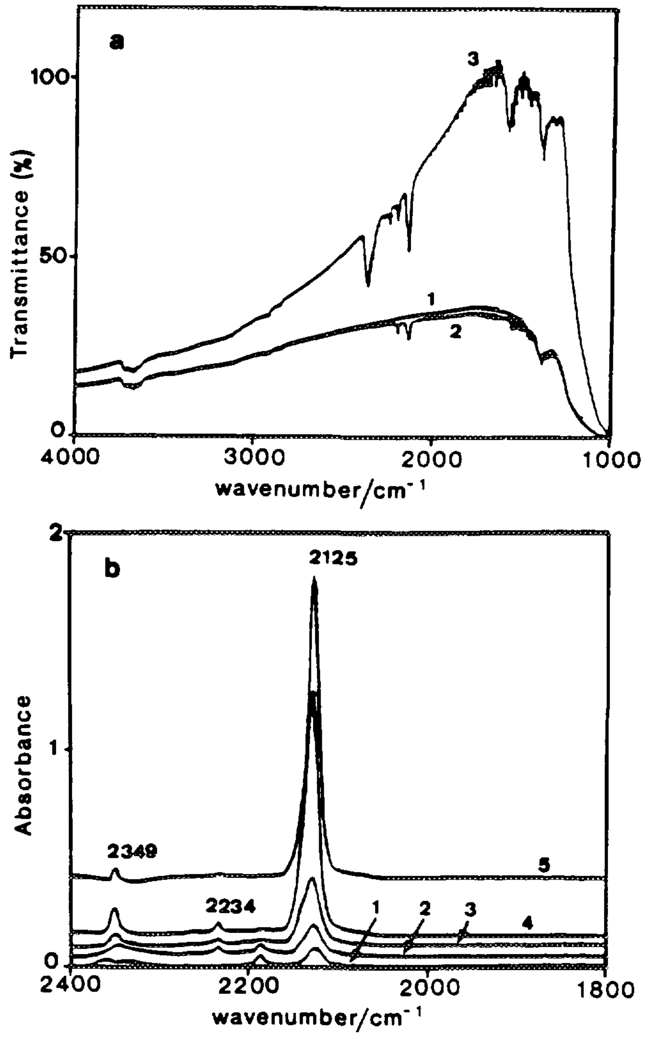

FIG. 3. IR spectra of NO interaction on R673 precovered with CO. (a) transmission spectra: 1, background; 2, 10 Torr of CO; 3, after inlet of 10 Torr of NO; (b) absorption spectra, run at RT: 1, 10 Torr of CO; 2, inlet of 10 Torr of NO, spectrum run after 15 min; 3, spectrum run after 15 h; 4, after heating at 373 K; 5, after heating at 473 K.

