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Nitric Oxide Adsorption and Nitric Oxide–Carbon Monoxide Interaction on Ru/ZnO Catalyst

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The adsorption of NO and the interaction of NO–CO mixtures on Ru/ZnO has been studied by FTIR and mass spectroscopic experiments. NO is adsorbed initially on Ru^0 and Ru^{2+} surface sites present on the reduced catalyst; however, a slow NO dissociation process leads to NO species adsorbed on more oxidized Ru^{3+} sites and to NO_2 species adsorbed on the support. CO reacts at 423–573 K with the NO species dissociated on the Ru sites giving isocyanate and carbonate species spilled over to the support and resistant to decomposition up to 573 K, whereas CO is adsorbed on Ru^0 and Ru^{2+} sites. The formation of large amounts of CO_2 and N_2 has been shown by mass spectroscopic experiments to occur only at $T \geq 473$ K. The opposite reaction of NO interacting with preadsorbed CO leads to CO displacement producing NO and CO species on oxidized Ru and carboxylates or carbonates on the ZnO phase. In this case, with NO predominating in the NO–CO mixture, higher quantities of N_2O, N_2, and CO_2 are formed already at room temperature, whereas isocyanate species are formed in small quantities also at higher temperatures. The mass spectral and FTIR results confirm previous literature data showing that the isocyanates compete with the production of N_2 and CO_2 during the NO–CO reaction on supported metal catalysts. © 1993 Academic Press, Inc.

INTRODUCTION

A previous characterization in our laboratory (*1*) of Ru/ZnO prepared from $Ru_3(CO)_{12}$ carbonyl impregnated and thermally decomposed on ZnO showed a profound effect of the semiconducting ZnO support on the adsorbing properties of the resulting metal: the ruthenium is highly dispersed and is reduced with difficulty to Ru^0 in the usual conditions of reduction, i.e., in H_2 at 623 K. As a consequence of the metal–support interaction, the carbon monoxide is adsorbed geminally on grafted oxidized Ru^{x+} ($x = 2, 3$) ions at room temperature and as species bridged to Ru^0 between 423 and 523 K.

In this paper we study on the same sample the interaction of NO and the activity in the NO–CO interaction by FTIR and mass spectroscopy.

NO is adsorbed as linear species on Ru(001) showing a band at 1800 cm^{-1} (*2*); on supported Ru (*3–6*), bands between 1800 and 1880 cm^{-1} are assigned to NO adsorbed on Ru^0 at 1800 cm^{-1}, on partially oxidized Ru at 1815 cm^{-1}, and on Ru^{2+} and Ru^{3+} at 1860 and 1880 cm^{-1}, respectively.

The NO–CO reaction has been studied on various catalysts because of its interest in the treatment of car exhaust emissions (*7*). Recently it was shown (*8*) that for Pt supported on reducible oxides such as TiO_2 the catalysts reduced at high temperature are more active in NO dissociation, probably as a consequence of an electron donation from the reduced TiO_2 to the adsorbed NO; great amounts of CO_2 and N_2O, intermediates in the formation of N_2, are produced already at room temperature.

We have previously studied the NO–CO reaction on Pt/ZnO catalyst pretreated in different ways (*9*) and a significant effect of the pretreatment temperature and extent of reduction on the NO–CO reaction was evidenced. In this paper we show the importance of the CO/NO ratio and the sequence of adsorption in the formation of intermedi-

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ates such as nitrous oxide and isocyanates and in their resistance to thermal treatments.

EXPERIMENTAL

Ru/ZnO with 0.5 wt% Ru was prepared by impregnating $Ru_3(CO)_{12}$ on ZnO Kadox 25 and activating as previously described (*1*): the final treatment of our samples, hereafter designated R623, is a reduction in the IR cell for 30 min with a 3% H_2/N_2 mixture at 623 K, followed by outgasing from the same temperature to room temperature (RT) under vacuum. All the FTIR spectra were recorded at RT after the thermal and chemical treatments; the spectra were recorded at 2 cm^{-1} resolution and 200 scans by a Perkin–Elmer 1760 spectrometer equipped with a HgCdTe cryodetector. The mass spectra were recorded at the same time at room temperature by connecting the IR cell through a needle valve to a Vacuum Generators VG Micromass 100 instrument: the primary m/z peaks of the gas were utilized to follow the changes in the mass ratios of the mixtures.

