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Ru/ZrO$_2$ Catalysts

II. N$_2$O Adsorption and Decomposition

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Nitrous oxide decomposition studies on an Ru/ZrO$_2$ catalyst (activated by oxidation or reduction at 623 and 773 K) have been performed in a flow reactor at 1 atm total pressure. The reaction onset temperature is 573 K, while a complete conversion of reactant is achieved at 773 K. At a given temperature, the oxidized sample exhibits higher conversions with respect to the reduced one, while on the latter a significant induction period for a stable conversion with time on stream was observed. ***In situ*** **FTIR experiments have indicated that RuO$_3$ clusters can be found in a dynamic equilibrium with an RuO$_2$ surface layer at the reaction conditions. Ru surface atoms with a valence state greater than 4 and tetrahedrically coordinated were found to be able to interact with N$_2$O at room temperature. At 773 K, upon introduction of N$_2$O a drastic decrease in the N$_2$O vibrational modes is observed with a simultaneous rapid decrease of N$_2$O and increase of O$_2$ and N$_2$ in the gas phase. It was concluded that during the reaction N$_2$O acts as a reductant of the oxidized ruthenium surface (Ru^{6+}) sites and as an oxidant of RuO$_2$ (Ru^{4+}) sites.** © 2000 Academic Press

Key Words: **ruthenium; zirconia; N$_2$O decomposition; RuO$_x$ active phase; redox mechanism.**

1. INTRODUCTION

The study of ruthenium catalysts and electrocatalysts has been carried out thoroughly in the past 20 years in different laboratories (1). The question of the oxidation state of ruthenium in different media and under different oxidizing conditions at different temperatures is very important because of the volatility of fully oxidized Ruthenium. In particular, the stabilization of the oxide by a suitable support could be important to the development of Ru-based catalysts to be employed in an oxidizing atmosphere at high temperatures. Recently, Zeng *et al.* (2, 3) have reported good performances of Ru/Al$_2$O$_3$ catalysts in N$_2$O decomposition, a very important process in environmental catalysis (4, 5). In fact, N$_2$O is produced as a gaseous by-product of different important chemical processes (HNO$_3$ and adipic acid productions and combustion of waste). However, in the above-cited papers no data on chemical or spectroscopic characterization of the catalysts has been reported, in particular with reference to the nature and the coordination of the sites involved in the reaction. A large number of FTIR papers on the surface characterization and the catalytic properties of metallic Ru (6) are available in the literature, while, to our knowledge, no studies have been performed on ruthenium oxides, in spite of their relevance as electrocatalysts in Cl$_2$ production. This is probably due to the metallic nature of massive RuO$_2$ (7) and, in the case of highly dispersed supported catalysts, to the fact that the Ru–O stretching region is usually masked by the support absorption.

Under oxidizing conditions IR evidence of an Ru–O species was given by some of us for a Ru/ZnO catalyst (8). In the case of ZrO$_2$ the IR transparency of the region is sufficiently high to detect Ru–O surface species and study their changes during N$_2$O decomposition. In the first part of this work (9) we have reported an FTIR characterization of the Ru/ZrO$_2$ catalyst by O$_2$, CO, and NO adsorption. In this paper we will present a catalytic and FTIR study of N$_2$O decomposition on both a reduced and an oxidized Ru/ZrO$_2$ catalyst. We will also provide evidence for the formation of Ru–O species and their thermal stability and reactivity.

2. EXPERIMENTAL

The preparation of the Ru/ZrO$_2$ catalyst was described in detail elsewhere (9). ZrO$_2$ was prepared by dropping a 28% ammonia solution into an aqueous solution of ZrOCl$_2\cdot$8H$_2$O with stirring. After filtration, the precipitated zirconium hydroxide was washed several times and dried in an oven at 388 K for 15 h and then calcined at 823 K for 2 h in a stream of air (2.5 l/h). The catalyst was prepared by incipient wetness impregnation with an aqueous solution

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of RuCl$_3$, dried at 383 K for 15 h, and calcined at 773 K for 20 h. The Ru content was 0.6 wt%.

