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# Preparation, Characterization, and Activity of Cu/$TiO_2$ Catalysts

## II. Effect of the Catalyst Morphology on the Hydrogenation of 1,3-Cyclooctadiene and the CO–NO Reaction on Cu/$TiO_2$ Catalysts

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**The hydrogenation of 1,3-cyclooctadiene and the CO–NO reaction have been studied on Cu/$TiO_2$ catalysts, with reference to the effects of the preparation method and of the reductive pretreatments of the samples. In the hydrogenation of 1,3-cyclooctadiene at 433 K, a marked difference in activity is observed between catalysts prepared by a chemisorption–hydrolysis method (C) and those prepared by wet impregnation (I), the former showing turnover numbers about 100 times greater than the latter. This large difference in activity is ascribed to differences in the morphology of the copper species present at the surfaces of the two different kinds of catalysts: there are three-dimensional stepped small particles of Cu in the first case (C), very efficient in hydrogen dissociation, whereas there are isolated copper sites embedded in the reduced support in the second case (I), very much less active toward hydrogen dissociation. In the CO–NO reaction, C samples show a decrease in the activity on increasing the catalyst prereduction temperature, while an opposite behavior is observed on I samples. For this reaction the rate determining step is NO dissociation; the interpretation of the apparently conflicting data is that NO dissociation occurs efficiently on copper sites on mildly reduced C catalysts exposing three-dimensional copper particles and also on reduced titania sites formed in the high-temperature reductive treatments on I catalysts.**

## 1. INTRODUCTION

In Part I (1), it was shown by XRD, HRTEM, and TPR investigations and through the analysis of FTIR spectra following CO adsorption that the surface properties of Cu/$TiO_2$ are strongly affected by the preparation method, by the copper loading, and by the reductive pretreatment. In particular it was shown that at the surface of samples prepared by a wet impregnation method, irrespective of the copper loading (2–8 wt.% Cu) and reductive pretreatments (423 to 673 K in $H_2$), almost isolated copper atoms or small two-dimensional copper clusters are exposed which are to some extent rendered positive by the interaction with the support. On similarly loaded samples prepared by a chemisorption–hydrolysis method, in addition to the above-mentioned isolated copper species, well-dispersed, clean, and well-crystallized three-dimensional copper particles are present after mild reductive pretreatment. Moreover, by a study of the effect of reductive treatments on the overall IR transparency of the samples and on the intensity of the CO absorption bands, it was shown that by increasing the reduction temperature a defective suboxide of titania, strongly absorbing in the IR, is formed, covering a large fraction of the copper particles.

In this paper we report on the catalytic activity of the samples characterized in Part I in two reactions, namely the selective hydrogenation of 1,3-cyclooctadiene to cyclooctene and the CO–NO reaction.

The catalytic activity in hydrogenation reactions strongly depends on both the nature and the dispersion of metallic particles. In particular, the presence of Cu(0) was found to be mandatory for the hydrogenation of cyclic polyenes (2). This reaction is favored by a high specific Cu(0) area, which in turn depends on the preparation method and on the support (3). The origins of these effects have not yet been fully clarified. In this paper we will attempt a correlation between the catalytic activity of the samples and the chemical properties of copper sites of different nature present at the surface of the examined samples.

In the case of the CO–NO reaction, copper-based catalysts for NO reduction have recently become objects of great interest, in particular the NO decomposition and reduction over Cu/$Al_2O_3$ (4) and Cu-exchanged zeolites (5). Recently the catalytic reduction of NO by CO on Cu/$TiO_2$ prepared by wet impregnation was studied by some of us (6). The main results were the strong dependence of the activity on the reduction pretreatment temperature, the highest activity being observed on samples reduced at high temperature. Nitric oxide dissociation on defective titania

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in close contact with copper small clusters appeared to be the rate determining step of the reaction. Also for other metals, such as Pt catalysts (7), it was observed that the activity when the metal is supported on *n*-type semiconducting oxides is strongly dependent on the reduction pretreatment temperature. In this paper we compare the results of the NO–CO reaction on $Cu/TiO_2$ samples prepared by wet impregnation with those prepared by the chemisorption–hydrolysis method, the samples having been submitted to reductive treatments at different temperatures in both cases.

## 2. EXPERIMENTAL

### 2.1. *Catalyst Preparation*

The sample preparation is described in Part I (1).

### 2.2. *Catalyst Activation and Procedure for Cyclooctadiene Hydrogenation*

The catalyst (250–300 mg) was first treated with $H_2$ at 373 K for 20 min, followed by raising the temperature by 20 K every 20 min up to 473 K and removing each time the water formed under vacuum for 1 min. The catalyst was then transferred under $N_2$ into a 60-ml stainless steel (AISI 316) autoclave and the organic reactant (10 ml of a solution of 1,3-cyclooctadiene 1.6 M in *n*-dodecane) was added. Hydrogen was charged at 3 atm, the temperature was raised to 433 K, and stirring was begun (1000 rpm). The rate of $H_2$ uptake was measured by an electronic flowmeter. The initial rate was used to evaluate turnover frequencies. Turnover frequencies are expressed on the assumption that only copper sites are active, the copper surface area being that determined by $N_2O$ decomposition, as reported in Part I (1).

The same reaction was carried out in the pulse mode in a tubular microreactor placed in the injector port of a gas chromatograph. The catalyst (10–20 mg) was reduced with $H_2$ between 373 and 473 K, raising the temperature by 20 K every 20 min. The temperature of the microreactor was adjusted to 433 K before the reaction was commenced. The cyclooctadiene (see above) was then introduced with $H_2$ flow rates ranging from 20 to 150 ml/min and the products were analyzed using a nonbonded, poly(80%-biscyanopropyl–20%-cyanopropylphenyl-siloxane) capillary column.

### 2.3. *Catalyst Activation and Procedure for CO–NO Reaction*

Pelletized catalyst was placed in a quartz infrared cell, equipped with KBr windows, designed to treat the sample *in situ* in controlled atmospheres and at different temperatures. The reaction was carried out under static conditions on the catalyst prereduced at different temperatures as specified below. By connecting the IR cell through a needle valve to a mass spectrometer (VG Micromass 100), FTIR spectra and mass spectra could be taken at different times or reaction temperatures in the same experiment. All the IR spectra were recorded with the sample at room temperature (RT) using a Perkin–Elmer FTIR spectrometer, at a resolution of 2 $cm^{-1}$, the number of scans (100–200) being varied according to the transmission of the sample, with the aim of obtaining similar levels of noise. CO, from Matheson, was used without purification; NO, from Matheson, freshly distilled before use, was analyzed before the reaction with the mass spectrometer.

In the label of the examined samples (e.g., 4I573), the initial number indicates the nominal copper loading (wt.%), the letter I or C indicates the sample preparation method (see Part I (1)), and the following three figures indicate the reduction temperature of the sample, before the reaction, in Kelvin. The initial reaction temperature was RT for all the samples and for the less reactive ones the reaction mixture was heated to 473 K.