O_2, H_2, and CO gases (Matheson) with purity ≥99.8% were used without further purification, whereas NO was freshly distilled before use.

RESULTS

Figure 1, curve a, shows the IR absorbance spectrum produced by NO adsorbed at saturation (pressure ≈3 Torr, where 1 Torr = 133.3 Pa), taken as the difference with the background spectrum of the sample reduced at 623 K. An overall gain of transparency accompanies the NO adsorption, mainly in the low-frequency region as proved by the slope of the curve. The most intense band of the spectrum is at 1858 cm^{-1}, with a shoulder at ≈1810 cm^{-1}. A weak and broad band is formed at 1220 cm^{-1}, which grows slightly in intensity during the time of NO contact, as shown in Fig. 1, curve b. At the same time, the transmission further increases, and the frequency of the main band is shifted in a continuous way up to 1872 cm^{-1}; the shoulder at 1810 cm^{-1} also decreases and very weak bands are formed at 2230 cm^{-1} (N_2O gas) and 1920 cm^{-1}.

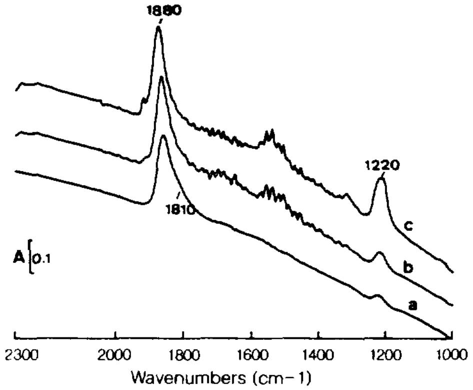

FIG. 1. IR absorbance spectra of NO adsorbed and oxidized on R623. NO adsorbed at 3 Torr at room temperature minus the R623 background: (a) spectrum recorded immediately, (b) after 20 min, and (c) after 16 h contact with 8 Torr O_2.

The increase in the IR transmission observed during the experiments indicates, as discussed in previous papers on similar samples (*3*, *9*, *10*), that the electrons produced in *n*-type semiconducting ZnO by reduction are trapped by the O atoms produced by NO dissociation. Therefore the shift of the band of adsorbed NO from 1810 to 1872 cm^{-1} can be related to a concurrent process of Ru oxidation (*3*). We confirmed this hypothesis by flowing O_2 at 8 Torr into the cell: as a result (Fig. 1, curve c) the main band is further shifted to 1880 cm^{-1} and also the bands at 1920 and 1220 cm^{-1} (see the following discussion) are intensified.

Figure 2, curve a, shows the spectrum of NO adsorbed at saturation on R623 and then contacted with CO. The IR spectrum is dominated by the absorption due to adsorbed NO at 1870 cm^{-1} with a minor band at 1220 cm^{-1}, as in Fig. 1, plus a pair of bands at 1577 and 1330 cm^{-1} assigned to carboxylate-like species adsorbed on the support (*11*).