Catalytic activity tests for N$_2$O decomposition were performed in a quartz flow reactor (0.21 g of catalyst) externally heated by an oven. The temperature was controlled with a thermocouple immersed in the catalytic bed. A feed (total flow 130 ml/min) made of a mixture of N$_2$O (750 ppm) in He was used, corresponding to a GHSV of 37,000 h^{-1}. Further experiments were performed in the presence of O$_2$ (N$_2$O (0.075%), O$_2$ (4%), and the remainder He) or O$_2$ + H$_2$O (N$_2$O (0.075%), O$_2$ (4%), H$_2$O (1.7%), and the remainder He). The inlet and outlet gas composition was analyzed by online gas chromatography using a Carbosphere column (2 m; 80/100 mesh) and a TCD detector. Except when differently specified, before a catalytic test the sample was activated in H$_2$ (reduced sample) or in air (oxidized sample) at both 623 and 773 K for 1 h.

The FTIR experiments were performed in an AABSPEC cell operating at different temperatures under a controlled atmosphere, using a Perkin-Elmer 2000 spectrometer with a resolution of 2 cm^{-1}. The composition of the gas phase during N$_2$O decomposition experiments was analyzed by a VG Micromass spectrometer, connected to the FTIR cell through a needle valve.

3. RESULTS AND DISCUSSION

3.1. Catalytic Data

Figure 1 reports the N$_2$O conversion at 623 and 773 K as a function of time on stream of the Ru/ZrO$_2$ after activation for 1 h in H$_2$ or in air at the same temperatures. The 623 K oxidized sample (Fig. 1, circles) exhibits a higher conversion than the reduced one (Fig. 1, triangles); moreover, on the sample reduced at 623 K an induction time to reach a stable conversion is observed, which is almost completely absent in the oxidized sample. At 773 K no induction time is observed, and the conversion of the reduced sample is ≈97% (Fig. 1, squares), while that of the oxidized sample is ≈100% (Fig. 1, diamonds).

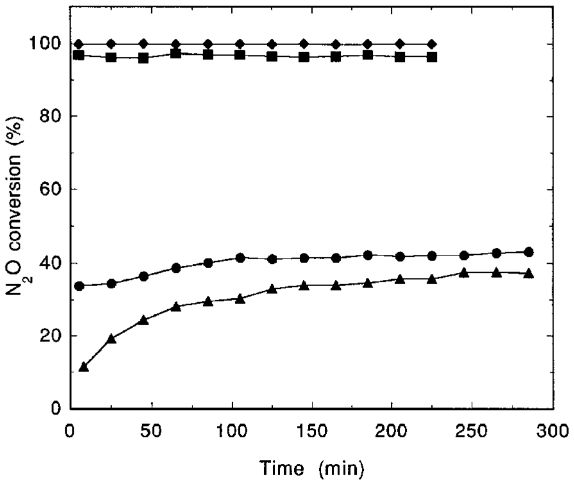

FIG. 1. N$_2$O conversion as a function of time. At 623 K, triangles, pretreated in H$_2$ for 1 h; circles, pretreated in air for 1 h. At 773 K, squares, pretreated in H$_2$ for 1 h; diamonds, pretreated in air for 1 h.

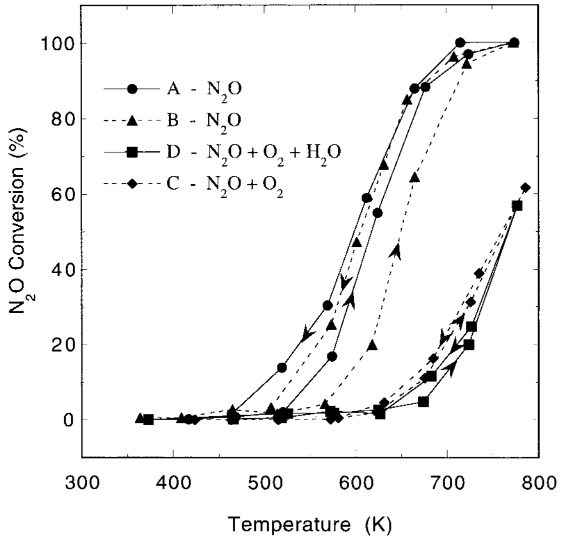

FIG. 2. N$_2$O conversion as a function of the reaction temperature for Ru/ZrO$_2$ catalyst: circles (curve A), oxidized sample; triangles (curve B), reduced sample (for both curves the feed was N$_2$O + He); diamonds (curve C), oxidized sample with an N$_2$O + O$_2$ + He feed; squares (curve D), oxidized sample with an N$_2$O + O$_2$ + H$_2$O + He feed.