## 3. RESULTS AND DISCUSSION

### 3.1. *Selective Hydrogenation of 1,3-Cyclooctadiene*

The selective hydrogenation of 1,3-cyclooctadiene to cyclooctene was studied in batch and pulse mode. The relative conversion of 1,3-cyclooctadiene to cyclooctene for the reaction carried out in pulse mode is in agreement with the turnover frequencies obtained in batch mode. The results obtained in batch mode at 433 K and 3 atm $H_2$ are reported in Table 1.

A very large difference in activity is observed between the catalysts prepared by the two methods, the turnover frequencies of C samples being about 100 times higher than those of the I samples, which are almost completely inactive.

The large difference in activity cannot be explained simply by the differences in Cu(0) specific surface area (see Table 1). Thus, comparable differences in $S_{Cu(0)}$ (64 vs 7 $m^2/g_{Cu}$), exhibited by $Cu/Al_2O_3$ samples prepared by the

**TABLE 1**

**Turnover Frequencies for the Hydrogenation of 1,3 Cyclooctadiene on Different $Cu/TiO_2$ Catalysts Compared with Their Specific Cu(0) Surface Areas[a]**

| Catalyst[b] | Turnover frequency[c] ($h^{-1}$) | $S_{Cu(0)}$ ($m^2/g_{Cu}$) |
|---|---|---|
| 4C | 530 | $64 \pm 3$ |
| 8C | 360 | $55 \pm 3$ |
| 4I | <5 | 11 |
| 8I | <5 | 9 |

[a] Reaction conditions: 433 K, 3 atm $H_2$; sample pretreatment: calcination at 623 K in $O_2$ for 4 hours; $T_{red} = 373–473$ K.

[b] Cu(wt.%): 4C = 4.3, 8C = 8.7, 4I = 4.6, 8I = 8.5.

[c] Moles of $H_2$/moles of exposed $Cu \cdot h$.

two methods, were found by some of us to give much lower differences in turnover (130 vs 9 $h^{-1}$) (3). Among the $Cu/TiO_2$ catalysts, the C samples are so much more active that some other factor must be taken into account.

The diene molecules are probably adsorbed on the samples prepared with both preparations both on the support and on the metallic particles. Therefore the difference in the activity is probably related to a different capability of the copper sites generated in the two preparations to dissociate $H_2$ and/or to coordinate in close contact both the olefin and the hydrogen. In Part I (1) evidence was provided that the main difference between the C and I samples consists in the presence in C samples of well-formed small Cu crystallites, exposing a significant fraction of step and edge sites whereas I samples expose only almost-isolated copper sites embedded in an amorphous layer of reduced titania. According to the model often used in describing the adsorption of hydrogen on metal surfaces, when the molecule approaches the surface it passes through a physisorption well and then crosses a barrier caused by Pauli repulsion between the $H_2$ $1\sigma_g$ orbital and the metal orbitals to enter a region of chemical interaction (8). If the barrier for dissociation is low enough, the molecule will end up as two chemisorbed atoms. For noble metals, Cu and low-index Ni and Fe surfaces the $H_2$ chemisorption is energetically activated, whereas on transition metals such as Pd and W and high-index Ni, Pt, and Cu planes the dissociative chemisorption is almost spontaneous (9). The energetics of this interaction of $H_2$ on metal surfaces is generally discussed by a one-dimensional representation of the $H/H_2$–metal potential as a function of the particle distance; instead it turns out that there is a distribution of barriers with different activation energy requirements depending on the chemisorption surface site. There is much experimental evidence that hydrogen dissociation occurs preferentially on stepped surfaces of different metals (10–12).

Therefore, samples C, exposing small metal particles with a large fraction of step sites, are expected to be very active in hydrogen dissociation. On the contrary, I samples, exposing isolated copper atoms embedded in reduced titania, are probably inactive in hydrogen activation because of their partial “positivization,” as shown by the close similarity of the CO IR absorption band frequency on these sites and that of the absorption band of CO adsorbed on $Cu^+$ ($d^{10}$) sites.

As for the higher specific turnover frequency of the 4C sample with respect to the 8C one (Table 1), we recall here that there are indications coming from the analysis of CO absorption spectra reported in Part I (1) that the 4C sample exposes small metal particles with mainly (111) microfacets and high fraction of step and borderline sites; the 8C sample, together with step, borderline, and (111) sites, exposes also (100) microfacets. Therefore, on the latter sample the (111) surface sites are a lower fraction of the total exposed copper sites. Recent measurements on different Cu planes (10) show that the Cu (111) plane presents the lowest activation barrier for $H_2$ dissociation with respect to other examined planes, such as the (100) and the (110) planes, accounting in this way for the specific turnover frequency differences observed.

### 3.2. *Mass Spectral Data on CO–NO Reaction*

Mass spectra of the gas phase composition and FTIR spectra of the adsorbed species were taken simultaneously at different stages of the reaction on differently prepared and pretrated samples. Since the reaction of CO and NO might be expected to yield $CO_2$, $N_2$, and $N_2O$, $m/z = 28$ (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 the $(m/z\ 44)/(m/z\ 30)$ ratio $(N_2O + CO_2)/NO$ is reported in Table 2 for the two differently prepared samples. Since this quotient is the ratio between two reaction products and a reactant, its value rises with the catalyst activity. It appears from the reported data that on the C sample with low copper loading (2%), by increasing the reduction temperature, a decrease in the activity is observed, this activity being restored by reoxidation followed by a second mild reduction (2C423(II)). On the I samples the opposite behavior is observed, since the activity increases by increasing the reduction temperature; moreover, by increasing the copper loading (4 and 8%), an absolute increase in the activity is observed and on these samples the activity remains quite high also after more severe reductive treatments up to 673 K.

The data reported in Table 2 are absolute data. As already shown in Part I (1) the exposed copper sites on the two catalysts strongly differ as regards their nature and their abundance depending on the preparation method and the reductive pretreatment. The opposite trends in catalytic activity observed by increasing the reduction temperature can possibly be rationalized by looking at the activity and reactivity

**TABLE 2**

**Ratio $[(N_2O + CO_2)/NO]^a$ Determined after CO–NO Interactions (Initial Ratios CO–NO 1 : 1) on Two Differently Prepared and Pretreated $Cu/TiO_2$ Samples**

| | Ratio $(N_2O + CO_2)/NO$ | | | |
|---|---|---|---|---|
| Sample | 15 min RT | 15 h RT | 15 min 373 K | 15 min 473 K |
| 2C423 | 0.24 | — | 4.0 | ≈∞ |
| 2C523 | 0.12 | — | — | — |
| 2C673 | 0.06 | — | 0.53 | 3.34 |
| 2C423(II) | 0.3 | — | 5.5 | ≈∞ |
| 2I523 | — | 0.08 | 0.33 | 1.25 |
| 2I623 | 0.1 | 0.25 | 2.0 | 5.0 |
| 2I673 | 0.27 | 0.77 | — | 11.1 |

[a] Mass spectrometric ratio: $(m/z\ 44)/(m/z\ 30)$.

of the copper sites and of the reduced titania exposed at the surface at the end of the different pretreatments. In order to obtain a deeper understanding of the mass spectral results on the NO–CO reaction presented in Table 2, we present and discuss below the FTIR spectra of the adsorbed phase during the same experiments.