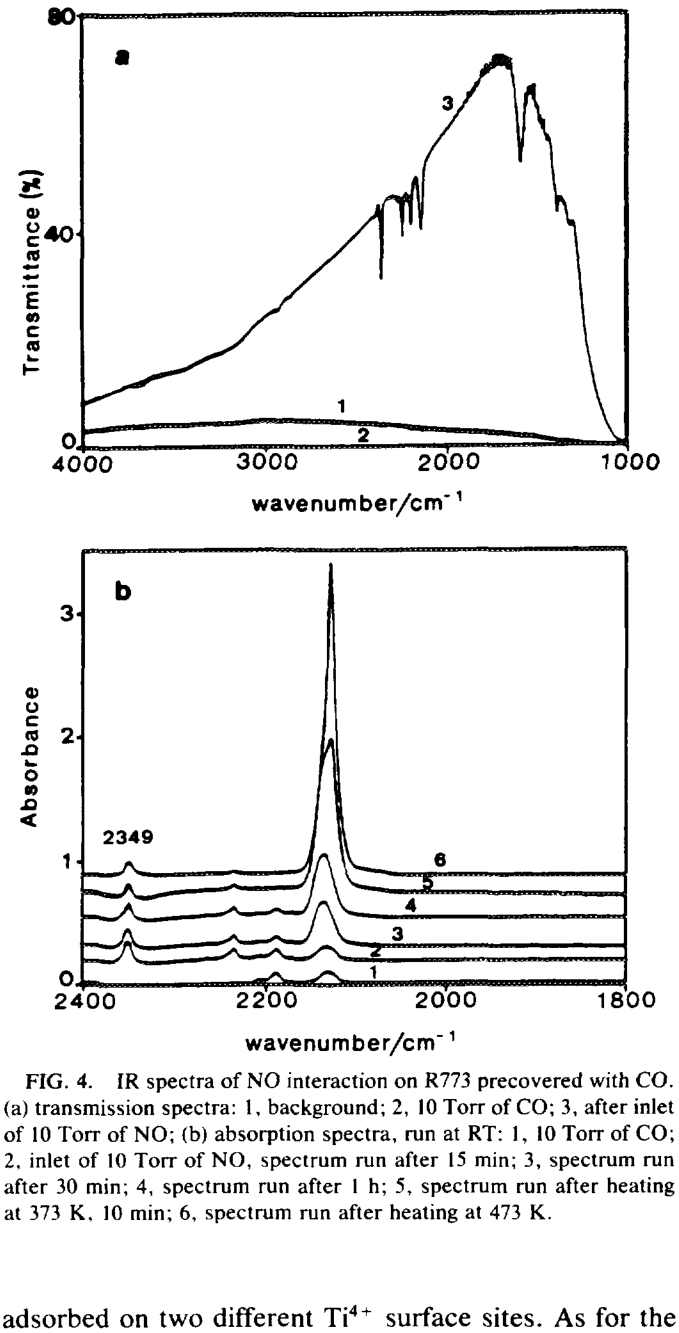

FIG. 4. IR spectra of NO interaction on R773 precovered with CO. (a) transmission spectra: 1, background; 2, 10 Torr of CO; 3, after inlet of 10 Torr of NO; (b) absorption spectra, run at RT: 1, 10 Torr of CO; 2, inlet of 10 Torr of NO, spectrum run after 15 min; 3, spectrum run after 30 min; 4, spectrum run after 1 h; 5, spectrum run after heating at 373 K, 10 min; 6, spectrum run after heating at 473 K.

adsorbed on two different Ti^{4+} surface sites. As for the bands at 2113–2131 cm^{-1}, they are due to CO adsorbed on Cu sites (11); the decrease in the intensity and the shift towards higher frequencies observed by increasing the temperature of the reductive treatments has been interpreted as an indication that copper sites, after strongly reductive treatments, are almost isolated and rendered partially positive by titania suboxides covering the Cu particles. Moreover, the XRD and HRTEM data previously presented suggest also an alloying effect to be responsible for the observed behaviour.

On the sample R573 the admission of NO at RT produces a quite small increase in the IR transmission (Fig. 2a, curve 3), the growth of a new component of adsorbed CO, at 2114 cm^{-1} (Fig. 2b, curve 2), the depletion of the 2186–2208 cm^{-1} bands, a weak band at 1892 cm^{-1} and a very weak one at 2235 cm^{-1}, which can be assigned to NO and N_2O adsorbed species, respectively. After a long contact time (15 h) bands at 1615, 1572, 1420, 1344 and 1221 cm^{-1}, assigned to carbonate- and nitrate-like species on TiO_2 (not shown for sake of brevity) were also detected. The heating of the catalyst in the CO–NO mixture at 473 K (Fig. 2b, curve 3) produces a further increment in the CO absorption, the integrated intensity becoming three times larger than at the beginning, without significant changes in other spectral regions. Mass spectra of the gas phase composition were taken at different stages of the reaction. Looking at the reaction CO + NO, m/z = 28 (CO and N_2), 30 (NO) and 44 (CO_2 and N_2O) were in particular examined: as an indication of the advancement of the reaction Table 1 reports the ratios of m/z 30/44. The data indicate that after a short contact time at RT almost no intermediates or reaction products, i.e. N_2O and CO_2, are formed. These appear after long contact time (15 h) and are increased by heating; however, on this sample the reaction is quite far from completion even after heating at 473 K.

The admission of NO on sample R673 causes an immediate and significant increase in the IR transmission (Fig. 3a, curve 3), and at the same time bands at 2234–2264 cm^{-1} and at 2349 cm^{-1} appear (Fig. 3a, curve 3 and Fig. 2b, curve 2); all these bands are quickly diminished by evacuation at RT. Bands are also detected at 1575 and 1330 cm^{-1}, irreversible by evacuation, related to carbonate-like species, while no bands are observed in the 1700–1900 cm^{-1} range, typical of NO-adsorbed species. After a long time of contact and after heating at increasing temperatures (Fig. 3b, curves 3–5) a substantial increase of a component in the CO absorption band at 2130 cm^{-1} is observed; at the same time the bands at 2186–2208 cm^{-1} decrease, and the bands at 2234–2264 cm^{-1} initially grow and finally, at 473 K, decrease.

The increase in the IR transmission, the simultaneous growth of bands at 2234–2264 and 2349 cm^{-1}, easily diminished by evacuation at RT and therefore easily assigned to N_2O and CO_2 molecular species, and the absence of bands in the 1700–1900 cm^{-1} range indicate that on this sample NO is easily dissociated, the resulting O and N atoms reacting immediately with CO and NO giving CO_2 and N_2O, respectively. The increase in the IR transmission can be explained by an electron transfer process of almost free electrons from reduced titania to oxygen atoms produced in the NO dissociation.

The increase of the band at 2130 cm^{-1}, assigned to CO adsorbed on Cu surface sites, up to a value six times larger than the initial one, and the decrease of the bands at 2186–2208 cm^{-1}, assigned to CO adsorbed on Ti^{4+} surface sites, indicate that the reoxidation by NO of the reduced titania leads to an increase of the exposed surface copper sites, chemisorbing CO quite strongly; the decrease in the intensity of the bands attributed to CO adsorbed on Ti^{4+} sites can be an indication that the increase of the exposed copper is associated with a decrease in the Ti^{4+}-exposed sites and/or that the reaction products, N_2O and CO_2, displace CO from Ti^{4+} sites.