In Fig. 2 the catalytic behavior of the catalyst pretreated under two different sets of conditions is reported: the sample was reduced in H$_2$ at 623 K for 1 h, cooled to room temperature, and then left for 18 h either in H$_2$ ("reduced", curve B) or in air ("oxidized", curve A). As can be seen, the oxidized sample is active at a temperature lower than the reduced one. Moreover, both conversion vs temperature curves exhibit a hysteresis loop which suggests the formation of an Ru active phase during the reaction with N$_2$O. However, the hysteresis cycle is wider for the reduced sample. Looking at the oxygen chemisorption data reported in the previous paper (9), it can be assumed that the "oxidized" sample is almost completely covered by an oxygen monolayer, filling all the hollow sites present at the surface of metallic ruthenium.

Curves C and D were obtained for the "oxidized" sample in the presence of O$_2$ and O$_2$ + H$_2$O, respectively. A lower catalytic activity is evident, although there is no appreciable difference when water is present. It appears evident that both oxygen and to a minor extent water can act as poisons for the active sites of the catalysts. Inhibition effects on N$_2$O decomposition by O$_2$ and H$_2$O have been previously reported in the literature for other catalysts (10) and ascribed to both competitive adsorption and the influence of these molecules on the nature and the reactivity of the exposed surface sites.

The role of zirconia alone in N_2O decomposition has been reported by some authors (11, 12). Miller *et al.* have found, by FTIR spectroscopy, that N_2O decomposition starts at temperatures above 623 K and becomes significant at about 723 K. Therefore, we have performed an activity test at 773 K loading the reactor with ZrO_2. Prior to the reaction, ZrO_2 was activated at the same temperatures as the catalyst for 1 h in air. A conversion of 6% was obtained compared to 100% observed with the Ru/ZrO_2 catalyst under the same experimental conditions. This result indicates that the effect of the support can be reasonably neglected in our experimental conditions. Similar differences were reported by Zeng and Pang (2) for alumina-supported catalysts: on pure alumina a 6% conversion at 753 K was observed, while a 0.26% Ru/Al_2O_3 catalyst yielded 100% conversion.

3.2. FTIR Study of the N_2O Interaction with Reduced and Oxidized Ru/ZrO_2

Figure 3a, curve I, shows a full-range absorption spectrum of N_2O interaction on a sample reduced at 773 K taken at RT. A strong band at 2244 cm^{-1}, accompanied by a shoulder at 2277 cm^{-1} and a weaker band at 1237 cm^{-1}, is evident. These are respectively blue shifted and red shifted to the ν_3 asymmetric stretching (2224 cm^{-1}) and the ν_1 symmetric stretching (1285 cm^{-1}) modes of the N_2O molecule in the gas. The shifts are +20 and +53 cm^{-1} for the ν_3 mode and −48 cm^{-1} for the ν_1 mode. Moreover, bands are observed at 2470 and at 3444 cm^{-1}, assigned to $2\nu_1$ and to $\nu_1 + \nu_3$ modes. Finally, weak negative bands are observed at frequencies typical of the Zr–OH stretching modes (3776 and 3661 cm^{-1}), more evident in the spectrum shown in Fig. 3b, curve I, indicating that a hydrogen bond interaction occurs between the adsorbed molecules and the OH surface groups of the support. The interaction of N_2O at room temperature on an Ru/ZrO_2 fully oxidized sample (Fig. 3a, curve II) produces spectra very similar to those observed on the reduced sample. However, in the 1100–900 cm^{-1} range, where the RuO_x bands already shown and discussed in the previous paper (9) are present, a perturbation of the Ru–O bands is evident. In particular, a negative band at 998 cm^{-1} and an increase of the intensity of the bands at 980 and 940 cm^{-1} are observed. These features are a clear evidence of the interaction of the N_2O molecules with ruthenium oxidized sites. As already discussed (9), the 998 cm^{-1} band can be assigned to oxygen bonded to ruthenium atoms with an oxidation state higher than 4 and/or more unsaturated or isolated, probably related to Ru–O species bonded on top to defect sites. In general, Ru^{3+} shows no coordination preferences, while Ru in a valence state >4 has a tendency for tetrahedral coordination (13). Therefore, it can be proposed that Ru surface atoms, with a valence state >4 and tetrahedrically coordinated, are able to interact with N_2O at RT, changing their coordination.