### 3.3. *FTIR Data of NO Interaction on CO Precovered Samples*

The full range IR transmission spectra and the absorption bands of the adsorbed species in the 2400–2000 cm$^{-1}$ range produced by interaction first of CO and then of NO on sample 2C423 are shown in Figs. 1a and 1b, respectively. A similar experiment made on sample 2I523 is illustrated in Fig. 2. From the transmission spectra reported in Fig. 1a it appears that the NO inlet causes changes in the 2400–2000 cm$^{-1}$ and the 1650–1200 cm$^{-1}$ ranges. The first range is shown in more detail in Fig. 1b and will be discussed below; the second range is typical for carbonate-like species and these absorption bands will not be discussed further. The main point to be stressed here is that no bands are observed in the 1900–1700 cm$^{-1}$ range, typical of the molecular NO stretching and no changes are produced by the NO interaction on the overall IR transmission profile. We recall here that it has been shown previously (13) that on *n*-type oxidic semiconductors the interaction with molecules of high electron affinity produces an increase in the IR transmission as a consequence of electron transfer from populated donor sites of the defective oxide to the acceptor molecule. This phenomenon is evident mainly in strongly reduced samples, i.e., those with large deviations from stoichiometry. The sample examined in Fig. 1a is very mildly reduced. However, in spite of the absence of adsorbed NO molecules and the absence of electronic effects due to the interaction with the oxidic support, reaction products of the CO–NO interaction are immediately evident. In Fig. 1b, curve 2, it is shown that in the first 15 min of interaction at room temperature bands relating to reaction products at 2350 and at 2260–2230 cm$^{-1}$, assignable to CO$_2$ and N$_2$O, are produced. Moreover, broad absorption at 2180–2220 cm$^{-1}$ appears; at the same time a band in the CO stretching region at 2120 cm$^{-1}$ develops, while the bands at lower frequencies, 2100–2070 cm$^{-1}$, decrease. The broad absorption at 2180–2220 cm$^{-1}$, irreversible on outgassing at RT, can be assigned on the basis of literature data (14, 15) to isocyanate species, while the 2100–2070 cm$^{-1}$ bands are assignable (see Part I (1)) to carbon monoxide adsorbed on three-dimensional copper particles. After prolonged interaction (Fig. 1b, curve 3) the main effect is a strong intensification of the band at 2120 cm$^{-1}$. After heating to 373 K, this band strongly decreases in intensity and shifts to 2115 cm$^{-1}$: at the same time the broad absorption at 2220–2180 cm$^{-1}$ is diminished and the CO$_2$ absorption band shifts to 2350 cm$^{-1}$ (not shown for sake of brevity).

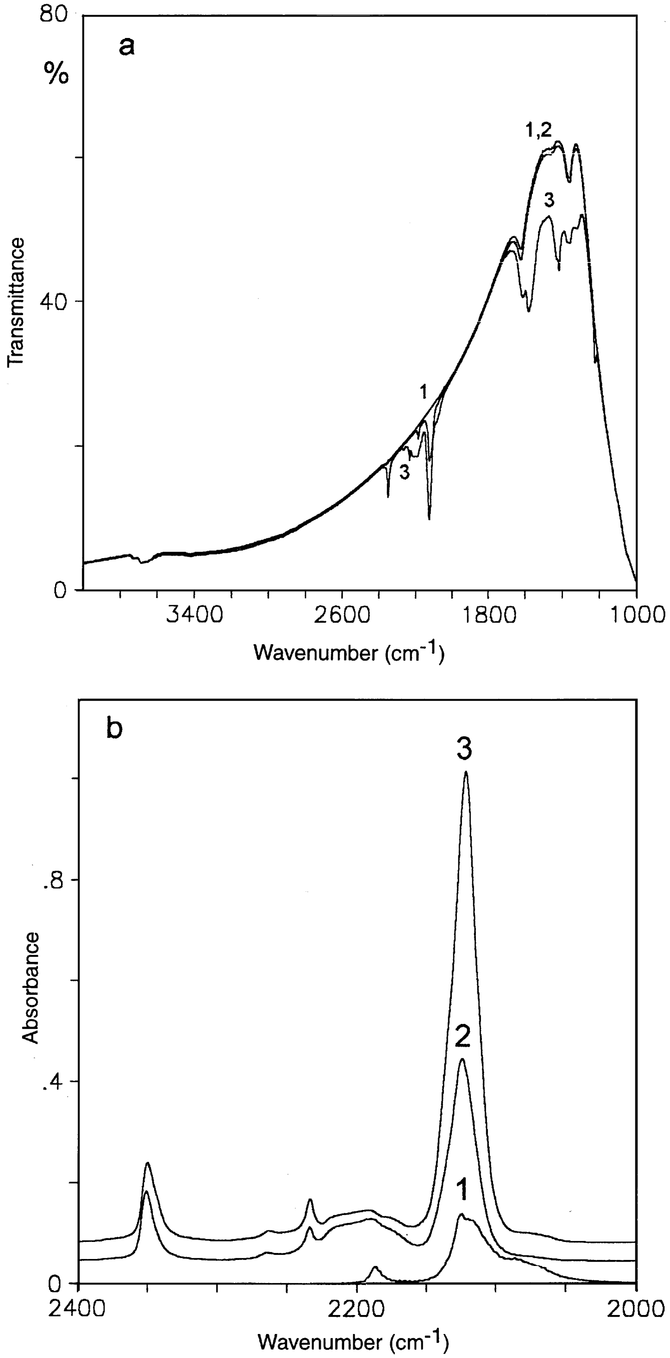

**FIG. 1.** FTIR spectra of NO interaction on sample 2C423 precovered with CO. (a) Full range transmission spectra of the clean sample (curve 1), precovered with CO by exposure to 10 mbar CO (curve 2), and after CO/NO interaction for 15 min (curve 3). (b) Absorption spectra in the 2400–2000 cm$^{-1}$ range after 10 mbar CO inlet (curve 1) and after CO/NO interaction for 15 min (curve 2) and 3 h (curve 3).