The mass spectra of the gas phase composition over this sample confirm substantially the IR spectroscopic data; in fact, as can be seen in Table 1, already after a short contact time at RT significant amounts of $m/z = 44$ (CO_2 and N_2O) are detected and the final ratio between the unreacted reagent NO and the reaction products, after heating at 473 K, is lower than on the R573 sample.

IR results, qualitatively quite similar to those observed on sample R673, are reported for sample R773 (Fig. 4); some differences can be detected in the relative intensities of the bands assigned to the different adsorbed species. In particular the intensity of the band of CO adsorbed on Cu sites, after heating the sample to 473 K, becomes 20 times larger than the initial one. The mass spectra of the gas phase composition reported in Table 1 (sample R773 (a)) show that the ratio between unreacted NO and the reaction products is significantly lower than in the previously examined samples at all the stages of the reaction; after heating at 473 K the reaction is almost complete, as indicated by the very small amount of residual NO.

3.3. CO Interaction on a R773 Sample Precontacted with NO

Figures 5a and 5b show the transmission and the absorption spectra of a sample R773, contacted first with NO and then with CO. As for the previously illustrated sample precovered with CO (Fig. 4), the interaction with NO produces a very large increase in the IR transmission (Fig. 5a, curve 2) and a weak absorption at 2234–2264 cm^{-1} assigned to N_2O. However, no bands are observed in this case in the 1700–1900 cm^{-1} range, typical of NO-chemisorbed species. These features indicate that NO is not molecularly adsorbed on this sample, also in absence of CO, but is only dissociated. The evolution of the spectra, after contact with CO (Fig. 5a, curve 3 and Fig. 5b, curves 1 and 2) is qualitatively quite similar to that observed in the previously illustrated experiment, with only minor differences in the relative intensities of the bands.

The results described so far clearly show that the strongly reduced Cu/TiO_2 samples are more active than the mildly reduced ones in the CO–NO reaction, showing therefore a behaviour similar to that previously found for Pt catalysts supported on *n*-type semiconductor oxides (2–3). The highest activity is found on the sample R773 and it is almost independent of the sequence of the adsorption of the two gases.

As shown by HRTEM data, by the electronic properties of the samples, by the surface composition, and by the reactivity tests, the differently H_2-reduced samples are really different catalysts before the interaction with the reaction mixture: R573 can be described as made of copper metallic particles of mean size 4.5 nm, supported on an almost stoichiometric titania, whereas the more strongly reduced R673 and R773 consist of smaller metal particles, mean particle size ≈ 2.5 nm, the exposed copper sites being only few in number and almost isolated as a consequence of a coating layer of nonstoichiometric TiO_x. The activity in the CO–NO reaction is related to an easy dissociation of the NO, determined by an electron transfer from the reduced surface to an antibonding orbital of the NO molecule. However, after NO interaction the IR transmission is quite high and similar for all the samples, either after a short contact time at RT (see Figs. 2a, 3a, 4a, and 5a) or after reaction at 473 K (not shown for sake of brevity). This observation induces the doubt that the

TABLE 1

Ratios of m/z 30/44 [$NO/(N_2O + CO_2)$] Detected after CO–NO Interactions on Differently Pretreated Cu/TiO_2 Samples

Sample	Ratio after CO–NO interaction			
	15 min at RT	15 h at RT	15 min at 373 K	15 min at 473 K
R573	—	12	3	0.8
R673	10	4	0.5	0.2
R773[a]	3.7	1.3	—	0.09
R773[b]	30	0.5	—	0.1
R773[c]	—	15	2.8	0.7

Note. The initial CO/NO ratio was taken ≈ 1 in all the experiments.

[a] Mass data relative to the IR experiment shown in Fig. 4.

[b] As [a], but Fig. 6.

[c] As [a], but Fig. 7.

