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Ru/ZrO_2 Catalysts

I. O_2, CO, and NO Adsorption and Reactivity

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The Ru/ZrO_2 catalyst's surface properties have been studied by quantitative chemisorption experiments on carbon monoxide and oxygen at different temperatures, by FTIR studies of oxygen, carbon monoxide, and nitric oxide adsorptions, and by FTIR studies of the CO–NO reaction. On the oxidized sample at least three FTIR absorptions are evident at 1008, 980, and 950–940 cm^{-1}. All the observed bands can be assigned to Ru–O surface species, differing in the oxidation state of ruthenium directly bonded to oxygen, the degree of metal–oxygen π bonding, and the coordination of the Ru atoms with the support. The larger heterogeneity of the bands observed on Ru/ZrO_2 catalyst, with respect to that previously detected on Ru/ZnO, can be taken as an indication that a significant role is played by the coordination properties and the surface features of the support. The strong increase of the band at 1008 cm^{-1} at temperatures higher than 573 K can be ascribed to the increase of the surface concentration of Ru–O surface species bonded to an Ru atom with an oxidation state higher than 4. The CO adsorption on the oxidized sample evidences the full reactivity of Ru–O species toward CO between room temperature (RT) and 473. CO and NO chemisorptions on reduced samples show that the two molecules are both molecularly and dissociatively adsorbed on the catalysts. The NO admission on preadsorbed CO produces immediately a significant modification of the adsorbed CO spectrum, i.e., a reduction of the intensity of the band assigned to CO adsorbed on Ru° sites and the appearence of additional bands that can be assigned to N_2O, NO, and carbonate species. These features indicate that NO is immediately dissociated on Ru already in the presence of preadsorbed CO and gives rise to N_2O and CO_2 already at RT. Upon heating at 373 K the N_2O absorptions and the bands ascribed to CO adsorbed species are depleted and that of CO_2 increases, indicating that the reaction $2CO + 2NO \rightarrow N_2 + 2CO_2$ may prevail on the catalyst. © 2000 Academic Press

Key Words: **ruthenium catalyst supported on zirconia; FTIR spectroscopy of Ru–O surface species; FTIR study of CO chemisorption; FTIR study of NO chemisorption; characterization of oxidized and reduced sample; CO–NO reaction.**

1. INTRODUCTION

During the past 20 years ruthenium catalysts supported on different oxides have been widely investigated. The high reactivity and selectivity of Ru in CO hydrogenation, in hydrogenolysis reactions, in aromatic hydrogenation, and in the $deNO_x$ processes are well known in the literature (1, 2). Recently, a review appeared concerning ruthenium-catalyzed reactions for organic synthesis (3). The adsorption of H_2, O_2, NO, N_2O, and mainly CO on ruthenium supported on the most common supports (4) has been extensively studied and compared with that obtained on unsupported Ru, mainly on the (0001) hexagonal basal face (5). In the adsorption of gases such as CO and NO, infrared techniques have been largely utilized in studies on both the supported and the unsupported samples. The study of the adsorption of these molecules is important for the characterization of the exposed surface sites and with respect to the catalytic properties of the ruthenium catalysts in the N_2O decomposition that will be reported in the next paper (6).

CO adsorption on Ru° surfaces produces a CO vibrational stretching band in the 1990–2060 cm^{-1} range, blue shifting with the increase of the coverage as a consequence of dipole–dipole and chemical effects. It was shown by Pfnur *et al.* (7) that on monocrystalline surfaces these effects lead to a decrease in the intensity of the IR band at high coverage. Recent studies at coverages higher than 0.25 of the monolayer of CO on a Ru surface precovered with 0.5 monolayer of oxygen atoms adsorbed on the threefold (hcp) sites have evidenced the formation of a CO bridge bonded species probably located on the threefold (fcc) sites, in addition to the linearly bonded species on the top sites.

A significant difference between monocrystalline and supported Ru catalysts concerns the broadness of the absorption bands on the supported ones: full width at half-maximum (fwhm) 8–12 cm^{-1} vs 40–80 cm^{-1}, respectively. The significantly higher broadness of the bands usually detected on the supported catalysts is probably due to the

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overlap of the absorption bands of CO adsorbed on crystallites of different size and/or differently contaminated by oxygen. Moreover, on supported reduced ruthenium catalysts, the Ru°–CO species on top bonded is often accompanied by other absorptions in the range 2140–1980 cm^{-1} assigned to $Ru^{x+}(CO)_{2,3}$ species. Their intensities depend on the catalyst preparation, reduction conditions, CO pressure, and contact time. However, these bands are always present in the experiments on CO interaction at room temperature (RT). Hadjivanov *et al.* (4) showed that these bands are formed at RT as a consequence of the oxidation of ruthenium sites produced by CO dissociation. In fact, these bands are not detected by CO adsorption at liquid nitrogen temperature and they are not observed at RT at low CO pressures and contact times, as will be shown in this paper.

The question of the oxidation state of ruthenium under reducing and oxidizing conditions at different temperatures is of fundamental importance. However, no direct information on this point can usually be obtained by IR because the Ru–O stretching region is, in the case of the most usual supports, masked by the support absorptions. Under oxidizing conditions, IR evidences of the existence of an Ru–O species were found by some of us for an Ru/ZnO catalyst. In this paper we will discuss a variety of Ru–O FTIR bands and their different thermal stability and reactivity toward CO.