On sample 2I523 the same interactions (Figs. 2a and 2b) do not produce IR-detectable reaction products, i.e. CO$_2$ and N$_2$O or NCO and carbonate-like adsorbed species; also after prolonged interaction, only a minor increase in the IR transmission is observed (Fig. 2a, curve 3, and Fig. 2b,

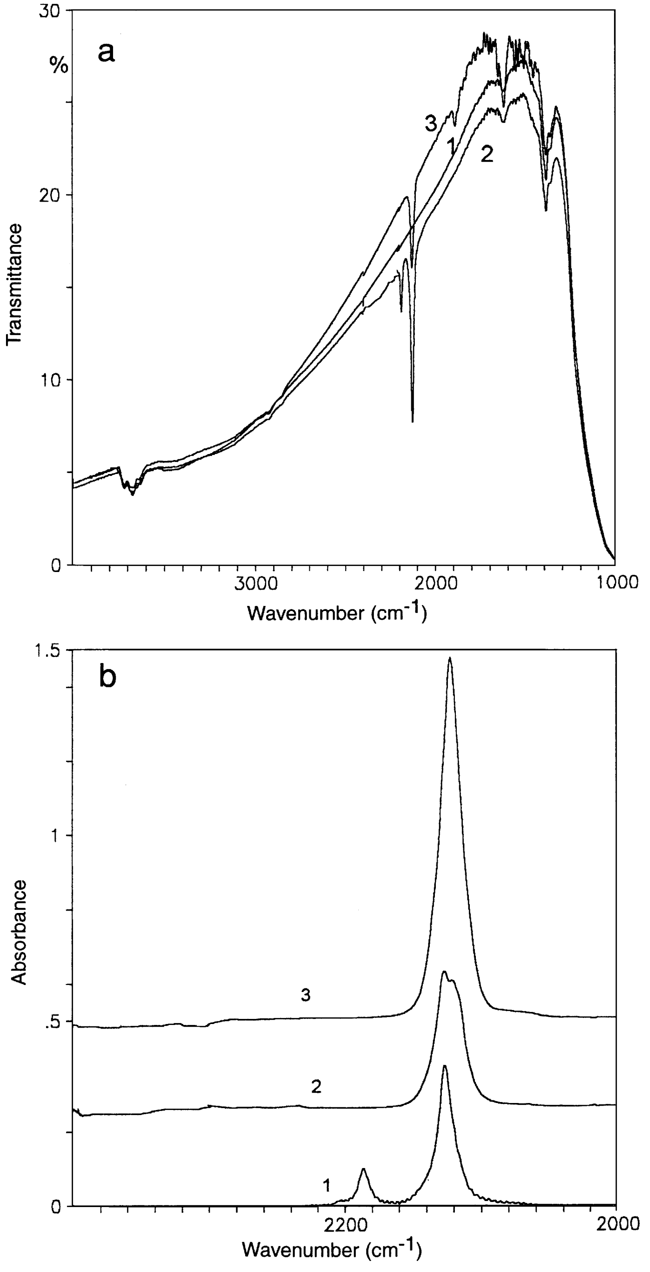

**FIG. 2.** FTIR spectra of NO interaction on sample 2I523 precovered with CO. (a) Full range transmission spectra of the clean sample (curve 1), precovered with 10 mbar CO (curve 2), and after CO/NO interaction for 15 min (curve 3). (b) Absorption spectra in the 2400–2000 cm$^{-1}$ range after 10 mbar CO inlet (curve 1) and after CO/NO interaction at RT for 15 min (curve 2) and at 473 K for 15 min (curve 3).

curve 2). The small increase in the IR transmission can be taken as an indication that small amounts of NO are dissociated at the surface of defective titania containing embedded copper atoms or possibly on a surface layer of nonstoichiometric copper titanate. By heating in the reaction mixture an increase in the intensity of the CO absorption band at 2114 cm$^{-1}$ is noticed (Fig. 2b, curve 3). The bands at 2120 and 2114 cm$^{-1}$, increasing in intensity by NO interaction, can be assigned to CO adsorbed on copper atoms oxidized by the NO dissociation. The increase in the intensity can be explained by taking into account that the absorption coefficient of the stretching of CO molecules adsorbed on Cu$^{+}$ sites is higher than that of CO molecules adsorbed on Cu$^{0}$ sites (16) or possibly that the surface exposed copper sites produced by the oxidation with NO can increase. The disappearance of the 2190 cm$^{-1}$ band, assigned to CO weakly adsorbed on Ti$^{4+}$ sites, is mainly related to a decrease in the CO partial pressure in the cell in the expansion into a larger volume during the NO interaction.

The copper loading and the pretreatments of the samples in the experiments reported in Figs. 1 and 2 are quite similar; the different reactivity must be related to the different nature of the exposed copper sites in the two samples, as evident from the characterization work (1). It can be proposed that on C samples NO molecules are dissociated on metallic copper sites exposed at the surface of the stepped particles and that the produced atoms adsorbed on the metallic sites react with CO and NO giving rise to the products $CO_2$, $N_2O$, and NCO; the absence of sites able to dissociate NO on the 2I523 sample inhibits all the reactions. A confirmation of this hypothesis comes from the study of the same interaction on C samples with a higher copper loading and reduced at different temperatures.

On sample 4C573 (Fig. 3a) the NO interaction on preadsorbed CO produces in a few minutes a significant increase in the overall transmission spectra; moreover, quite strong bands are produced in the 2400–2000 cm$^{-1}$ and 1650–1200 cm$^{-1}$ regions, while no bands are observed also in this case in the NO stretching region. The increase in the IR transmission is an indication that on this sample NO dissociation occurs also on the reduced titania, giving rise to an electron transfer reaction from the solid to the adsorbed species, as already discussed (6, 13). In Fig. 3b it is clearly shown that the bands at 2103 and 2071 cm$^{-1}$ gradually decrease and are almost completely depleted in 9 min of contact, that a broad absorption at 2220 cm$^{-1}$ grows, and also that the band at 2350 cm$^{-1}$, already assigned to $CO_2$, grows (Fig. 3b, curves 2–4); only in the last spectrum are components at 2234–2264 cm$^{-1}$, due to $N_2O$, observed (Fig. 3b, curve 5). Thus, there is a significant difference between the experiments on the 2C and the 4C sample in the rate of formation and in the relative intensity of $N_2O$ species in respect to the other reaction product, the $CO_2$. By increasing the copper loading and the reduction temperature (Fig. 4) the same kind of CO–NO interaction leads to quite similar features. The main differences are again in the relative intensities of the absorption bands; in particular the $CO_2$ to $N_2O$ band ratio is very high, while the broad absorption at 2220–2180 cm$^{-1}$ is quite weak. As already stated, spectra show that the relative amounts of $CO_2$, $N_2O$, and NCO in the CO–NO interactions are strongly dependent

