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Effect of noble metals in the decomposition of nitrous oxide over Fe-ferrierites

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The decomposition of nitrous oxide was studied over Fe-ferrierite, Me-ferrierites and Fe/Me-ferrierites (Me: Pt, Rh and Ru). Flow as well as batch experiments were carried out and showed a synergy between Fe and Me ions. Ions of noble metals in Fe-ferrierite increased the catalytic activity in the sequence $Pt < Rh \cong Ru$. Addition of NO substantially decreased the decomposition of N_2O over Rh/ferrierite and Ru/ferrierite, but not over bimetallic ferrierites. NO_x species created during the decomposition of nitrous oxide alone as well as with addition of NO, and employment of nitrous oxide labeled with ^{18}O allowed us to assume a changing decomposition mechanism in the presence of Me ions in Fe-ferrierites.

KEY WORDS: Fe-, Pt-, Rh- and Ru-ferrierites; synergy effects in Fe/Me-ferrierites; N_2O decomposition.

1. Introduction

Fe-ferrierite exhibits high activity in the decomposition of nitrous oxide, low deactivation and high oxygen resistance [1–10]. The presence of NO and NO_2 even increases the activity [5,9]. In contrast, the reactivity decreases in the presence of moisture [10] and thus the decomposition must proceed above 400 °C. Noble metals alone [11–14] or supported [15–18] are also known to efficiently decompose nitrous oxide, but the reaction is inhibited by nitric oxide, oxygen and water [15,18]. Pieterse *et al.* [10] successfully reduced this drawback using bimetallic zeolite – Fe/Co-mordenite and Fe/Ru-ferrierite. The synergy between metallic and bimetallic systems in Fe/Ru-ferrierite has been tentatively ascribed to a change in the effect of NO [10].

We have studied the decomposition of nitrous oxide over Fe-ferrierite with various iron loading values [3–9]. It appeared that iron located in cationic positions, most probably in β-sites, serves as an active center for the N_2O decomposition [3]. Consequently, Fe-ferrireites containing less than 1 wt% of iron (Fe/Al of about 0.06, most β-sites occupied) exhibit the highest activity related to the Fe content. Decomposition of ^{18}O labeled nitrous oxide showed that the recombination of oxygen atoms from N_2O proceeds with the participation of zeolite oxygens, as neither the isotopomers $^{18}O_2$ nor $^{18}O^{16}O$ were solely formed [7,9]. The analysis of surface species desorbed after the decomposition of nitrous oxide and nitrous oxide + nitric oxide allowed us to assume that NO_x species are active intermediates in the N_2O decomposition. They play the role of oxygen scavengers and of oxygen carrier through the zeolite lattice [9]. As the activity of NO_x species as well as the recombination of oxygen atoms can be changed in bimetallic Fe/Pt-, Fe/Rh- and Fe/Ru-ferrierites, the decomposition of N_2O in a flow reactor and the decomposition of $^{15}N_2{}^{18}O$ in a batch reactor were examined. The role of added nitric oxide and the equilibration of $^{16}O_2$ + $^{18}O_2$ mixtures were also studied. Preliminary results are reported.

2. Experimental

2.1. Samples

Fe-ferrierite (Si/Al = 8.9) was prepared from NH_4-ferrierite (originally NaK-ferrierite, TOSOH Co, ion exchanged with ammonium nitrate) by treatment in $FeCl_3$ solution in acetyl-acetone (for details see Refs. [19,20]). Pt-, Rh- and Ru-ferrierites were prepared by ion-exchange with NH_4-ferrierite using 1 mmol per l solution of tetraammonium salts in water (25, 50 and 50 ml per g of zeolite, respectively). The bimetallic ferrierites were prepared from Pt-, Rh- and Ru-ferrierites by subsequent exchange of iron similarly for the Fe-ferrierite. Samples are denoted Fe/Me-ferrierites.Their composition is given in table 1.

2.2. Measurements

Flow experiments were performed in a classical quartz U shaped flow-reactor. Individual components of the reaction mixture were fed using a set of mass-flow controllers (KARA-CZ) into a mixing-line, where they were diluted by helium as a carrier gas. The resulting

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Table 1
Composition of samples

Sample	Si/Al	Fe wt%	Me wt%	Fe/Al
H-fer	8.9	*	–	–
Fe-fer	9.1	0.98	–	0.1
Pt-fer	9.1	*	≅0.53	–
Rh-fer	9.2	*	≅0.05	–
Ru-fer	9.1	*	≅0.05	–
Fe/Pt-fer	8.9	1.05	≅0.51	0.2
Fe/Rh-fer	9.0	1.82	≅0.07	0.5
Fe/Ru-fer	9.1	1.19	≅0.05	0.3

*150 ppm of Fe in the parent zeolite.

flow of 300 cm^3 min^{-1} was then adjusted, corresponding to GHSV of approx. 90,000 h^{-1}. The on-line analysis of N_2O and NO/NO_2 was performed using an Advance Optima IR analyzer (ABB Co., Germany) and a chemiluminescence analyzer (VAMET-CZ). N_2 and O_2 were monitored regularly, using a Hewlett-Packard 5890 II GC Chromatograph. Steady-state conversions reached typically within 20 min were compared. In some cases, NO was added to the N_2O/He mixture in amounts of 27, 50, 100 and 500 ppm. The corresponding effect on the N_2O decomposition was the highest between 27 and 50 ppm where the effect of a further 50–500 ppm added did not exceed the lower NO addition values by more than 10%.