To our knowledge, the studies concerning the characterization of Ru/ZrO_2 surfaces seem to be very few and they do not report detailed characterization results (8). In the present work results on the characterization of Ru/ZrO_2 catalysts obtained by performing FTIR studies of CO, NO, and O_2 chemisorption and determining the amounts of CO and O_2 chemisorption will be presented. In the following paper (6) results concerning the adsorption and reactivity of N_2O gas on the same Ru/ZrO_2 catalysts will be presented.

2. EXPERIMENTAL

2.1. *Materials*

ZrO_2 was prepared by dropping a 28% ammonia solution into an aqueous solution of $ZrOCl_2 \cdot 8H_2O$ with stirring. After filtration, the precipitated zirconium hydroxide was washed several times with slightly warm ammonia solution (pH 8) until the disappearance of chloride ions ($AgNO_3$ test). The precipitate was dried in an oven at 388 K for 15 h and calcined at 823 K for 2 h in a stream of air (2.5 l/h). The resulting BET surface area was 55 m^2/g. The catalyst was prepared by incipient wetness impregnation of the ZrO_2 support with an aqueous solution of $RuCl_3$, followed by drying at 383 K for 15 h and a subsequent 20 h calcination at 773 K. The Ru content was 0.6 wt%.

2.2. *Methods*

O_2 and CO chemisorptions measurements were performed by a pulse-flow technique, using a Gow-Mac TC detector (9). Prior to each measurement, the sample was subjected to a thermal pretreatment which involved exposure to H_2 at 773 K for 1 h, followed by He purge at the same temperature for 3 h. The sample was then cooled in He flow to 298 K for the O_2 and CO chemisorption experiments. Additional O_2 chemisorptions were performed at different temperatures, in the range 298–570 K, after the above described pretreatment procedure (H_2 exposure at 773 K).

FTIR experiments were performed in a cell operating at different temperatures under a controlled atmosphere, using a Perkin-Elmer FTIR 1760 and a Perkin-Elmer 2000 FTIR spectrometer, at a resolution of 2 cm^{-1}. The experiments were carried out on samples preliminarly calcined at 773 K (O773) or reduced in H_2 at 773 K (R773). At the end of each reduction treatment H_2 was evacuated at the same temperature. The curve-fitting analysis of the FTIR bands was performed by adding three Lorentzian curves. The graphical representation of the RuO_x surface phase has been made by Moldraw (10).

3. RESULTS AND DISCUSSION

3.1. *Quantitative Chemisorption Data*

In Table 1 are reported the quantitative data of O_2 and CO chemisorption performed on the sample reduced at 773 K. Taking as a reference the coverage observed on metallic Ru monocrystalline samples by interaction with CO and O_2 at RT (7, 11), a stoichiometry $O/Ru_s = 1$ and $CO/Ru_s = 0.7$ can be assumed. In this respect the chemisorption data obtained at room temperature are somehow odd and do not allow a meaningful calculation of the dispersion. On the other hand, they indicate that the majority of the Ru atoms are exposed on the surface.

The O_2 chemisorption performed at temperatures higher than 298 K shows that the O/Ru ratio smoothly increases and at 570 K a value of 2.22 is found. A ratio larger than 2 can be taken as an indication that at the surface of the RuO_2 surface layer some RuO_3 clusters are produced. This hypothesis will be discussed more deeply after the presentation of the spectroscopic data in the next section.

3.2. *FTIR Absorptions of Ru–O Surface Species*

Figure 1a shows the transmittance spectra of an O773 sample and an R773 sample in the full spectral range. It