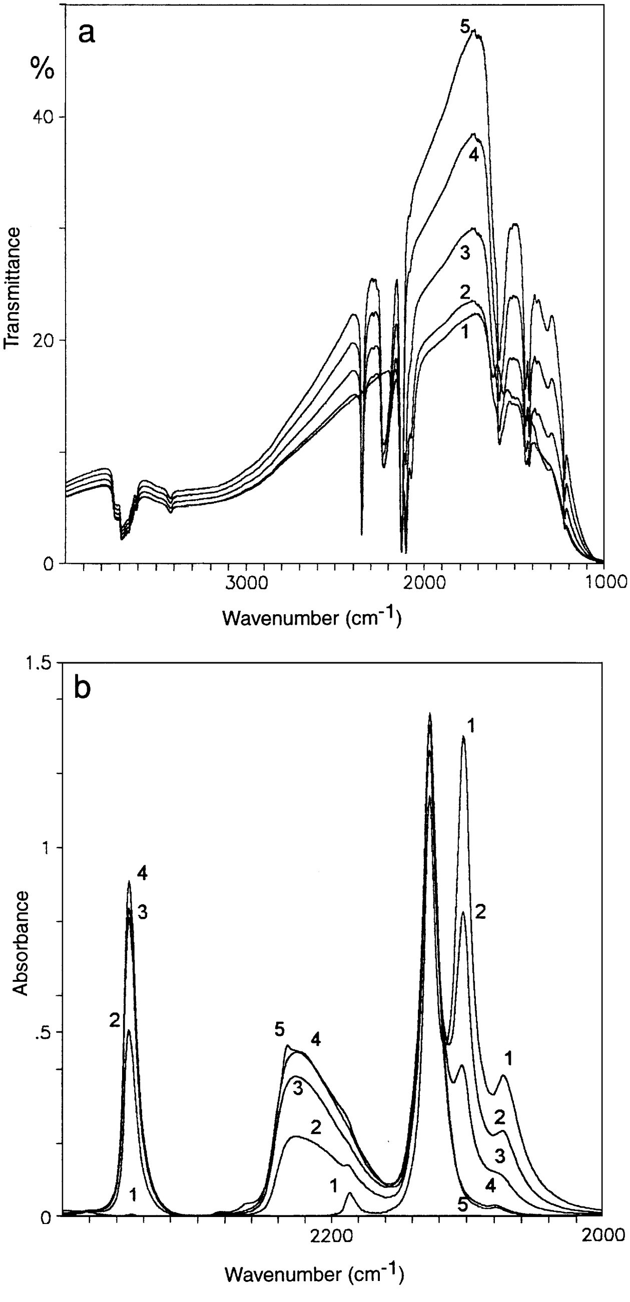

**FIG. 3.** FTIR spectra of NO interaction on sample 4C573 precovered with CO. (a) Full range transmission spectra of the sample precovered with 10 mbar of CO (curve 1) and after different CO/NO interaction times: 3 min (curve 2), 6 min (curve 3), 9 min (curve 4), 15 min (curve 5). (b) Absorption spectra in the 2400–2000 cm$^{-1}$ range after CO interaction (curve 1) and after different contact times with CO/NO: 3 min (curve 2), 6 min (curve 3), 9 min (curve 4), 15 min (curve 5).

on different factors, viz. the extent of reduction of the supported metal and of the support, the metal loading, and the preparation method of the samples.

On the basis of the illustrated data some observations can be made on the effect of the metal loading and the preparation method on the activity and the selectivity toward the different product formation. As regards the metal loading effect, it is evident that at high metal loading, CO$_2$ formation is favored over N$_2$O and NCO formation; this point will be discussed below. Moreover, it appears that: (i) on the samples prepared by wet impregnation, NCO species are not formed at all after either mild or strong reductive pretreatments (Figs. 2 and 5); (ii) on the sample prepared by

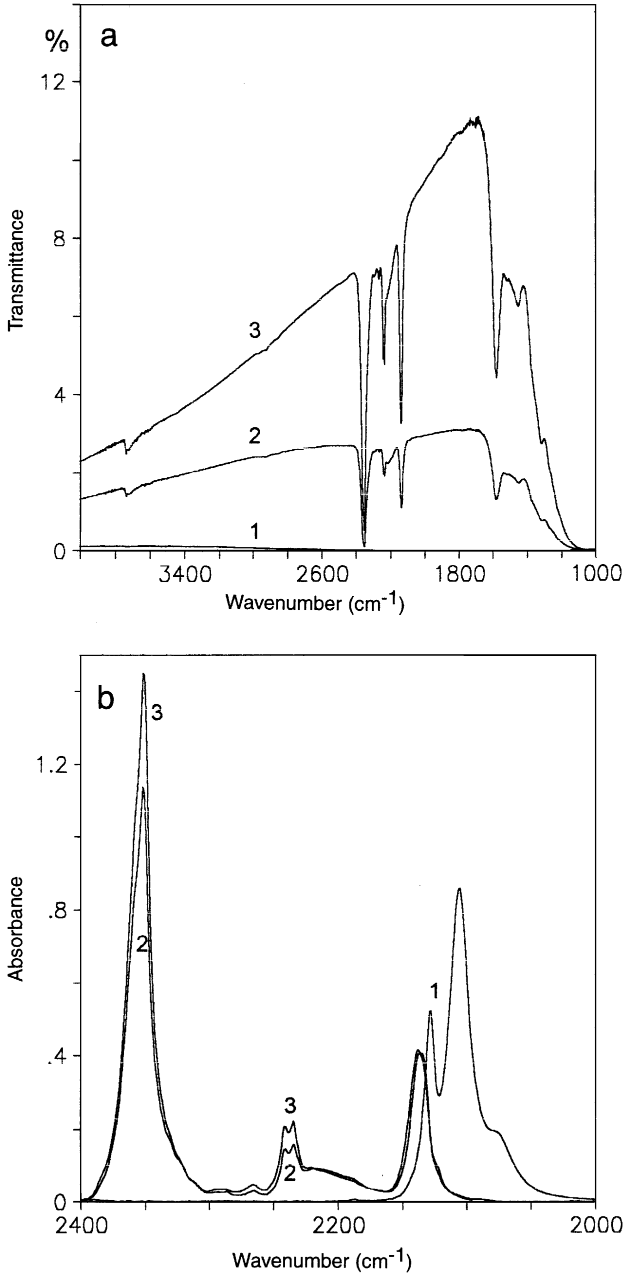

**FIG. 4.** FTIR spectra of NO interaction on sample 8C673 precovered with CO. (a) Full range transmission spectra of the clean sample (curve 1) and after CO/NO interaction for 5 min (curve 2) and 10 min (curve 3). (b) Absorption spectra in the 2400–2000 cm$^{-1}$ range of sample 8C523 precovered with CO (curve 1) and of 8C673 after CO/NO interaction for 5 min (curve 2) and 10 min (curve 3).