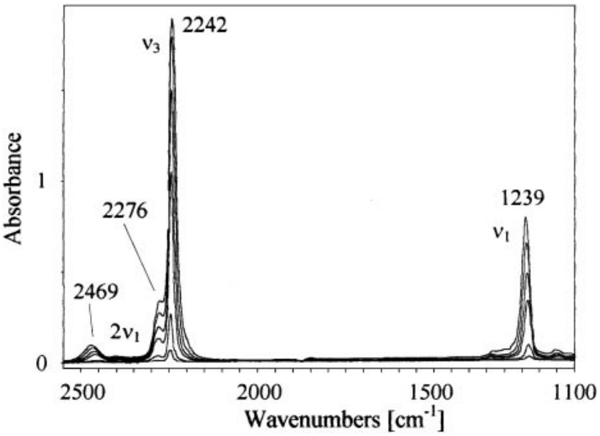

FIG. 4. FTIR spectra of N_2O adsorbed on the Ru/ZrO_2 reduced sample at the equilibrium pressure 10^{-2} mbar (lowest curve) up to 20 mbar (highest curve).

In Fig. 4 the spectra of the adsorbed N_2O on the reduced sample, in the range 2550–1100 cm^{-1}, taken at different

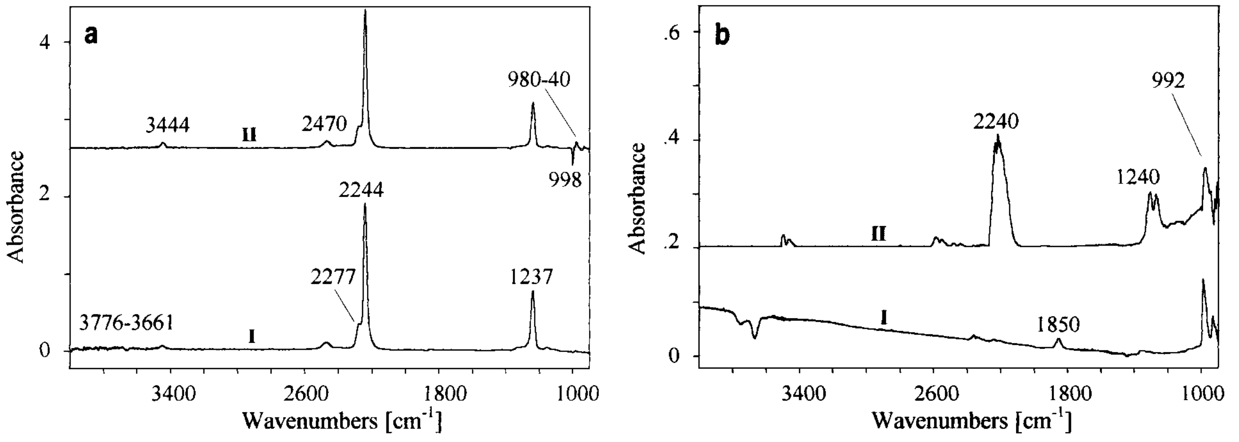

FIG. 3. FTIR spectra of Ru/ZrO_2 catalyst. (a) Curve I, interaction at RT with 20 mbar of N_2O on the sample reduced at 773 K; curve II, interaction on the sample oxidized at 773 K under the same conditions. (b) Curve I, interaction with 20 mbar of N_2O at 773 K on the sample reduced at 773 K; curve II, interaction with 20 mbar of N_2O at 773 K on the sample oxidized at 773 K.