Heating in contact with the CO–NO mix-

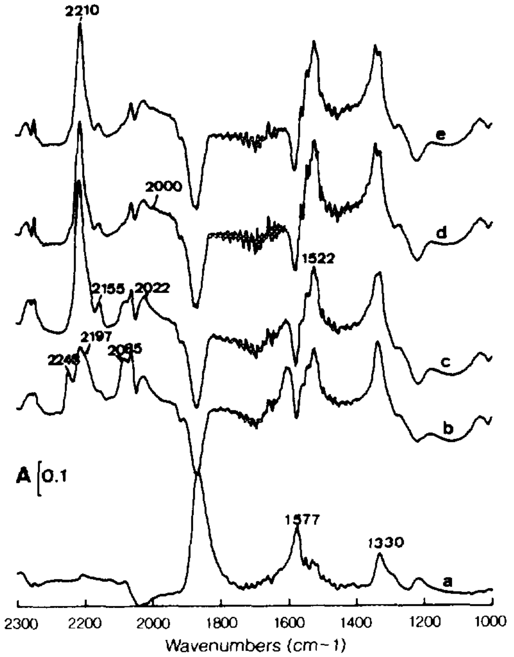

FIG. 2. IR absorbance spectra of NO+CO adsorption on R623. Curve a: NO adsorbed at 3 Torr and then contacted with CO at 20 Torr and room temperature (NO/CO ratio = 0.4) minus the R623 background. Curve b: sample heated 15 min at 423 K in the previous CO/NO mixture minus the spectrum reported in curve a. Curves c, d, e: Like b, but samples heated 15 min at 473, 523, and 573 K, respectively.

ture at 423 K gives the spectrum of Fig. 2, curve b. This is reported as the difference between the spectrum after the 423 K heating and that of curve a; the same accounts for curves c, d, and e showing the effect of heating at 473, 523, and 573 K, respectively. A strong decrease is observed both for the bands of adsorbed NO at 1870 and 1220 cm^{-1} and for the band at 1577 cm^{-1}. New species give bands at 2248, 2208, 2197*sh*, 2155*w*, 2085, 2060, 2022 cm^{-1}. Some carbonate-like bands (*11*) increase or are shifted in frequency by the heating treatment at 1522, 1340–1330, and 1040 cm^{-1} and then remain at nearly the same frequency; some components with slightly increasing intensity are formed during the heating at higher temperature (curves c–e).

The composition of the gas phase initially in contact with this sample, determined by quadrupole mass spectroscopy, showed a 30/28 *m*/*z* ratio of 0.4. On heating to 423 K, the 30/28 *m*/*z* ratio decreases sixfold with respect to the room temperature ratio and the NO *m*/*z* peak nearly disappears; at the same time, the 44 *m*/*z* signal is strongly magnified. The mass spectral experiments can be ambiguous as they concern the products expected from the CO–NO reaction: the product N_2 shows the same 28 *m*/*z* peak as the reactant CO; moreover, the products CO_2 and N_2O have the same 44 *m*/*z* peak. Nevertheless, the decrease of $m/z = 30$ and the growth of $m/z = 44$ confirm an NO dissociative reaction.

After heating to 473 K, the NO species at 1870 and 1220 cm^{-1} are fully eliminated ("negative" bands), whereas the band at ≈2210 cm^{-1} reaches its maximum intensity, then decreases at 523 and 573 K. The band at 2248 cm^{-1} decreases, whereas that at 2155 cm^{-1} resists the thermal treatments. No other relevant changes are observed at this temperature except the elimination of the band at 2085 cm^{-1} and the growth of a weak and broad band at ≈2000 cm^{-1}.

The mass spectral analysis shows that the NO is fully eliminated, and a *m*/*z* ratio 44/28 = 2 is obtained; this ratio decreases to 1.8 at 523 K and to 1.54 at 573 K, while the IR spectrum does not change significantly.

An experiment similar to that reported in Fig. 2, but with CO adsorbed before NO, is illustrated in Fig. 3. The sample was the same as in the previous experiment and had been previously reduced by CO at 623 K: This treatment should lead to a well-reduced Ru catalyst (*1*). The CO adsorption at RT (curve a) therefore shows a band with maximum at 2058 cm^{-1}, typical of CO adsorbed on Ru^0 (*1*), with only a minor component at 2113 cm^{-1}. Flowing NO into the cell to give a mixture with a ratio NO/CO = 1.6 led to the spectrum, recorded immediately, reported in Fig. 3, curve b. The spectrum of adsorbed CO is strongly perturbed,