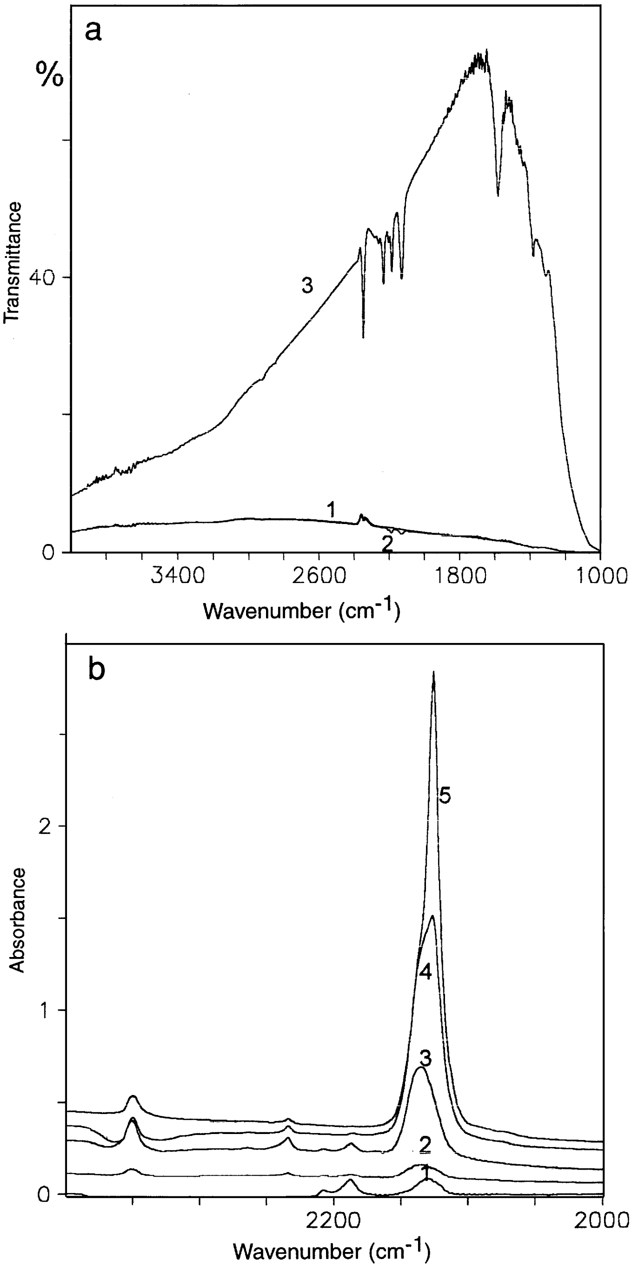

**FIG. 5.** FTIR spectra of NO interaction on sample 2I673 precovered with CO. (a) Full range transmission spectra of the clean sample (curve 1), after interaction with 10 mbar of CO (curve 2), and after inlet of 10 mbar of NO and 5 min of interaction (curve 3). Absorption spectra in the 2400–2000 cm$^{-1}$ range after different CO/NO interactions: 10 mbar of CO (curve 1), inlet of 10 mbar of NO and 5 min interaction (curve 2), 30 min interaction (curve 3), after heating at 373 K (curve 4), after heating at 473 K (curve 5).

chemisorption hydrolysis a broad absorption in the NCO stretching region is observed at all the examined copper loadings (2–8%) and after all the reductive pretreatments (from 423 to 673 K); (iii) the relative intensity of this absorption in respect to $CO_2$, CO and $N_2O$ is maximum on the 4% sample. Isocyanate species can be adsorbed on the oxidic support and on copper sites in different oxidation states. On oxidic supports their stability is primarily determined by the chemical and electronic properties of the support (14a); the absence of isocyanate species on the $Cu/TiO_2$ samples prepared by wet impregnation was interpreted in a previous paper (6) as due to a destabilization of these species on the reduced, highly conductive titania. However, in the C sample examined in this work, absorptions in the spectral region characteristic of NCO species are observed also on the strongly reduced samples. Therefore the previously made hypothesis that isocyanate species were lacking on $Cu/TiO_2$ as a consequence of the high conductivity of reduced titania appears questionable; it is more likely that the formation and stabilization of these species depends on the oxidation state of copper and on the nature and structure of the borderline region between metal and support. Recently Solymosi and Bansagi (14b) studied the adsorption of HNCO on H–ZSM-5 and on Cu-containing ZSM-5, $SiO_2$, and $Al_2O_3$ catalysts. Their data clearly show that the location of the absorption bands due to NCO species bonded to Cu depends on the oxidation state of the copper, i.e., 2230–2240 cm$^{-1}$ for $Cu^0$–NCO, 2200–2210 cm$^{-1}$ for $Cu^+$–NCO, and 2180–2185 cm$^{-1}$ for $Cu^{2+}$–NCO. On the basis of these literature data the broad absorption in the 2220–2180 cm$^{-1}$ range can be assigned to different Cu and Ti–NCO species coexisting on the surface.

Looking at the transmission section of the previously illustrated experiments, it appears that the transmission profiles of the samples reduced at different temperatures differ substantially as regards the shape. These differences, as already discussed previously (1, 6), are due to the presence in the most strongly reduced samples of almost free electrons in the reduced titania, absorbing/reflecting the IR radiation. The C673 and 1673 samples show at the end of the reductive treatment a very low residual transparency; on both of them the admission of NO causes an immediate and significant increase in the IR transmission (Figs. 4a, 6a, and 5a).

After a long time of contact a substantial increase of a component in the CO absorption band at 2130 cm$^{-1}$ is observed on the 2I673 sample (Fig. 5b) and on 2C673 (Fig. 6b). On the 2I673 sample the increase of the band at 2130 cm$^{-1}$, assigned to CO adsorbed on isolated Cu surface sites, up to a value six times 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, on the wet impregnated samples, to an increase of exposed copper sites. The increase of the 2130 cm$^{-1}$ band is significantly smaller on the sample prepared by the chemisorption–hydrolysis method, showing, before NO interaction, the bands at 2103 and 2071 cm$^{-1}$ assigned to CO adsorbed on Cu sites exposed on small copper particles. In order to explain these differences it can be proposed that in the wet impregnated samples a nonstoichiometric