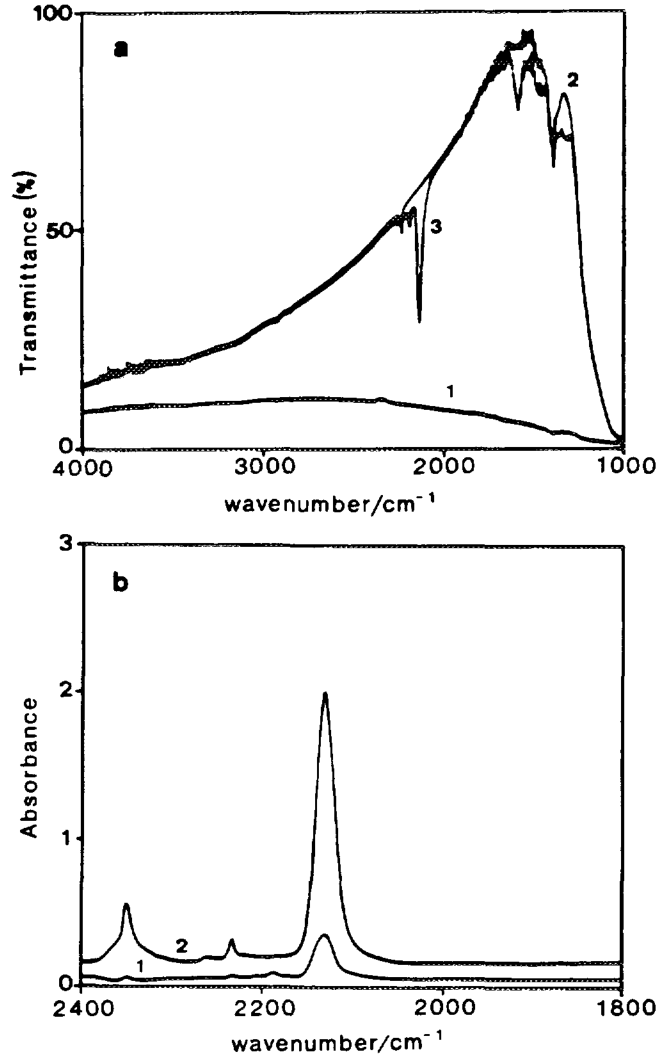

FIG. 5. IR spectra of CO interaction on R773 precovered with NO. (a) transmission spectra: 1, background; 2, 10 Torr of NO; 3, after inlet of 10 Torr of CO; (b) absorption spectra, run at RT: 1, spectrum run after 15 min of contact with NO–CO mixture; 2, spectrum run after heating at 473 K.

observed differences in the CO–NO reaction on the differently pretreated samples could be a transient phenomenon, significant only in a first run. If this were the case the importance of the observed differences between the differently pretreated samples would vanish; in order to investigate this point we present next results on the CO–NO interaction on sample R773 not freshly reduced but precontacted with these gases and outgassed at 473 K, the final temperature of the reaction. At the end of this treatment the sample shows a high transmission, as a consequence of the fact that the oxygen atoms previously produced by NO dissociation are not desorbed or fully reacted with CO. The sample pretreated in this way is labeled R773V473.

3.4. CO–NO Mixture Interaction on Sample R773V473

The transmission and absorption IR spectra produced by readsorption of 10 Torr of a 1 : 1 CO–NO mixture on R773V473 are shown in Figs. 6a and 6b, respectively. Almost no changes are observed in the IR transmission of the sample by admission of the mixture (Fig. 6a, curve 2) in respect to that of the clean R773V473 sample (Fig. 6a, curve 1); the CO present in the mixture produces immediately a very strong absorption at 2130 cm^{-1} (Fig. 6a, curve 2 and Fig. 6b, curve 1) and furthermore very weak bands at 2234 cm^{-1} and 2350 cm^{-1}, assigned to N_2O and CO_2, are detected; no bands due to CO adsorbed on Ti^{4+} sites or to NO molecularly adsorbed can be seen. After a long contact time at RT (15 h, Fig. 6b, curve 2)