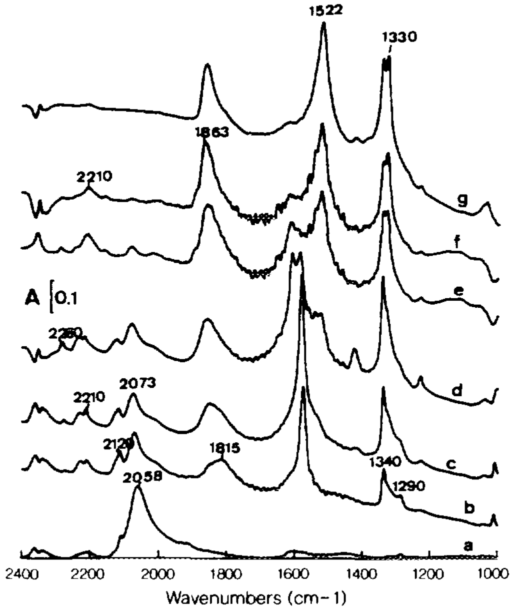

FIG. 3. IR absorbance spectra of CO+NO adsorption on R623 reduced at 623 K with CO. Curve a: CO adsorbed at 5 Torr and room temperature minus the background. Curve b: the same as curve a but subsequently contacted with 5 Torr NO (NO/CO ratio = 1.6). Curves c and d: as b, but after 15 and 200 min, respectively. Curves e, f, and g: after heating for 15 min in the NO/CO mixture at 423, 473, and 523 K, respectively.

and a competitive NO adsorption is shown by the bands at 1815 and 1852sh cm^{-1}; a CO oxidation is proved by the growth of intense carboxylate or carbonate bands at 1577, 1340, and 1290*sh* cm^{-1}, whereas new bands are formed or enhanced at 2073, 2120, 2210, 2230, 2280, and ≈2350 cm^{-1}. The formation of N_2O and CO_2 species is proved by the latter three bands and by the presence of a considerable amount of $m/z = 44$ with m/z ratio 44/28 = 0.8. The CO oxidation by NO is confirmed by the development of the IR spectrum with time reported in curves c and d: the carbonate bands at 1577 and 1340 cm^{-1} grow and new components, mainly after 200 min, form at 1608, 1522, 1423, and 1230 cm^{-1}. Also the spectrum of adsorbed NO is changed, with a decrease in the 1815 cm^{-1} component and an increase in the 1852 cm^{-1} component, shifted finally to 1863 cm^{-1}. By heating at 423 K, curve e, the spectrum in the carbonate range is strongly modified with the overwhelming of the component at 1522 cm^{-1} and the rise of another component at 1330 cm^{-1}; this behavior is confirmed also by increasing the temperature to 523 K (curves f and g). Moreover, in the temperature range between 423 and 523 K, the bands at 2280 and 2230 cm^{-1} tend to decline, while the band at 2210 cm^{-1} reaches its maximum intensity at 423 K and then declines. Also the CO bands at 2073 and 2120 cm^{-1} decrease already at 423 K and disappear at 523 K. The CO_2 band at 2350 cm^{-1} is stronger at 423 K, but in this case quantitative data can be seriously perturbed by a different concentration of CO_2 background in the room during the period of the experiments. At 523 K, only the NO species at 1863 cm^{-1} and the carbonate species at 1522, 1340–1330, and 1040 cm^{-1} remain on the surface.

The mass spectral results reveal a profound modification of the NO–CO mixture already after heating at 423 K. The nitric oxide is strongly diminished, the 30/28 m/z ratio is lowered from 1.6 to 0.25, and also the signal at m/z 44($N_2O + CO_2$) is formed in great amount, the 44/28 m/z ratio reaching the value 2.85.

At 473 K, the signal at m/z 30 of NO is nearly absent and only species with m/z 44 and 28 remain in the cell, but with a ratio (1.24 declining to 0.85 at 523 K) favoring the m/z 28 (N_2) with the increase of the temperature.

DISCUSSION

(*a*) *NO Adsorption*

The experiment of NO adsorption reported in Fig. 1 is easy to interpret. The shoulder at 1810 cm^{-1} can be assigned, following the literature (*2–6*), to NO chemisorbed on a reduced Ru^0 site, but the major part of the NO is evidently adsorbed on oxidized Ru^{2+} sites as linear and monomeric species at 1858 cm^{-1}: these sites are already present on the R623 sample and can adsorb CO as geminal species (*1*). Moreover, an absorption at 1870 cm^{-1} or at higher wavenumbers increases for high contact times of NO (curve b) or after O_2 adsorption (curve c). This can be assigned to NO adsorbed on Ru^{3+} sites formed by an NO dissociation process on the Ru and/or on the ZnO defect sites: the oxygen atoms (or the small amounts of N_2O detected in the spectrum) produced in the NO dissociation can oxidize the ruthenium to Ru^{3+}. The oxidative reaction induced by NO dissociation is proved also by the presence of the band at 1220 cm^{-1} increasing from curve a to c and assigned to a NO_2^- species chemisorbed on the ZnO (*10*); also the weak band at 1920 cm^{-1} can be assigned to an oxidized NO_2 species (*4*).