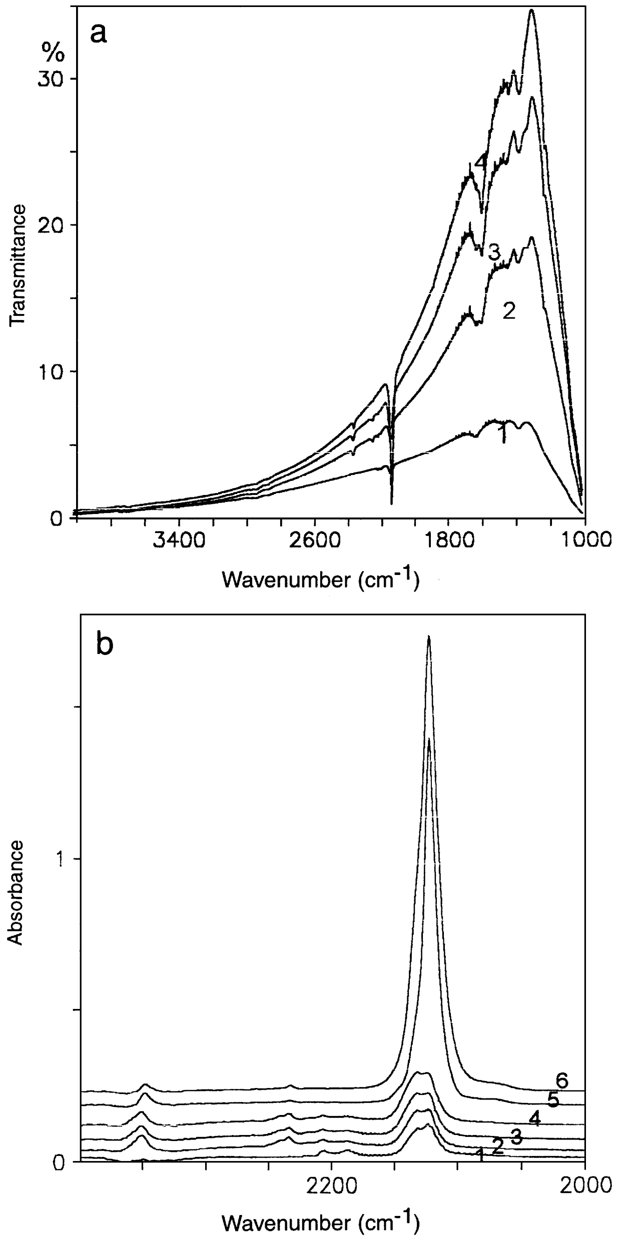

**FIG. 6.** FTIR spectra of NO interaction on sample 2C673 precovered with CO. (a) Full range transmission spectra of the sample precovered with CO (curve 1) and after CO/NO interaction for 1 min (curve 2), 15 min (curve 3), and 15 min at 473 K (curve 4). (b) Absorption spectra in the 2400–2000 cm$^{-1}$ range of the sample precovered with CO (curve 1) and after CO/NO interaction for 5 min (curve 2), 10 min (curve 3), 15 min (curve 4), 15 min at 373 K (curve 5), and 15 min at 473 K (curve 6).

surface layer of copper titanate or, alternatively, a defect-rich amorphous layer of composition TiO$_x$, incorporating copper atoms and small clusters, is formed during the reductive treatments. This phase, by NO interaction, can be reoxidized to TiO$_2$, giving rise to the exposure at the surface of greater amounts of copper sites. As already proposed in the discussion of the HRTEM and TPR data presented in Part I (1), the formation of the amorphous layer could be favored by the presence of anionic impurities at the surface of titania.

Summarizing the previously reported results, on the C samples mildly reduced NO is dissociated on copper small particles, as shown by the depletion of the bands at 2103 and 2070 cm$^{-1}$, not accompanied by the appearance of bands in the NO stretching region. The adsorption of NO on single crystal copper (100) and (110) surfaces studied by EELS revealed that at temperatures above 100 K the adsorption is dissociative and that all species containing nitrogen are desorbed or dissociated below room temperature (17). On samples reduced more severely, both I and C, the inlet of NO produces a very strong increase in the IR transparency, explained by an electron transfer process of free electrons from the reduced titania to the oxygen atoms produced in the NO dissociation. There is, therefore, an indication that *NO dissociation can occur on the examined catalysts on two different kinds of sites, on copper small particles, and on defective reduced titania.*

The high activity in the CO–NO reaction observed on C Cu/TiO$_2$ samples already at RT is interesting. It was important from both a fundamental and a practical point of view to ascertain whether this high activity is a transient phenomenon, typical only of the freshly reduced catalysts and significant only in a first reaction run, or whether it is a permanent phenomenon. In Fig. 7, a comparison is presented of the absorption spectra produced by three

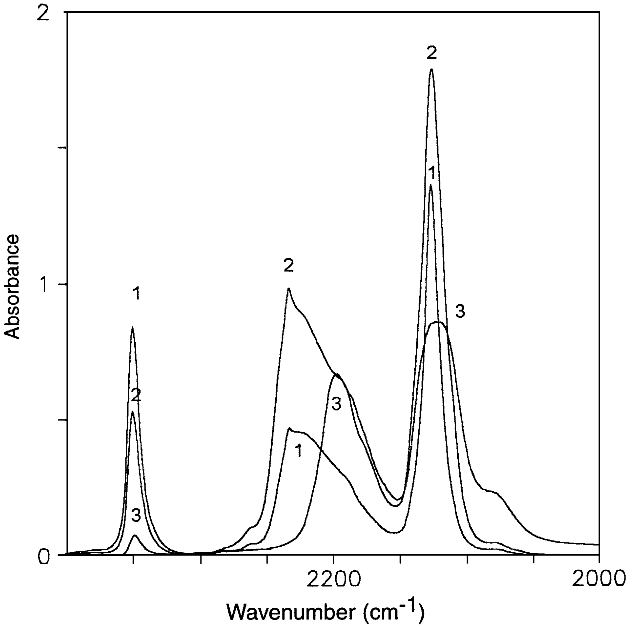

**FIG. 7.** FTIR absorption spectra of different CO/NO interactions on sample 4C523: 10 mbar of NO on a freshly reduced sample precovered with 10 mbar of CO (curve 1); readsorption of 10 mbar of CO and of 10 mbar of NO, after outgassing of the first interaction (curve 2); readsorption, first of 10 mbar of NO and then of inlet of 10 mbar of CO, after outgassing at RT of the previous gas phase (curve 3).

successive CO–NO interactions, all performed on the same 4C523 sample; the first one is on a freshly reduced sample (curve 1), the second one after outgassing at RT the previous reaction mixture and by readsorption firstly of CO and then of NO (curve 2), and the last one after outgassing at RT the previous reaction mixture and readsorbing firstly NO and then CO (curve 3). It can be observed that in the second run of the reaction, with the reagents introduced as in the first run, only limited differences are observed in the reaction products and in the adsorbed species formed; in particular the absorption band of the produced $CO_2$ appears weaker, but stronger bands are observed at 2260–2150 $cm^{-1}$ and in the CO stretching region. These features indicate that in the second run the reaction proceeds with almost the same rate as on the freshly reduced sample. In the last interaction (curve 3) the absorption band of the produced $CO_2$ is almost absent; in the 2260–2150 $cm^{-1}$ region the band is narrower, showing a maximum at 2200 $cm^{-1}$; and the components at 2260–2230 $cm^{-1}$, assigned to $N_2O$, are completely lacking, as also are some components of the absorption band related to NCO species. In particular, the bands at 2230–2240 $cm^{-1}$ and 2220–2210 $cm^{-1}$ are almost completely absent, bands which, according to the assignment of Solymosi and Bansagi (14b), relate to NCO groups bonded to reduced copper sites, $Cu^0$ and $Cu^+$. The absorption band of the CO stretching appears significantly broader and less reversible by outgassing. It is important to notice that the absorption frequencies of CO adsorbed on reduced isolated copper sites and on oxidized copper sites are almost the same, the main difference between the two species being their resistance to outgassing, as also reported by other authors (16).