TABLE 1

O_2 and CO Chemisorption Data on Sample Reduced at 773 K

Chemisorption temperature (K)	O/Ru	CO/Ru
298	1.3	0.8
373	1.5	
469	1.77	
570	2.2	

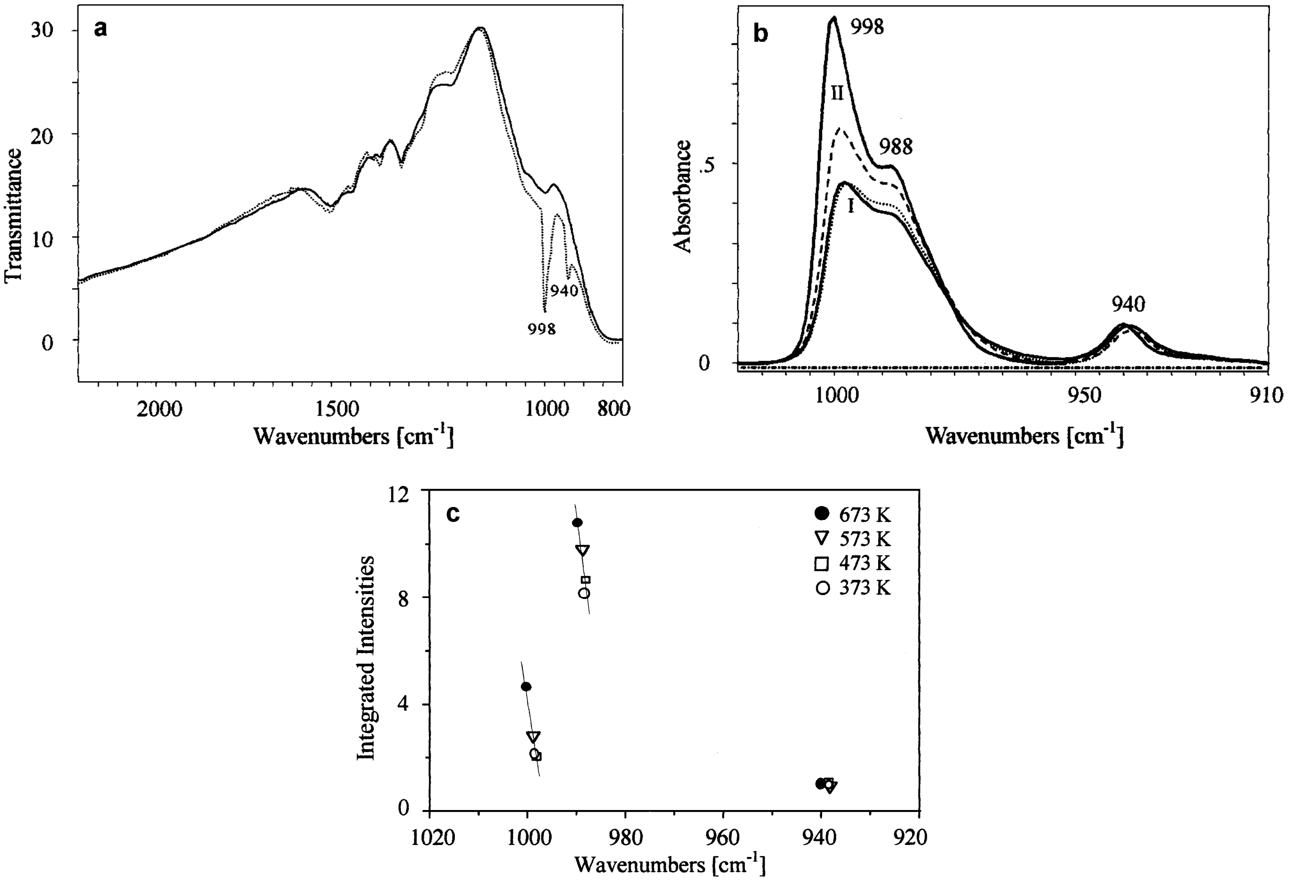
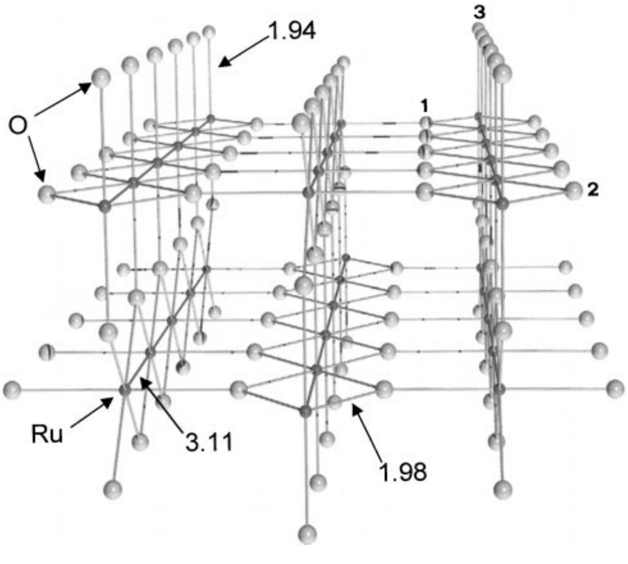


FIG. 1. FTIR absorptions of Ru–O surface species. (a) Comparison between the transmission spectra of the O773 sample (full line) and the R773 sample (dashed line) in the 2400–800 cm^{-1} range. (b) Absorbance spectra in the 1100–900 cm^{-1} range produced by oxygen interaction on a R773 sample at increasing temperatures: dash-dotted curve, interaction at RT; thin line, interaction at 373 K; dotted line, interaction at 473 K; dashed line, interaction at 573 K, bold line, interaction at 673 K. (c) Integrated intensities vs the frequency maxima of the bands obtained by the curve fitting of the spectra reported in panel b.

appears evident that the only difference between the two spectra is observed in the 1100–900 cm^{-1} region. At least three absorptions are evident at 998, 988, and 940 cm^{-1} as shown more clearly in Fig. 1b. At lower frequencies the sample is fully absorbing as a consequence of the support absorption. These absorptions (Fig. 1b) are quite broad and probably structured, although, for the sake of brevity, we will consider them as three bands.

Figure 1b shows the formation of these bands starting from a reduced sample (R773) by increasing gradually the temperature under an oxygen atmosphere. Oxygen interaction at RT (dash-dotted curve) does not produces an IR band in the 1100–900 cm^{-1} spectral region in spite of a significant amount of chemisorbed oxygen reported in Table 1 (O/Ru ratio = 1.3). This behavior can be understood on the basis of a LEED study, showing that O$_2$ on monocrystalline Ru(0001) is dissociatively adsorbed in the hollow sites (12). In these sites the oxygen atoms are bonded in a totally symmetric way to three Ru atoms (positions 1 in Scheme 1). The vibrational spectra of this phase exhibit a



SCHEME 1

single band, shifting from 516 cm^{-1} at low coverages up to 596 cm^{-1} at high coverages (12) attributed to the stretching mode of atomic oxygen normal to the surface, in hollow sites. On the basis of these data, we propose that the oxygen adsorbed at RT produces an IR absorption in a region obscured by the support absorption. The Ru/O ratio larger than 1 obtained in the quantitative chemisorption experiments at RT (see Table 1) is probably related to the penetration of some oxygen into the subsurface region.