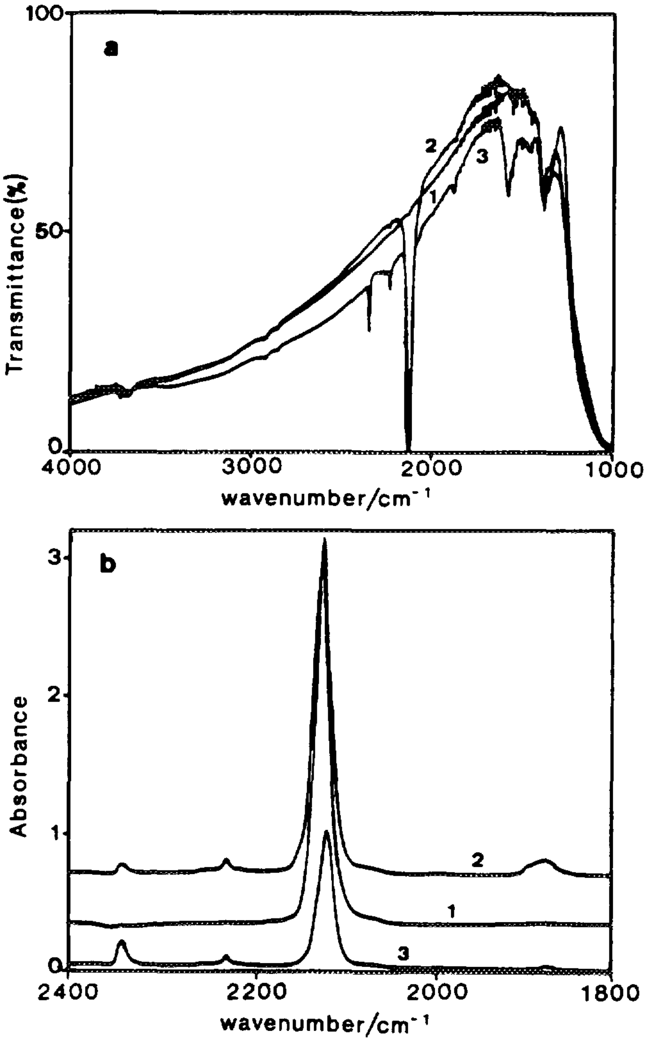

FIG. 6. IR spectra of the interaction of a CO–NO mixture on R773V473: (a) transmission spectra: 1, background; 2, interaction with CO–NO mixture, spectrum run after 15 min; 3, spectrum run after 15 h; (b) absorption spectra, run at RT: 1, spectrum run after 15 min of contact with the CO–NO mixture; 2, spectrum run after 15 h of contact; 3, spectrum run after heating at 473 K.

the N_2O and CO_2 bands become more intense and a weak absorption at ≈ 1870 cm^{-1} appears. By heating at 473 K the CO and NO absorption bands reduce their intensity while the CO_2 band becomes stronger (Fig. 6b, curve 3). The mass spectroscopic data (Table 1, sample R773(b)) show that the reaction proceeds as on the freshly reduced one. This observation is quite important because it indicates that the activity is related to the initial reduction state of the catalysts. In fact, as observed by HRTEM, after interaction with the reaction mixture, the metallic particles remain smaller and the reactivity remains higher than in the mildly reduced case, indicating that the interaction with the reaction mixture does not restore the initial dispersion and composition of the metallic phase nor the stoichiometry of the oxide; therefore, also after the reaction the catalysts remain different.

3.5. CO Interaction with a Sample R773V473 Precovered with NO

The interaction at RT with 10 Torr of NO on R773V473 (Fig. 7a, curve 2 and Fig. 7b, curve 1) produces bands at 1767, 1880, 1886, and 1924 cm^{-1}. These bands, not observed after the same kind of interaction on the clean R773 sample (Fig. 5a), are in the NO stretching region. The band at 1767 cm^{-1} shows its maximum of intensity in the spectrum run immediately (Fig. 7b, curve 1); it decreases with the time of contact and is completely removed by admission of CO (Fig. 7b, curve 2). The band is apparently not related to any other one and, in agreement with the assignment made by Hierl *et al.* of a band at a similar frequency detected on Cu/Al_2O_3-reduced samples (5, 6) and on the basis of EELS data of NO adsorption on Cu° single crystal (14), can be assigned to NO adsorbed on Cu° sites. The decrease in the intensity of this band with contact time indicates that in the presence of NO alone Cu° sites are gradually oxidized. The other bands at higher frequency are less quickly reduced in intensity and depleted by CO interaction (Fig. 7b, curves 2 and 3); on the basis of their frequency and of their higher resistance they can be assigned to the adsorption on oxidized copper sites (6). In fact bands at these frequencies, significantly more intense than those shown in Fig. 7, were observed by NO interaction on calcined Cu/TiO_2 samples (not shown for sake of brevity); furthermore, their intensity is higher on the samples containing a higher copper content.

In contrast with the clean R773 sample no IR transmission changes are observed and almost no N_2O bands are detected. The bands due to N_2O and CO_2 remain weak also after heating at 473 K; the mass spectroscopic data confirm that on this sample the reaction does not proceed as on the last two illustrated experiments but occurs in a way more similar to that of the first experiment, on the mildly reduced sample: in fact the final ratio of m/z 30 over m/z 44 at 473 K is in this case 0.7, quite close to 0.8, the value observed on the mildly reduced sample.

From this experiment it appears evident that the readsorption of NO, before CO admission, produces fully oxidized copper sites that are less efficient or inactive in the reaction. Hierl *et al.* (5) observed, on Cu/Al_2O_3 samples, that NO reoxidizes the copper metallic particles by a dissociative chemisorption; they recently confirmed in a study of the CO–NO reaction on the same catalysts (6) that Cu° and Cu^+ are the relevant copper oxidation states in this reaction. Our results agree with these conclusions.

3.6. Adsorption Sites of the Reaction Products or Intermediates

The experiment illustrated in Fig. 8 confirms that the N_2O formed in the previously illustrated interactions is weakly adsorbed on titania and does not occupy copper sites. In fact it can be seen that the admission of CO to a reduced sample on which bands produced by a previous interaction with NO were present at 2234, 2241, and 2264 cm^{-1} (Fig. 8a, curve 1), does not change at all their frequency or intensity (Fig. 8a, curve 2); at the same time a strong absorption at 2130 cm^{-1}, assigned to CO molecules chemisorbed on Cu surface sites, grows, and the bands at 1925–1887 cm^{-1}, assigned to NO adsorbed on copper oxidized sites (5), decrease.