equilibrium pressures (10^{-2} mbar to 20 mbar) are shown. The intensity of all bands strongly depends on the N$_2$O pressure; moreover, their frequency shifts with the coverage. Starting from the low equilibrium pressures, the ν_1 symmetric stretching mode blue shifts from 1230 up to 1239 cm^{-1}, the ν_3 mode red shifts from 2246 to 2242 cm^{-1}, and similar shifts are also observed on the other bands. All bands are completely depleted by outgassing at room temperature. The observed spectroscopic features are very similar to those reported by Miller and Grassian (11) and assigned to nitrous oxide molecules adsorbed on surface Zr^{4+} Lewis acid sites, through the oxygen atom. However, in Ref. (11) the low coverage values of the ν_3 and ν_1 modes are at 2242 and 1233 cm^{-1}; therefore, at low coverage a contribution of the interaction with the ruthenium surface sites cannot be excluded in our sample.

By heating the reduced sample in an N$_2$O atmosphere at 373 K a new weak band at 983 cm^{-1} is produced in the region of the Ru–O vibrational modes (9) and the intensities of the N$_2$O related bands are to some extent reduced (not shown for the sake of brevity). We can observe that on pure zirconia the N$_2$O decomposition is quite limited, as discussed above in the catalytic section. In addition, no bands in the 1000–900 cm^{-1} spectral region have been previously observed (14). An adsorbed oxygen species, produced by N$_2$O decomposition, has been previously (11) identified on pure ZrO$_2$ by DRIFT experiments, showing an IR band at 810 cm^{-1}, i.e., at a frequency significantly lower than in our case. By heating the reduced sample up to 773 K and by recording the spectrum at the same temperature (Fig. 3b, curve I), the molecularly adsorbed N$_2$O-related bands are completely depleted. At 2230 cm^{-1} only a weak absorption due to some residual N$_2$O in the gas phase is observed and a weak band is detected at 1850 cm^{-1} in the region of NO adsorbed on Ru sites. At the same time, the Ru–O bands in the 992–931 cm^{-1} range are significantly increased in intensity. During the same experiment NO is also detected in the gas phase by mass spectrometry. Lintz and Turek (15) reported experimental evidences of NO formation as a by-product of N$_2$O decomposition on Cu–ZSM5. The results reported above suggest that under our experimental conditions N$_2$O decomposition occurs mainly on the exposed Ru° sites, giving rise to the adsorption of the fragments on ruthenium and producing an RuO$_x$ surface layer, similar to that observed in presence of oxygen. These bands have been assigned to an RuO$_x$ surface phase, with $x > 2$.

On the oxidized sample (Fig. 3b, curve II) N$_2$O molecules can be observed in the gas phase, no NO-adsorbed molecules are produced during the reaction, and an increase of the high-frequency mode in the Ru–O stretching region is also observed. However, during the N$_2$O reaction, the main difference between the reduced and the oxidized samples concerns the mass spectra taken during the experiments, where, in addition to the quite rapid decrease of N$_2$O ($m/z = 44$) and N$_2$ ($m/z = 28$), the growth of O$_2$ ($m/z = 32$) has been detected only on the already oxidized sample. It can be concluded that in the decomposition reaction, N$_2$O acts as an oxidant on the reduced sample and as a reductant of the fully oxidized ruthenium.

3.3. *Reaction Mechanism*

In the adsorption and decomposition mechanism of N$_2$O on oxides the electron transfer from a metal ion to the N$_2$O molecule is assumed to be a crucial step for N$_2$O decomposition (16, 17). Catalysis requires not only an easy reducibility of low oxidation state metal ions but also the recoverability of the ion from the high oxidation state to the original one. This process may occur faster on some supports. In particular, ZrO$_2$ is a solid electrolyte in the reaction temperature range (18) and this property can play a role in improving the mobility and the desorption of oxygen.

The reaction mechanism of the N$_2$O decomposition on metal oxides is usually considered to be either adsorption or desorption controlled. N$_2$O is a soft Lewis base and it is known that it can bind metal atoms or ions in an end-on fashion through its terminal nitrogen or oxygen. The adsorption-controlled mechanism involves an electron transfer from a low oxidation state metal cation to the adsorbed molecules as the rate-determining step. The desorption-controlled mechanism assumes as the rate-determining step the desorption of the reaction products, i.e., N$_2$ and mainly O$_2$.