The 988 and the 940 cm^{-1} absorptions increase (full line curve) at 373–473 K. However, as is evident from both the spectra and the results of the curve fitting reported in Fig. 1c, the bands are not correlated. In fact, the absorption at 940 cm^{-1} reaches its maximum intensity at 373 K, while the absorption at 988 cm^{-1} gradually increases in intensity from 373 up to 673 K. Similarly, the higher frequency component at 998 cm^{-1} increases rapidly in the temperature range 573–673 K. Therefore, the bands cannot be assigned to a single surface species, containing more than one oxygen atom, but to different surface species, formed in the different temperature ranges.

Unfortunately, very few data concerning the vibrational features of ruthenium–oxygen bonds in solid materials can be found in the literature as a consequence of the metallic nature of bulk RuO_2.

On the basis of the literature concerning homogeneous ruthenium complexes (13), Ru–O stretching frequencies in the 800–950 cm^{-1} range should be expected. Indeed, we have previously detected a band at 972 cm^{-1} on Ru/ZnO oxidized samples (14) and Hadjivanov *et al.* (4) have observed an absorption band at 1895 cm^{-1} on Ru/TiO_2, assigned to a $2\nu(Ru^{4+}–O)$ overtone.

Taking into account the quantitative chemisorption data previously illustrated it can be proposed that, in the temperature range 373–473 K, at O/Ru ratios significantly larger than one, a complete filling of all the hollow surface sites (oxygen atom 1 in Scheme 1) occurs. Additional oxygen is then chemisorbed, bridge or on top bonded to the surface ruthenium atoms, giving rise to a RuO_2- like layer (oxygen atoms 2 and 3 in Scheme 1). The low integrated intensity, the lower frequency and the maximum intensity obtained at relatively low temperatures seem to indicate that the band at 940 cm^{-1} is related to bridge bonded oxygen (atoms 2 in Scheme 1), while the band at 988 cm^{-1} can be assigned to on top oxygen (atom 3 in Scheme 1). At temperatures higher than 473 K, as the quantitative O/Ru ratios is significantly larger than 2, the further growth of the higher frequency component at 998 cm^{-1} can be taken as an indication of the presence of Ru–O surface species where the Ru atom has an oxidation state higher than 4. These are probably top species located in defects in the bridge oxygen rows. Indeed, RuO_3 clusters at the surface of monocrystalline RuO_2 have been already postulated on the basis of XPS data analysis (15).

3.3. *FTIR Spectra of CO Adsorbed on Oxidized Sample*

Figure 2a shows FTIR spectra, in the 2400–1000 cm^{-1} range, obtained by subtracting the spectrum of the clean O773 sample from that obtained by contacting the sample with subsequent small doses of CO. Figures 2b and 2c show the same experimental data in more detail in the ranges 2300–1900 and 1020–910 cm^{-1} respectively. The experiment well documents that a partial consumption of the 1000–940 cm^{-1} bands is accompanied by a simultaneous, gradual increase of absorptions due to products of CO oxidation, carbonate-like species, and Ru^{x+} carbonyls (main peaks at 2135, 2075–45, 2004 cm^{-1}). From the first five curves, it appears that, initially, mainly the components at 980 and 940 cm^{-1} are consumed while the bands at 2135, 2075–2045, and 2004 cm^{-1}, typical of ruthenium carbonylic species, and bands at 1557, 1311, and 1060 cm^{-1}, typical of carbonate species on the support, are produced. In addition, at 2196 cm^{-1} an absorption band is observed. On the basis of the literature data and of the behavior with the outgassing, this band can be assigned to CO weakly adsorbed on Zr^{4+} surface sites (16).

The contact with higher CO pressures and longer contact times produces a stronger reduction of the intensity of the 998 cm^{-1} band and the further increase of the carbonate-like species and of the Ru^{x+} carbonyls already observed at lower CO pressures; moreover, some new components appear, at 1446, 1422 cm^{-1}, at 1800–1700 cm^{-1}, and at 1300–1200 cm^{-1}.

Looking at the large amount of literature data summarized in Ref. (4), the carbonylic species can be assigned mainly to two different surface complexes: the bands at 2135 cm^{-1}, associated with a component at 2055 cm^{-1}, can be assigned to the asymmetric and symmetric stretching of an $Ru^{3+}(CO)_2$ species, while the bands at 2070 and 2004 cm^{-1} can be assigned to those of an $Ru^{2+}(CO)_2$ species. The Ru ions with an oxidation state lower than 4 are produced by the reducing action of carbon monoxide, as evidenced by the concomitant increase of the carbonate species on the support. As for the other bands an assignment to carbonate-like species adsorbed on the support can be proposed. In fact, their spectroscopic features are very similar to those observed on ZrO_2 alone (bands at 1557, 1311, 1060, and 870–865 cm^{-1}). Moreover, minor bands of monodentate carbonates are also produced at 1446, 1422 cm^{-1}. Finally, the weak bands at 1800–1700 cm^{-1} and at 1300–1200 cm^{-1} can be assigned to the asymmetric and symmetric stretching of a side–on CO_2 species, possibly interacting with the RuO_x phase (17).