(*b*) *NO+CO Adsorption*

Some dissociation of NO at RT is evidenced in Fig. 2, curve a, by the formation, with CO, of carboxylate groups at 1577 and 1330 cm^{-1} on the ZnO phase (*11*), by a very weak band at 2205 cm^{-1}, assigned to an isocyanate group, and by the detection of traces of the m/z 44 peak of the N_2O and CO_2 species. At RT, the NO–CO reactivity is very low; however, already at 423 K the isocyanate species becomes intense and gains its maximum intensity at 473 K, forming at the expense of the adsorbed NO at 1870 cm^{-1}. At 423 K, other bands appear in the same spectral region, at 2248, 2208, and 2197 cm^{-1}, and these can be assigned to isocyanate species bonded to different sites of the support and/or of the ruthenium.

Recent data for the Ru(001) surface (*12*) show that an isocyanate species at 2170 cm^{-1} is formed by exposure to CO of a Ru surface that had preadsorbed and dissociated NO: the maximum intensity is reached by this species at 300–330 K, but at 373 K it fully decomposes. An isocyanate species characterized by a band at 2180 cm^{-1} is formed at 300–473 K on Ru supported on silica by CO interaction with preadsorbed NO (*5*). However, following the hypothesis previously advanced by Solymosi and coworkers (*13*), on supported transition metals the isocyanate species is formed by CO interaction with a metal–*N* species produced by NO decomposition and migrating by a spillover mechanism on to the support, where it can be stabilized to different extents depending on the nature and ionicity of the support. The isocyanate asymmetric stretching mode frequency is higher for the more covalently bonded group [i.e., 2318 cm^{-1} on silica (*13*), 2267–2246 cm^{-1} on alumina (*13*, *14*)], and on these supports high stability is shown at higher temperatures. The frequency is lower and the thermal stability is reduced for more ionic isocyanates: on TiO_2, an *n*-type semiconductor support like ZnO, the frequency is shifted to 2210 cm^{-1} (*13*). The assignment of the bands in the frequency range 2300–2200 cm^{-1} to isocyanate species spilled over onto the support has been exhaustively proved by experiments on HNCO adsorption (*13*) and confirmed recently by observations on the CO–NH_3 reaction on Ru/Al_2O_3 using isotopically labeled gas (*14*). Therefore the band at 2210 cm^{-1}, formed with high intensity at $T \geq 423$ K, is assigned to isocyanate species formed on the Ru and then migrating on to ZnO, as on Pt/ZnO (*9*), where it was found at 2220 cm^{-1}. We cannot exclude a priori the possibility that some isocyanate groups are adsorbed on the oxidized Ru sites: The transient bands at 2248 and 2197 cm^{-1}, formed at 423 K and disappearing at higher temperatures, could therefore be tentatively assigned to isocyanates on Ru^{x+} (x = 3 and 2, respectively) sites.

The weak band at 2155 cm^{-1}, resistant to high temperature, can be assigned to a cyanide group (*15*) formed by reduction of the isocyanate.

During the reaction, some carboxylate species are converted to different bidentate or polydentate carbonates with maxima shifted to 1522, 1340–1330, and 1040 cm^{-1}. Moreover, at $T \geq 423$ K, the CO substitutes for the NO in the Ru coordination, and the

1870 cm^{-1} band completely disappears; however, notwithstanding the preponderance of reducing CO gas in the mixture, the frequencies at 2085 and 2022 cm^{-1} are in agreement with CO adsorbed on Ru^{2+} sites in geminal form (*1*, *16*) rather than on Ru^0. The Ru^0–CO species, formed by Ru^{x+} reduction at 523–573 K by CO, can be correlated with the band at 2060 cm^{-1} and with the broad and weak band at ≈2000 cm^{-1} (see curves d and e).