Figure 8b shows a full range absorption spectrum of N_2O adsorbed on a R773 sample. The bands at 2264–2234 cm^{-1}, coincident with those observed by NO interaction shown in Fig. 8a, assigned to ν_3 (asymmetric) modes of N_2O-adsorbed molecules, are clearly correlated with other weaker bands in the 1252–1219 cm^{-1} range assigned to ν_1 (symmetric) modes of the same molecules; in the same spectrum combination modes, at 3454–3490 cm^{-1}, assigned to $\nu_1 + \nu_3$, and at 2480–2496 cm^{-1}, assigned to $2\nu_1$ absorptions, are also detected. Comparison of the spectra produced by interaction with N_2O and with those produced by NO (Fig. 8b, curves 1 and 2, respectively, in insets l and r) indicates that in the NO-produced spectrum a species characterized by bands at 2289 and 1240 cm^{-1} is missing. The other observed bands are almost perfectly coincident with those observed on pure TiO_2 by Ramis *et al.* (15). These bands were assigned to vibrational modes of N_2O molecules chemisorbed on two different surface sites Ti^{4+}, bonded through the nitrogen or the oxygen. The species not observed in the NO interaction is characterized by a ν_3 mode blue-shifted and by a ν_1 mode red-shifted with respect to those of the free molecule. A shift of the symmetric mode towards low frequencies is characteristic of oxygen-bonded species (16). Therefore it can be concluded that the N_2O species not observed after NO interaction on reduced Cu/TiO_2 samples is an oxygen-bonded species.

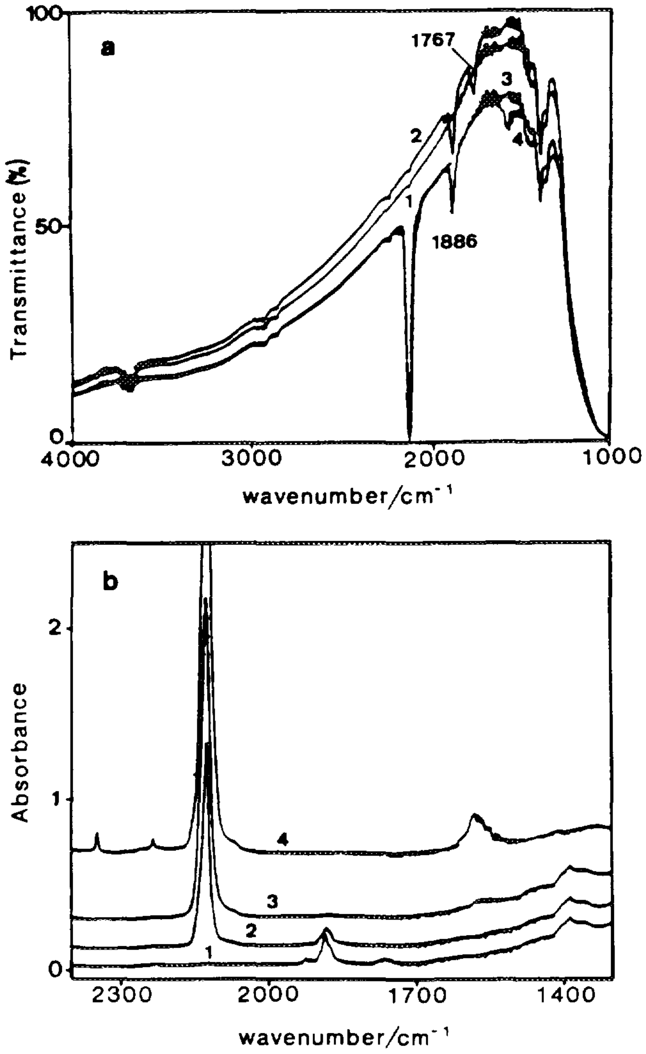

FIG. 7. IR spectra of CO interaction on R773V473 precovered with NO: (a) transmission spectra: 1, background; 2, 10 Torr of NO, spectrum run after 15 min; 3, inlet of 10 Torr of CO, spectrum run after 15 min; 4, spectrum run after 15 h; (b) absorption spectra: 1, 10 Torr of NO, spectrum run after 15 min; 2, inlet of 10 Torr of CO, spectrum run after 15 min; 3, spectrum run after 15 h; 4, spectrum run after heating at 473 K.

Also the CO_2 species formed in the reaction, on the basis of experiments of coadsorption of CO and CO_2, not shown for sake of brevity, can be assigned to species adsorbed on the support.

3.7. Reaction Mechanism

The main results relevant to understanding the mechanism of the reaction can be summarized in this way:

(i) the reaction proceeds faster and in a more complete way on the samples reduced at higher temperature;

(ii) these samples are initially characterized, before interaction with the reaction mixture, by a low IR transmission, as a consequence of the absorption/reflection of the radiation by the almost free electrons produced by reduction;

(iii) the free electron absorption remains unaltered by CO interaction, and superimposed on it are bands due to molecularly adsorbed CO; the absorption due to CO chemisorbed on surface copper sites is significantly weaker than on the more mildly reduced ones.