Figure 2d shows the same kind of experiment reported in Fig. 2a, although in the present case the sample has been heated in CO at increasing temperatures. As a reference, the first spectrum in the figure is the difference spectrum between an oxidized sample and a reduced sample. The

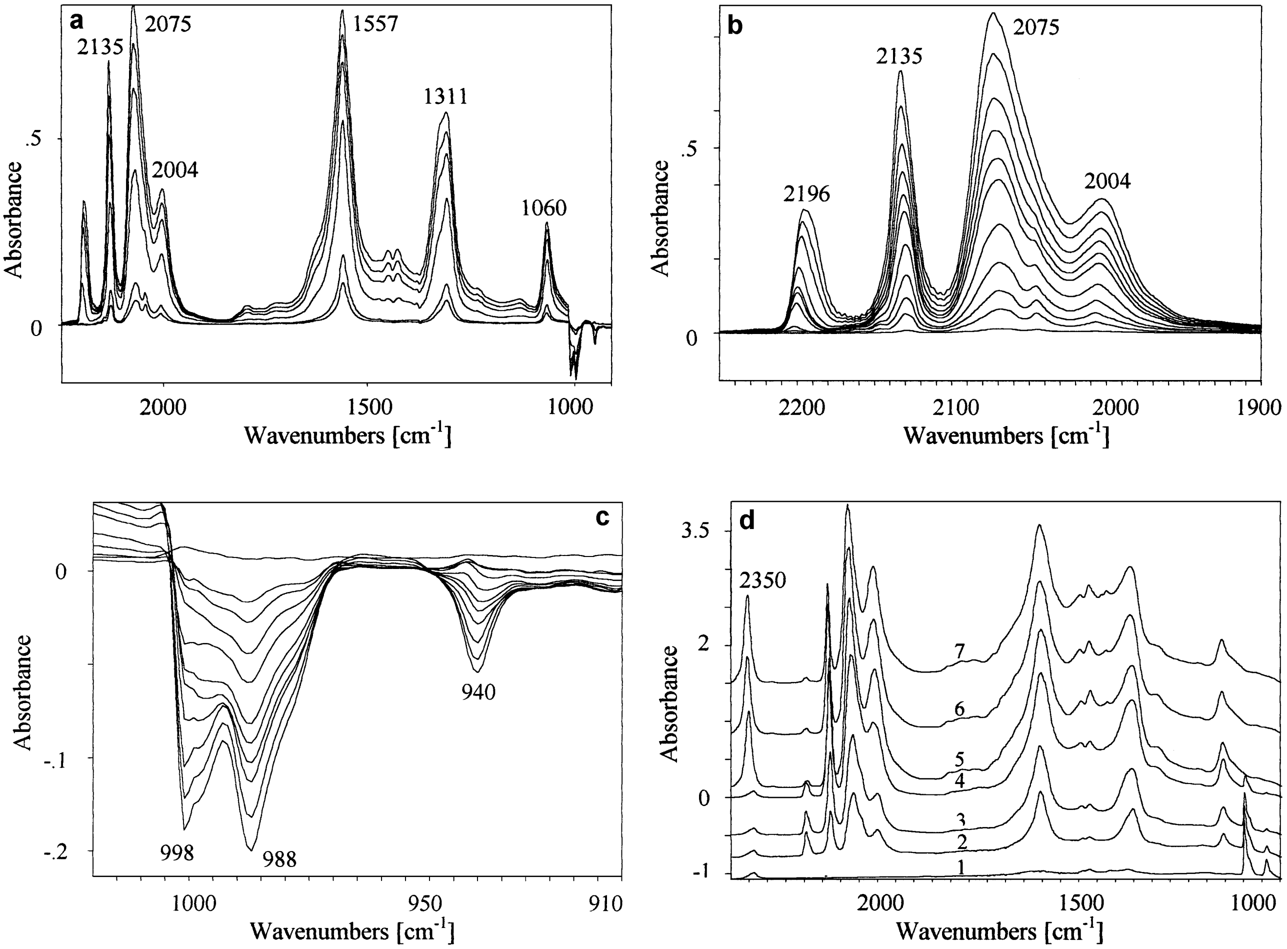


FIG. 2. FTIR difference absorption spectra produced by CO interaction on the O773 sample, taken as background. (a) Subsequent CO small doses, at RT, first two lower curves, 10^{-3} mbar equilibrium pressures; up to last curve, equilibrium CO pressure, 10^{-2} mbar up to 23 mbar. (b) Abscissa magnification from 2300 to 1900 cm^{-1}. (c) Abscissa magnification of the 1040–900 cm^{-1} region. (d) Spectra produced by CO at full coverage on the O773 sample, taking as background the spectrum of the sample R773: curve 1, difference between the spectra of the oxidized sample (O773) and the reduced sample (R773); curve 2, 20 mbar of CO at RT on O773; curve 3, after 2 h of contact; curve 4, in CO at 373 K for 15 min; curve 5, in CO at 473 K; curve 6, in CO at 573 K; curve 7, in CO at 673 K.

experiment proves the full reactivity of Ru–O species toward CO between RT and 473 K. At this temperature all the Ru–O groups disappear; the CO adsorbed on the Zr^{4+} is almost completely depleted and, in addition to the carbonates and Ru carbonyl groups, also the formation of linearly, weakly adsorbed CO_2 (band at 2354 cm^{-1}) is observed. No further changes are observed for treatment above 473 K. The analysis of the gas phase after the 673 K treatment with the Micromass linked to the IR cell shows the presence of masses $m/e = 28$ and 44, i.e., residual CO and CO_2.

In summary, from the above data it appears evident that the Ru/ZrO_2 calcined catalyst examined here is constituted by a well-dispersed and easily reducible RuO_x phase. By contact with CO at RT the RuO_x phase is gradually reduced, giving rise to sharp and well-defined bands ascribed to carbonates on the support and to $Ru^{x+}(CO)_2$ surface complexes.