The mass spectroscopic experiments clearly indicate the presence of CO_2, as confirmed by the FTIR results of Fig. 2 showing both the CO_2 gas phase at 2350 cm^{-1} and the carbonates formed by CO_2 adsorbed on the support.

The mass data at 473–573 K can be interpreted in terms of the simple reaction

$$2CO + 2NO \rightarrow 2CO_2 + N_2 \qquad (1)$$

with the prevailing of m/z 44 over m/z 28: at 473 K the m/z ratio 44/28 of the products is exactly 2 as in Eq. (1). The literature (*7*) shows that on supported Ru this reaction is faster than on other noble metals and nearly complete at 473 K.

A contribution to the products CO_2 and N_2 from isocyanate decomposition is relevant only at $T \geq 523$ K, i.e., when the isocyanate band begins to decrease; however, the m/z ratio 44/28 decreases to 1.8 and then to 1.54 at 573 K, showing that the isocyanate species delays reaction (*1*).

Finally, we note that the isocyanate species formed on Ru/ZnO occurs at a slightly different frequency and is more stable than the species formed on Pt/ZnO (*9*). The different frequency and thermal stability of the isocyanate species adsorbed on the same ZnO support could be attributed to the different contact area and dispersion of the metallic phase (*13*). Another contribution to the different stability of this species can be attributed to differences in the electronic properties of the support in contact with differently reduced metals. Our previous papers (*1*) on the same Ru/ZnO catalyst show that Ru is not easily reduced. On Pt/ZnO samples it was shown (*9*) that by reduction at 573 K, a PtZn intermetallic phase is formed, in ohmic contact with a highly conductive ZnO. As a consequence, the different electronic state of the support makes the decomposition of the adsorbed isocyanate easier by decreasing the positive charge carried by the surface cations coordinating the anionic isocyanate species.

(*c*) *CO+NO Adsorption*

The experiment reported in Fig. 3 has been performed on a well-reduced sample, i.e., reduced with H_2 and then with CO at 623 K (*1*): the good reduction to zero-valent ruthenium is confirmed (curve a) by the intense band at 2058 cm^{-1}, assigned to CO adsorbed linearly on Ru^0 with only a minor band at 2113 cm^{-1} assigned to CO on Ru^{x+} (x = 1 or 2) (*16*, *17*). The total absence of bands in the carbonate region confirms the good reduction of the sample. However, the NO adsorption, with this gas prevailing in the NO–CO mixture, displaces CO from Ru^0 already at RT; carbon monoxide is partially oxidized already at RT and nitrous oxide is quickly formed by the reaction of NO with N produced by NO dissociation. N_2O is an intermediate in the N_2 formation (*8*). The main reaction at RT is therefore

$$CO + 2NO \rightarrow CO_2 + N_2O \qquad (2)$$

Carbon monoxide is partially replaced by NO on Ru^0 with the band at 1815 cm^{-1}; the Ru^0 is also oxidized at RT, as shown by the rise with time of the bands at 1852–1860 cm^{-1} (NO on Ru^{2+}) and at 2120 and 2073 cm^{-1} (CO geminally adsorbed on Ru^{3+}). (*1*) Carbonate-like bands grow at the same time at 1577 and 1340 cm^{-1}, accompanied for longer times of contact by bands at 1608, 1423, and 1230 cm^{-1} assigned to bicarbonate groups (*11*). The formation of CO_2 is attested by the band at ≈2350 cm^{-1}, whereas the band at 2230 cm^{-1} is assigned to the asymmetric stretching mode of physisorbed N_2O; the weak band at 2280 cm^{-1} can be assigned to N_2O chemisorbed through the terminal nitrogen to ions Ru^{x+}

or Zn^{2+} of the support, in agreement with the literature on chemisorbed N_2O (*18*). Some contribution of the reduced support to the formation of N_2O can be invoked for the supported ruthenium because this gas is not found or is found in only small quantities on unsupported Ru monocrystals (*2*).