(iv) The electronic absorption is completely destroyed by NO adsorption, without the growth of NO molecular vibrational bands, and after NO interaction the intensities of the bands of the CO species molecularly adsorbed on copper surface sites strongly increase; this different behaviour can be related to the fact that NO, as a consequence of an electron transfer from the reduced solid to

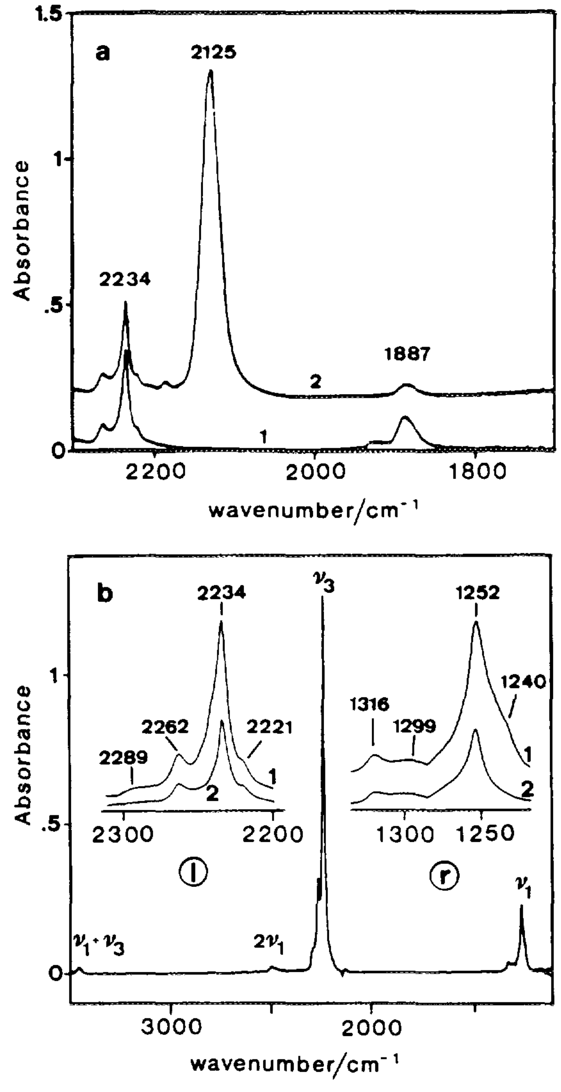

FIG. 8. IR absorption spectra. (a) 1, 10 Torr of NO on R673; 2, inlet of 10 Torr of CO; (b) 10 Torr of N_2O on the same sample; insets l and r: 1, magnification of ν_3 and ν_1 regions of the N_2O absorption spectrum; 2, spectrum produced by NO interaction.

an antibonding orbital, is easily dissociated, according the reaction

$$NO + e^- \rightarrow N + O^-.$$

(v) on the strongly reduced samples the NO–CO interaction quickly produces CO_2, N_2O, and carboxylate and/or carbonate-like adsorbed species, and there is no evidence at any stage of the interaction for the formation of isocyanate, as on other catalysts (3, 4, 6);

(vi) the reaction proceeds also by readmission of the reaction mixture after outgassing without desorption of the oxygen atoms previously produced in the NO dissociation; however, if NO is readmitted before CO the reaction proceeds in a less efficient way, as a consequence of a more deep oxidation of the copper particles.

The differences in the behaviour of the differently pretreated samples discussed in Section 3.2 clearly show that the rate-determining step in the CO–NO reaction on these catalysts is the NO dissociation, while the CO activation has a secondary role. In fact the mildly reduced sample, the less active one, shows a quite strong band of CO adsorbed on copper sites, but does not dissociate the NO; the samples reduced in a more drastic way show initially a very weak CO absorption band but a high activity in the NO dissociation. The low intensity of the CO absorption band on the strongly reduced samples and its shift towards high frequencies has been interpreted (11) as an indication that on these samples the copper sites are almost isolated. The isolated nature of the copper sites initially exposed at the surface of the R773 sample is further demonstrated by experiments (not shown for sake of brevity) of adsorption of a 1 : 1 ^{12}CO–^{13}CO mixture: two bands at 2123 cm^{-1} and at 2075 cm^{-1}, related to the two different isotopic species adsorbed on copper sites, show exactly the same intensity. The lack of any intensity transfer from the low-frequency band to the high-frequency one is a clear indication that no dipole–dipole coupling between the adsorbed CO is acting on this sample, confirming that the adsorption sites are isolated. After interaction with NO the two bands show a significant increase in intensity, but the high-frequency one increases more than the other one: this is a clear indication that under reaction conditions the surface becomes richer in Cu, and therefore the copper sites become less isolated than in the freshly reduced sample. Moreover, as already discussed in the previous paper (11), the adsorbed CO is more strongly bonded, after interaction with NO, indicating that in the reaction mixture Cu^+ ions are formed.