3.4. *FTIR Spectra of Adsorbed CO on Reduced Sample*

Figure 3 shows the spectra in the carbonyl region (2300–1900 cm^{-1}) of CO adsorbed on the R773 sample at increasing doses and contact times. For the sake of clarity the figure is divided into two parts, but the experiment is the same. Figure 3a (small doses, increasing contact times) shows the development of a broad band, initially centered at 2016 cm^{-1}, shifting with increasing coverage up to 2052 cm^{-1}. A peak at 2135 cm^{-1} appears at high pressures, accompanied by a component at 2075 cm^{-1} (Fig. 3b). At the same time a peak at 2201–2194 cm^{-1} is produced at higher frequencies together with shoulders at 2100 and 2060 cm^{-1}. The final CO pressure in this experiment is 21 mbar. However, the most impressive effect is the strong increase in intensity of the 2000–2060 cm^{-1} bands. The integrated intensities of the bands at 2000–2030 cm^{-1} and

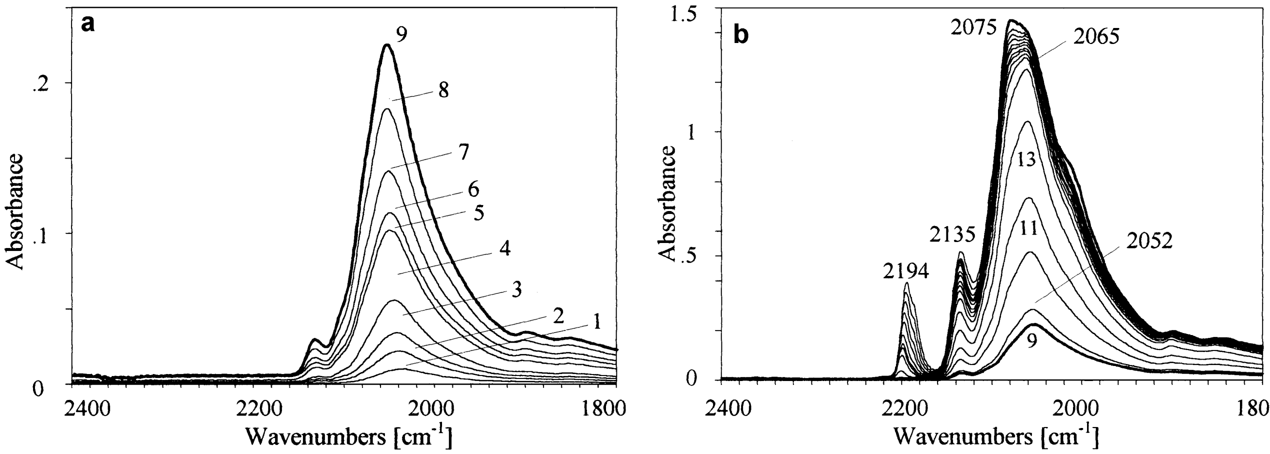


FIG. 3. FTIR difference absorption spectra in the 2300–1900 cm^{-1} range produced by CO interaction on the R773 sample. (a) Nine subsequent small doses, final equilibrium pressures <10^{-3} mbar. (b) Increasing equilibrium CO pressures up to 21 mbar.

2040–2060 cm^{-1}, as shown by a curve fitting of the spectra (not shown for the sake of brevity), grow by a factor larger than 10.

The main band shown in Fig. 3a can be assigned, in agreement with the literature (11), to CO linearly adsorbed on Ru° sites or Ru$^{\delta+}$ sites exposed at the surface of small particles. Actually, the EELS and IRAS data of CO adsorbed on monocrystalline (0001) surfaces exhibit, at very low coverages, an absorption band at a frequency even lower than 2000 cm^{-1}. The higher frequency observed in our case could be explained by the different experimental conditions, i.e., UHV in the monocrystalline samples and HV in our microcrystalline samples. In our case some oxygen may be adsorbed on the metal particles or, more likely, ruthenium may be present as very thin, bidimensional particles, to some extent modified and made electropositive by the interaction with the oxidic support, due to the low metal loading of our samples and the high dispersion revealed by chemisorption data. It is well known that oxygen coadsorbed with carbon monoxide can act as an electronegative ligand, reducing the ability of the metal to back-donate electrons into the $2\pi^*$ orbital of the CO ligand, thereby reducing the CO bond order. In the recent and very detailed work of Schiffer *et al.* (18) concerning a TDS, IRAS, LEED, and XPS study of the coadsorption of CO and oxygen on Ru(001), it was shown that, on an oxygen precovered surface, CO produces a vibration at 2025 cm^{-1}, increasing in intensity with increasing coverage and blue shifting up to 2051 cm^{-1} at the maximum coverage of 0.25 of a monolayer. Under these conditions, as shown by the analysis of LEED-IV data performed by Narloch *et al.* (19), the CO molecules are located on top of Ru atoms whereas the O atoms occupy hcp hollow sites.

Another significant difference between monocrystalline and supported Ru catalysts, already clearly documented in the paper of Hoffman and Robbins (20), is the broadness of the absorption bands on the supported samples (fwhm 8–12 cm^{-1} on the monocrystalline samples and 40–80 cm^{-1} on the supported ones). The significantly higher broadness of the bands detected on the supported catalysts is probably due to the overlap of the absorption bands of CO adsorbed on crystallites of different size and/or differently contaminated by oxygen.

Figure 3b shows that, at increasing pressures, new bands arise at 2201–2187 cm^{-1}. On the basis of the literature data and their behavior with the outgassing, they can be assigned to CO weakly adsorbed on Zr^{4+} surface sites (16).