The weak band at 2210 cm^{-1}, assigned to the isocyanate species, is formed already at RT and remains at low concentration at higher temperatures (see Fig. 3, curves e and f) and vanishes at 523 K (curve g). At this temperature, only a carbonate species remains on the surface, as for the NO–CO mixture, but with residual Ru^{3+}–NO groups.

It follows from the discussion so far that the NO–CO reactivity, i.e., the formation of N_2O and isocyanate intermediates and of the products CO_2 and N_2, is strongly influenced on supported catalysts by:

(i) the extent of reduction of the supported metal and of the semiconducting support;

(ii) the sequence of admission of NO and CO, with formation of species adsorbed with different stability on the metal;

(iii) the relative pressure of CO and NO, as found by Solymosi *et al.* (*13*) on Rh/Al_2O_3.

As previously discussed, Ru is reduced with more difficulty than Pt, at least on ZnO, and it is easily oxidized by NO itself. Higher temperatures of reduction are therefore required to reduce the ruthenium. Moreover, if NO is adsorbed before CO, after an initial step of dissociative adsorption on the reduced catalyst, molecular NO species strongly adsorbed on Ru^{x+} sites are formed; these hinder the CO activation and therefore the formation of isocyanates or of the products in great amounts at $T \leq 423$ K. In fact, on Ru the NO is adsorbed as species that are more stable than adsorbed CO, and the latter does not displace NO until 423–473 K (Fig. 2, curves b and c). The opposite behavior is shown by Pt/ZnO (*9*) and Pt/TiO_2 (*8*).

This behavior follows exactly that found for a similar CO–NO adsorption experiment on Ru/SiO_2 (*5*): NO depletes CO with formation of two bands at 1815 and 1860 cm^{-1}, and the isocyanate species is not formed under these conditions at 300–473 K, whereas this occurs for the opposite NO–CO adsorption.

If CO is adsorbed before NO, as in the experiment reported in Fig. 3, it can be molecularly chemisorbed and activated on free Ru sites; the subsequent admission of NO on the well-reduced sample partially displaces CO at RT producing N and O atoms that can easily react with activated CO leading to the formation of the products, N_2O and CO_2, already at RT.

As for the effect of the reaction mixture composition on the intermediate and formation of reaction products, we note that the predominance of CO content in the NO–CO mixture favors the formation of isocyanate species, whereas the predominance of NO favors the formation of N_2O and of a Ru^{x+}–NO ($x = 2, 3$) species, more resistant than CO to higher temperatures (*4a*) and dissociated with more difficulty. A similar behavior has been found on Ru/TiO_2 (*19*).

On Pt/TiO_2 (*13*) and Pt/ZnO (*9*), a minor stability to the heating of the isocyanate groups was observed: This could be due simply to the different stability of these species in the borderline region between the metal and the *n*-type semiconducting reduced supports. However, *n*-type semiconductors are characterized, if reduced, by a significant concentration of almost free electrons that can destabilize the adsorbed anionic isocyanates by decreasing the positive charge of the surface cations coordinating the anionic isocyanate species.

These factors and the stability of isocyanates on both the metal and the support sites can influence the relative ratio of the products (CO_2 and N_2) at temperatures between 473 and 523 K. At these temperatures, the mass spectral data for the CO–NO sequence of adsorption (the m/z ratio 44/28 is 1.24 and 0.85 at 473 and 523 K) favor N_2 instead of CO_2, and therefore the reaction should be different from reaction (1). At $T < 473$ K, the NO is easily dissociated to N+O on the metal producing first N_2O following reaction (2) and then N_2 if NO prevails in the NO–CO mixture: because both N_2O and isocyanate species are formed by the same mechanism, i.e., by reaction of NO or CO with the Ru–N intermediate formed by NO dissociation (5), the formation of isocyanate and N_2O species compete.

Otherwise with a CO–NO mixture enriched in CO (part b) the isocyanate species is formed in good quantity and fills the Ru sites until 423 K (see the bands at 2248 and 2197 cm^{-1}): at this temperature the isocyanate groups partially (and fully at 473 K, see the band at 2210 cm^{-1}) spill over to the support, leaving the Ru sites free for reaction (1). The isocyanate is therefore a poison for the reaction giving the desired CO_2 and N_2 products, at least for $T \leq 473$ K.

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