On R773 the XRD and HRTEM results provide evidence for the formation of Cu–Ti intermetallic compounds. Furthermore, the observation that on this sample the mean metallic particle size is lower than on the samples treated in milder conditions indicates that the formation of the intermetallic compound is accompanied by an increase in the dispersion of the metallic phase. These findings, supported by the coincidence of the spectral features of these samples with those of samples coming from amorphous alloys (11), suggest that the catalytically active phase is Cu and TiO_x interdispersed at an atomic level. XPS data (17) showed that the surface of Ti–Cu alloy prepared *in situ* by co-condensation in high vacuum conditions is covered by a TiO_x-type overlayer, as a consequence of the high affinity of titanium towards oxygen. Therefore we can hypothesize that high activity in the CO–NO reaction shown, already at RT, by strongly reduced Cu/TiO_2 samples is related to the presence of a highly defective reduced titania, TiO_X, on which NO is easily dissociated, in close contact with Cu° and Cu^+ sites on which CO is adsorbed.

Two reactions are thermodynamically favoured at 298 K between NO and CO:

$$2NO + 2CO \rightarrow N_2 + 2CO_2 \quad [1]$$

$$2NO + CO \rightarrow N_2O + CO_2. \quad [2]$$

The mechanisms and the pathways of these reactions have not been unambiguously determined; for example, controversy persists as to whether N_2O (or isocyanate or both) are formed as intermediates in the N_2 formation. Because CO_2 and N_2O are immediately detected on our most active samples we have evidence that reaction [2] occurs easily on this catalyst.

On the basis of the presented experimental data the following sequence of surface reaction steps can be suggested:

$$NO \rightarrow NO_{ad} \quad [3]$$

$$CO \rightarrow CO_{ad} \quad [4]$$

$$NO_{ad} + e^- \rightarrow N_{ad} + O^-_{ad} \quad [5]$$

$$N_{ad} + NO_{ad} \rightarrow N_2O \quad [6]$$

$$2NO_{ad} \rightarrow [(NO)_{2\,ad}] + e^- \rightarrow N_2O + O^- \quad [6\ bis]$$

$$CO + O^- \rightarrow CO_2 + e^- \quad [7]$$

$$CO + O^- \rightarrow [CO_2^-] + O^{2-}_{ret} \rightarrow CO_3^{2-} + e^- \quad [8]$$

$$N_2O + e^- \rightarrow N_2 + O^-. \quad [9]$$

Nitric oxide is molecularly adsorbed on fully oxidized copper sites, while carbon monoxide is molecularly adsorbed mainly on Cu° and Cu^+, the bond with Cu^{2+} ions being very weak (5, 10); therefore on well-reduced samples the two molecules do not compete for the same sites. The dissociation of the NO occurs easily on reduced titania (13, 18), according to reaction [5], and can also occur on Cu° sites.

The proposed sequence indicates N_2 formation as a secondary product involving N_2O as intermediate; this pathway has been already suggested earlier (19), and in our case it is supported by IR and mass spectroscopic data. In the proposed elementary steps N_2O is formed by reaction of NO with atomic nitrogen produced in the NO dissociation or by decomposition of a NO dimer. We do not have direct evidence for NO dimer formation on Cu/TiO_2 samples in our experimental conditions, but on Cu^+-exchanged zeolites; there is evidence for a dinitrosyl species at 77 K (9); we cannot therefore exclude a dinitrosyl species as precursor in the N_2O formation.

The complete absence of isocyanate species formed according to the reaction $N + CO \rightarrow NCO$ is quite unexpected; NCO species are often observed after CO–NO interaction on metal catalysts supported on TiO_2 and other oxides (20) and were observed by Hierl *et al.* (6) on Cu/Al_2O_3 samples. It is generally accepted that the isocyanate species are adsorbed on the oxidic support and that their stability is primarily determined by the chemical and electronic properties of the support (20); probably the absence of isocyanate species on our samples indicates that NCO is not stable on them. Previously we observed, on Pt/ZnO samples differently prereduced (3), that lower amounts of isocyanate species are formed on the more strongly reduced samples than on the mildly reduced ones. It can be hypothesized that the isocyanate species are unstable and immediately decompose on highly conductive solids.

The spectra reported in Figs. 3 and 4 show that N_2O decomposes above 373 K, indicating that on these catalysts the reaction $2NO + 2CO \rightarrow N_2 + 2CO_2$ can be complete in quite mild conditions, without side-reactions or side-products.

4. CONCLUSIONS

The results presented in this paper show that:

—the catalytic reduction of NO by CO starts at RT and proceeds at quite low temperatures on Cu/TiO_2 samples;

—the activity depends strongly on the reaction pretreatment temperature, the highest activity being observed on the samples reduced at high temperature;

—these samples, if freshly prepared, are characterized by small metal particles exposing almost isolated and partially positive copper sites in close contact with a defective reduced titania;

—nitric oxide dissociation on defective titania in close contact with small metal particles is the determining step of the NO–CO reaction;

—CO activation on reduced copper sites is also needed, the reaction being strongly inhibited in the presence of oxidized copper produced by exposure of the sample to NO alone, on which molecularly adsorbed NO species are formed and where CO is not bonded;

—the activity remains high by repeating the reaction with a new CO–NO mixture without the intervening of a new high-temperature pretreatment.

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