The bands observed at high coverages and at increasing contact times at 2135, 2100, and 2075 cm^{-1} can be assigned, in agreement with Hadjivanov *et al.* (4), to CO mono or twin adsorbed on Ru^{x+} oxidized sites ($x = 3$ and/or 2) produced by the disaggregation of CO on the surface of Ru° thin rafts. This effect is evidenced by the large intensity increase of the broad band at ~2050 cm^{-1}. By outgassing at high temperature two main absorptions remain, with almost the same intensity, at 2070 and 2004 cm^{-1}, that can be assigned to the asymmetric and symmetric stretching vibrations of Ru^{2+}(CO)$_2$ species produced by the dissociation of CO on the surface of Ru° thin rafts. A comparison of the carbonyl stretching region at full coverage between a sample reduced for the first time, and the same sample after many subsequent oxidation–reduction treatments, showed that in the latter the intensity of the bands of CO adsorbed on ruthenium surface sites does not decrease but, on the contrary, increases slightly.

No bands are produced in the Ru–O 1100–900 cm^{-1} region. This fact can be interpreted considering that, as discussed for oxygen interaction in Section 3.2, the oxygen atoms produced are bonded in a fully symmetric way to three ruthenium atoms in hollow sites.

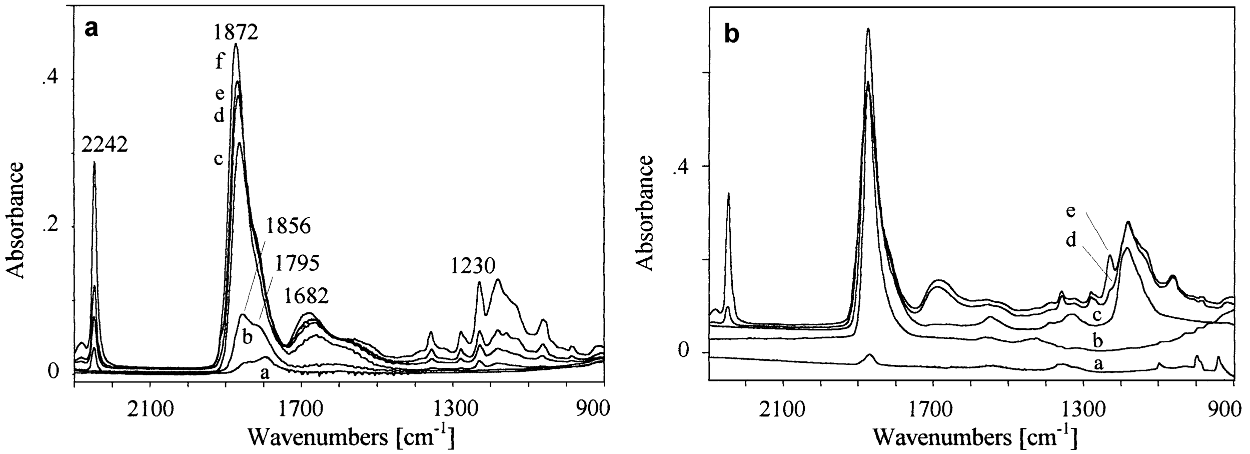


FIG. 4. FTIR difference absorption spectra in the 2300–900 cm^{-1} range produced by NO interaction on the R773 sample at increasing coverages at RT. (a) Curve a, 5×10^{-3} mbar; curve b, 9×10^{-2} mbar; curve c, 0.3 mbar; curve d, 0.6 mbar; curve e, 6 mbar; curve f, 10 mbar, 1 h. (b) NO outgassing at increasing temperatures: curve a, 10 mbar of NO; curve b, outgassed at RT; curve c, outgassed at 373 K; curve d, outgassed at 523 K; curve e, outgassed at 623 K.

3.5. FTIR Spectra of NO Adsorption on Reduced Sample

Figure 4a shows the spectra produced upon increasing the NO pressure. It appears evident that at the beginning only a weak band at 1795 cm^{-1}, accompanied by a shoulder at 1850 cm^{-1}, is produced (curve a). Upon increasing the NO pressure (curve b), the 1856 cm^{-1} component increases without other changes in other spectral regions. These components, on the basis of literature data, can be assigned to NO molecularly adsorbed on Ru° and Ru$^{\delta+}$ surface sites, respectively. At an NO pressure of 0.3 mbar (curve c) a significant growth of the absorption is observed, shifting up to 1872 cm^{-1}; moreover, additional components are detected at 2245, 1682, 1547, 1358, 1279, 1230, 1181, and 1060 cm^{-1}.

The blue shift of the band assigned to the stretching mode of NO molecularly adsorbed on ruthenium surface sites, and the strong intensity increase, can be explained considering that, under these conditions, some NO is dissociated and the formed oxygen atoms give rise to ruthenium oxidized sites (see curve a, bands in the 900–1000 cm^{-1} range). On these sites the NO can be adsorbed giving rise to a species strongly bonded and probably characterized by a higher absorption coefficient. At the same time, by reaction of NO with N atoms, N_2O molecules are produced, as indicated by the bands at 2246 and 1230 cm^{-1}, that can be outgassed at RT (Fig. 4b). The additional bands observed in the 1700–1060 cm^{-1} range, irreversible to the outgassing, can be assigned, on the basis of literature data, to nitrite and nitrate species (21).

On the basis of these results it appears evident that at high coverages and high contact times both of the test molecules used in the surface characterization of the catalyst dissociate, causing an increase in the Ru exposure and dispersion (4).