From these experimental data it can be deduced that the readsorption of NO before CO produces more oxidized copper sites, less efficient in the reaction. The lower activity of copper oxidized sites produced in the last interaction compared to the fully reduced ones confirms our previous results on the impregnated $Cu/TiO_2$ samples (6) and those of Hierl *et al.* on $Cu/Al_2O_3$ samples (4) that reduced copper sites are needed for the CO–NO reaction.

### 3.4. *Relationship between Surface Structure of the Catalyst and Activity in the CO–NO Reaction*

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

$$\text{(a)}\ 2NO + 2CO \rightarrow N_2 + 2CO_2$$

$$\text{(b)}\ 2NO + CO \rightarrow N_2O + CO_2.$$

The mechanisms and the pathways of the two reactions have not been unambiguously determined; in particular, controversy persists as to whether $N_2O$ and NCO are intermediates in the $N_2$ formation.

In order to have an efficient catalyst for the CO–NO reaction, both the molecules must be activated. The best catalysts for NO reduction with CO are Pt group metals (7), but these metals are expensive. Previously quoted work (4, 5) showed that reduced copper catalysts can also be active in this reaction. The following steps can be proposed in a general scheme:

$$CO \xrightarrow{Cu} Cu^0\text{–}CO_{ad} \tag{1}$$

$$NO \xrightarrow{Cu} N_{ad} + O_{ad} \rightarrow \tfrac{1}{2}N_2 + Cu_2^+O^- \tag{2}$$

$$Cu_2^+O^- + CO \rightarrow CO_2 + 2Cu^0 \tag{3}$$

$$NO + e^- \xrightarrow{TiOx} N_{ad} + O_{ad}^- \tag{4}$$

$$NO + N_{ad} \rightarrow N_2O \tag{5}$$

$$N_{ad} + N_{ad} \rightarrow N_2 \tag{6}$$

$$N_{ad} + CO \rightarrow NCO_{ad} \tag{7}$$

$$N_2O_{ad} \rightarrow N_2 + O_{ad}. \tag{8}$$

Carbon monoxide, as shown by FTIR, is molecularly adsorbed on small copper particles and on isolated copper atoms or clusters, whereas nitric oxide does not appear to be molecularly adsorbed at all; in fact no bands are produced in the NO stretching region. However, the presence of oxidation products of CO and NO immediately after NO inlet at RT on 2C473 (Fig. 1b) indicates that NO is dissociated on copper small particles, according to reaction (2) and, on the samples reduced at high temperature, also on reduced titania, following reaction (4). Cu(111) and Cu(100) surfaces are well known for their ability to dissociate nitric oxide even at temperatures as low as 80 K (17). Taking into account that NO dissociation is probably the rate determing step in the CO–NO reaction, the highest activity observed on the C samples when mildly reduced appears related to the high dissociative NO activity of copper metal particles and, furthermore, on these samples, $Cu^0$ sites are readily restored by CO, following reaction (4). The increase observed in the $CO_2/N_2O$ band intensity ratios when increasing the copper loading on the C samples is probably related to a surface structure sensitivity of the selectivity for $N_2O$ formation. In Part I (1) an increase in metal particle size with increase of metal loading was inferred from an analysis of the CO absorption bands, and therefore an effect of metal particle size can be suspected, favoring reaction (a) with respect to reaction (b). Particle-size-dependent effects have been observed on Rh catalysts in the selectivity for the CO–NO reaction (18) and studies of this reaction over Rh(110) and Rh(111) have demonstrated that the selectivity in these reactions is strongly sensitive to the structure of the Rh catalyst metal surface (19); in fact on the (110) surface there was a much stronger tendency toward

$N_2$ production than on the (111) surface. It was suggested that on the (110) surface NO dissociation is less inhibited and leads to greater steady-state concentration of adsorbed N atoms, thus producing more favorable conditions for N atom recombination, relative to the NO + N atom reaction to make $N_2O$. A similar explanation can be also proposed in our case.

On the C samples reduced at high temperature the decrease in the exposed $Cu^0$ sites, produced by the decoration with $TiO_x$ suboxides shown by in the IR experiments discussed in Part I (1), produces a decrease in the activity. This indicates that on these samples the decrease in the number of active sites for reaction (3) is not balanced by the increase of the active phase for the NO dissociation according to path (4) on the $TiO_x$ suboxide.

On the I samples the Cu and $TiO_2$ are interdispersed at an atomic level already in the mildly reduced samples, possibly as an amorphous copper titanate surface layer. The low activity of these samples indicates that the isolated copper atoms exposed at the surface of these samples are far less active in NO dissociation than in the hydrogen dissociation, discussed previously. By increasing the reduction temperature a reduced, defective, electron-rich, nonstoichiometric titania phase is produced, as shown by the decrease in the IR transparency observed, and this phase can be efficient in the dissociation of NO following the reaction (4). On these samples, by increasing the reduction temperature, increasing amounts of almost free electrons are produced that can be efficiently transferred to NO molecules and thereby dissociate them, as a consequence of an electron transfer from the reduced solid to an antibonding orbital of the NO. This explains the higher activity of the high-temperature-reduced I samples.

## 4. CONCLUSIONS

A marked difference in activity is observed in the hydrogenation of 1,3-cyclooctadiene between the catalysts prepared by a chemisorption–hydrolysis method (C) and those prepared by wet impregnation (I), the former showing turnover frequencies about 100 times greater than the latter. This large difference in activity is mainly ascribed to differences in the morphology of the copper species present at the surface of the two different kinds of catalysts: there are three-dimensional stepped small particles of Cu in the first case (C), very efficient in hydrogen dissociation, and isolated copper sites embedded in an amorphous reduced layer in the second case (I) samples. In the CO–NO reaction, C samples show a decrease in activity on increasing the catalyst prereduction temperature, while the opposite behavior is observed on I samples. In this reaction the generally accepted rate determining step is the NO dissociation and this can occur on small copper metal particles and on reduced titania: on mildly reduced C samples the characterization work (1) showed that well-formed three-dimensional copper particles are present, while on I samples reduced at high temperature a reduced titania phase is formed. On this basis the apparently conflicting data can be explained. Moreover, it was also shown that reduced copper sites are also necessary for CO activation, and in fact the reaction activity decreases when oxidized copper is produced by exposing the reduced samples to NO alone.

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