In the previous spectroscopic experiments it has been shown that N$_2$O is molecularly and weakly adsorbed at RT on the support both in the oxidized and in the reduced sample. Moreover, we observed (i) a reducing action of N$_2$O on ruthenium sites with an oxidation state greater than 4 in the oxidized sample, and (ii) an oxidative effect of N$_2$O on the metallic or not fully oxidized sites in the reduced sample.

Ruthenium in an oxidation state greater than 4 usually prefers a tetrahedral coordination (19) and low coordination facilitates the interaction with molecules such as N$_2$O.

In previous examples of catalytic N$_2$O decomposition, it has been proposed (20) that N$_2$O can act either as an oxidant or as a reductant for the active sites. For example, the mechanism proposed for N$_2$O decomposition on Cu–ZSM5 (21, 22) involves the presence of both Cu$^+$ and Cu^{2+}. Fu and Korchak (20b) found that N$_2$O can both reduce Fe^{3+} to Fe^{2+} and oxidize Fe^{2+} to Fe^{3+} in FeY zeolite and Christopher and Swami (20a), in studies on perovskite-type catalysts, assumed N$_2$O as both the oxidant and the reductant in order to explain their reaction mechanism.

Let us now recall (i) the larger induction time observed (see Fig. 1) in the attainment of the equilibrium conversion at 623 K on the reduced sample with respect to the oxidized one, (ii) the differences observed between samples differently pretreated, and (iii) the hysteresis loops reported in Fig. 2. These findings seem to be a clear indication that

(i) the active phase on our catalyst is a highly oxidized one and (ii) the reaction appears to be controlled by the oxygen desorption. On reduced or partially oxidized catalysts the oxygen atoms produced in the dissociation reaction remain strongly bonded on the surface, according to the following reactions:

$$Ru + N_2O \rightarrow RuO + N_2 \tag{1}$$

$$RuO + N_2O \rightarrow RuO_2 + N_2. \tag{2}$$

Moreover, on the reduced or partially oxidized catalysts we have evidence that also the N–N bond is broken, giving rise to NO formation, following the reaction

$$RuO + N_2O \rightarrow (NO)RuO + \frac{1}{2} N_2. \tag{3}$$

Finally, on highly reactive and coordinatively unsaturated ruthenium sites the following reaction probably occurs:

$$RuO_2 + N_2O \rightarrow RuO_3 + N_2. \tag{4}$$

RuO_3 is in equilibrium with RuO_2 and O_2:

$$2RuO_3 \Leftrightarrow RuO_2 + O_2. \tag{5}$$

The presence of Ru in a formally +6 oxidation state does not imply the existence of a RuO_3 discrete solid phase.

The oxygen atoms giving rise to these species can be considered, from the point of view of their reactivity, similar to the extralattice oxygens (ELO) postulated on Cu–ZSM5 catalysts (23). The oxygen atoms produced in the first two reactions are strongly bonded to the ruthenium atoms, yielding a stable RuO_2 surface phase, from which oxygen is hardly removed.

However, on some ruthenium centers a further oxidation can occur by interaction with N_2O. The evolution of molecular oxygen can occur according to the reaction

$$RuO_3 + N_2O \rightarrow RuO_2 + N_2 + O_2, \tag{6}$$

thereby regenerating the active sites.

In the above-reported scheme, N_2O acts as a reductant of the Ru^{6+} sites and as an oxidant of Ru^{4+}. On this basis the negative effect on the conversion of oxygen and the absence of any further effect of water can be also understood.

CONCLUSIONS

On the basis of the results reported in this work the following remarks can be made:

—N_2O decomposition on Ru–ZrO_2 starts at 573 K and heating to 773 K is necessary to reach 100% conversion.

—The oxidized sample exhibits a conversion at low temperatures higher than the reduced one. In the latter an induction time to achieve a stable conversion is required associated with the oxidation of the Ru active sites.

—RuO_3 clusters in dynamic equilibrium with the RuO_2 surface have been evidenced by FTIR experiments under the given reaction conditions.

—Formally surface Ru^{6+} appears to be capable of interacting with N_2O at RT.

—In the reaction N_2O acts as an oxidant of the ruthenium reduced sites and as a reductant of the overoxidized sites.

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