3.6. CO–NO Coadsorption and Reaction Experiments

Figure 5 shows the FTIR spectra obtained by adsorption of 20 mbar of CO (curve a) on an R773 sample followed by 20 mbar of NO (curve b). The NO admission produces immediately a significant modification of the adsorbed CO spectrum, i.e., a reduction of the intensity of the band at 2058 cm^{-1} assigned to CO adsorbed on Ru° sites and some additional bands at 2243, 1820–1757, 1560, 1454–1422, 1309, 1233, 1185, and 1060 cm^{-1} that can be assigned to N_2O, NO, and carbonate species. Moreover, these features indicate that NO is immediately dissociated on Ru in the presence of preadsorbed CO and gives rise to CO and NO adsorbed on oxidized sites and to $N_2O + CO_2$ at RT according to

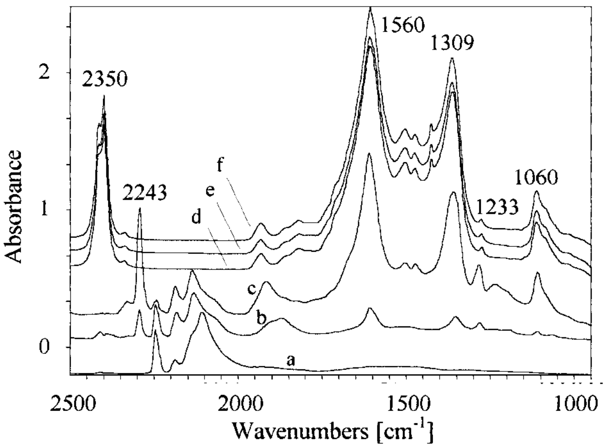


FIG. 5. FTIR difference absorption spectra of the CO–NO interaction on the R773 sample at increasing temperatures: curve a, 20 mbar of CO; curve b, inlet of 20 mbar of NO at RT, spectrum run after 15 min; curve c, in the mixture at RT, after 17 h; curve d, heated at 373 K; curve e, heated at 423 K; curve f, heated at 473 K.

reaction [1]:

$$CO + 2NO \rightarrow N_2O + CO_2. \qquad [1]$$

Upon increasing the contact times, an increase of the bands assigned to N_2O, NO, and carbonate species is observed (curve c); moreover, a new component is evident at 2280 cm^{-1}. Upon heating at 373 K (curves d–f), the N_2O absorptions and the bands ascribed to CO adsorbed species are depleted and the CO_2 asymmetric stretching band at 2350 cm^{-1} and the band of the carbonate-like species appear. These features may indicate that at 373 K (i) N_2O is completely decomposed and only the reaction [2],

$$2CO + 2NO \rightarrow N_2 + 2CO_2, \qquad [2]$$

occurs on the catalyst, and/or (ii) the latter reaction prevails over reaction [1]. Upon further increasing the temperature no further changes are observed. Moreover, at variance with similar experiments made on supported Ru catalysts or on monocrystalline Ru(001) surfaces, no isocyanate species are detected in these experiments. According to the mechanism proposed by Solymosi and Sarkany (22) on transition metals, the isocyanate species are formed by CO interaction with a metal–N species, produced by NO decomposition. The dissociation of nitric oxide on a ruthenium (0001) surface was studied by scanning tunneling microscopy (23). The distribution of nitrogen atoms after the dissociation allowed the identification of the active sites, which are formed by low coordinated metal atoms of atomic steps. On the supported samples the isocyanate species are formed by CO interaction with N atoms produced by NO decomposition and migrated by a spillover mechanism onto the support, where they can be stabilized to different extents, depending on the nature and ionicity of the support. On zirconia, isocyanate species are not formed.

4. CONCLUSION

In this paper it has been shown that the Ru/ZrO_2 catalysts exhibit interesting surface and catalytic properties, related to the peculiar properties of ruthenium, ruthenium oxides, and zirconium oxide. In particular:

—On the oxidized sample at least three FTIR absorptions are evident at 1000, 980, and 950–940 cm^{-1}. All of these bands can be assigned to Ru–O surface species, differing for (i) the oxidation state of ruthenium directly bonded to oxygen, and (ii) the degree of metal–oxygen π bonding. The larger heterogeneity of the bands observed on this Ru/ZrO_2 catalyst, with respect to that previously detected on Ru/ZnO, can be taken as a strong indication that a significant role is played by the coordination and surface features of the support. The strong increase of the band at 1008 cm^{-1} at temperatures higher than 573 K can be tentatively assigned to an Ru–O surface species bonded to an Ru atom with an oxidation state higher than 4.

—The CO adsorption on an oxidized sample evidences the full reactivity of Ru–O species toward CO between RT and 473 K and the formation of different carbonyl species on Ru^{3+} and Ru^{2+} surface sites. At low coverages and contact times, a CO band is mainly detected on the reduced sample. This band can be ascribed to CO molecularly adsorbed on Ru° sites and red shifting by decreasing the coverage. At high coverages and contact times, evidence has been found of CO dissociation. Similar features were observed also in the NO adsorption on the Ru/ZrO_2 reduced catalyst.

—The NO admission on preadsorbed CO produces immediately a significant modification of the adsorbed CO spectrum, i.e., a reduction of the intensity of the band assigned to CO adsorbed on Ru° sites and some additional bands that can be assigned to N_2O, NO, and carbonate species. These features indicate that NO is immediately dissociated on Ru in the presence of preadsorbed CO and gives rise to CO and NO adsorbed on oxidized sites and to N_2O and CO_2 at RT. By heating at 373 K the N_2O absorptions and the bands ascribed to CO adsorbed species are depleted while that of CO_2 increases, indicating that the reaction $2CO + 2NO \rightarrow N_2 + 2CO_2$ may prevail on the catalyst.

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