Batch experiments were performed on the zeolite samples (100 mg) pretreated *in situ* at 450 °C in vacuum, followed by oxidation in 5 kPa of oxygen to remove the traces of carbon. Then the samples were again evacuated, and the temperature was decreased to 280 °C. The decomposition of 500 Pa of ${}^{15}N_2{}^{18}O$ (Medical Isotopes Inc., USA, 99 at %), in some cases with 50 Pa of ${}^{14}N^{16}O$ (MG 2.5) was measured in a 160 ml reaction volume. A negligible amount of the gas phase was led into a Balzers QMG 420 quadrupole mass spectrometer via a needle valve; the gas composition was calculated using characteristic ions calibrated using pure compounds. Temperature-programmed desorption (TPD, 5 °C/min) was measured after the reaction (usually lasting 80 min); the gases were rapidly evacuated and the temperature was decreased to 150 °C. The gases during TPD were led directly into the mass spectrometer without any leak. The equilibration of a 1:1 mixture (300 Pa) of ${}^{16}O_2$ (99.9 at.%) and ${}^{18}O_2$ (85 at.%, Technabsexport, Russia) was also examined at 280 °C.

3. Results

The Fe loading (see table 1) lies between 0.98 and 1.8 wt%, i.e. above the value of the highest activity per Fe in ferrierite [3,4]. Iron ions are located predominantly in the cationic positions, together with β- also in α-sites. Location of the noble metals ions in the cationic positions also seems to be very probable as follows from IR data and D_2 exchange.

The decomposition of nitrous oxide under the flow conditions is displayed in dependence on the reaction temperature for all the samples in figure 1A. The bottom part stands for bimetallic ferrierites (Fe-ferierite is added for comparison) and the top part for monometallic ferrierites. It can be seen that Ru-ferrierite is more active than Rh- and Fe-ferrierite. Pt-ferrierite was virtually inactive and therefore is not shown in the figure. Bimetallic systems exhibit the highest conversion for Ru/Fe-ferrierite and Rh/Fe-ferrierite up to 400 °C. Above this temperature, the activity of Pt/Fe-ferrierite is similar to that of Rh/Fe-ferrierite and the activity of Ru/Fe-ferrierite decreases. The activity of monometallic Fe-ferrierite also increases above 400 °C, which partially explains the increase in bimetallic Pt/Fe-ferrierite. Nevertheless, the N_2O decomposition over bimetallic ferrierites is always higher than that over Fe-ferrierite including Pt/Fe-ferrierite, regardless the absence of activity over monometallic Pt-ferrierite.

The activity in bimetallic systems is not equal to the simple sum of the Fe-ferrierite and Me-ferrierites as follows from figure 1B, in which the ratios of the sums of monometallic ferrierites to the respective bimetallic ferrierite are displayed. It can be seen that only at 400 °C are all three bimetallic systems more active than the sum of the monometallic ferrierites. The sum of the individual monometallic systems in all the other cases is higher than that for the bimetallic ferrierite except for Pt/Fe-ferrierite.

The addition of NO increases the conversion of nitrous oxide in almost the same way for bimetallic ferrierites and Fe-ferrierite in contrast to monometallic Rh- and Ru-ferrierites, whose activity decreases substantially (see figure 1C). Consequently, the sum of the individual monometallic ferrierites related to the bimetallic ferrierites above 300 °C lies near a value of 1 (see figure 1D).

The batch decompositions of ${}^{15}N_2{}^{18}O$ and ${}^{15}N_2{}^{18}O$ + NO over Fe/Pt-ferrierite in dependence on time are depicted in figure 2A and B, respectively. Section a shows the decomposition at 280 °C, section b the release of dioxygen isotopomers during the decomposition, section c the % of ${}^{18}O$ in dioxygens, and section d the gas products released during the subsequent TPD. The same parameters are given in sections e–h for the ${}^{15}N_2{}^{18}O$ + ${}^{14}N^{16}O$ (1:0.1) mixture. The presence of NO therefore: (i) accelerates the decomposition of nitrous oxide (e versus a), and (ii) less ${}^{18}O$-enriched oxygen is released (g versus c) and ${}^{14}N^{16}O^{2}$ + ${}^{14}N^{16}O$ greatly predominates over the ${}^{15}N$ oxides in the TPD products (h versus d).

The decomposition of ${}^{15}N_2{}^{18}O$ (empty columns) and ${}^{15}N_2{}^{18}O$ + ${}^{14}N^{16}O$ (solid columns) is compared in figure 3A for mono- and bimetallic-ferrierites at 280 °C after 40 min. The effect of noble metals is similar as that under flow conditions. The values of the sum of monometallic ferrierites related to the respective bimetallic ferrierite for the decomposition of nitrous oxide at

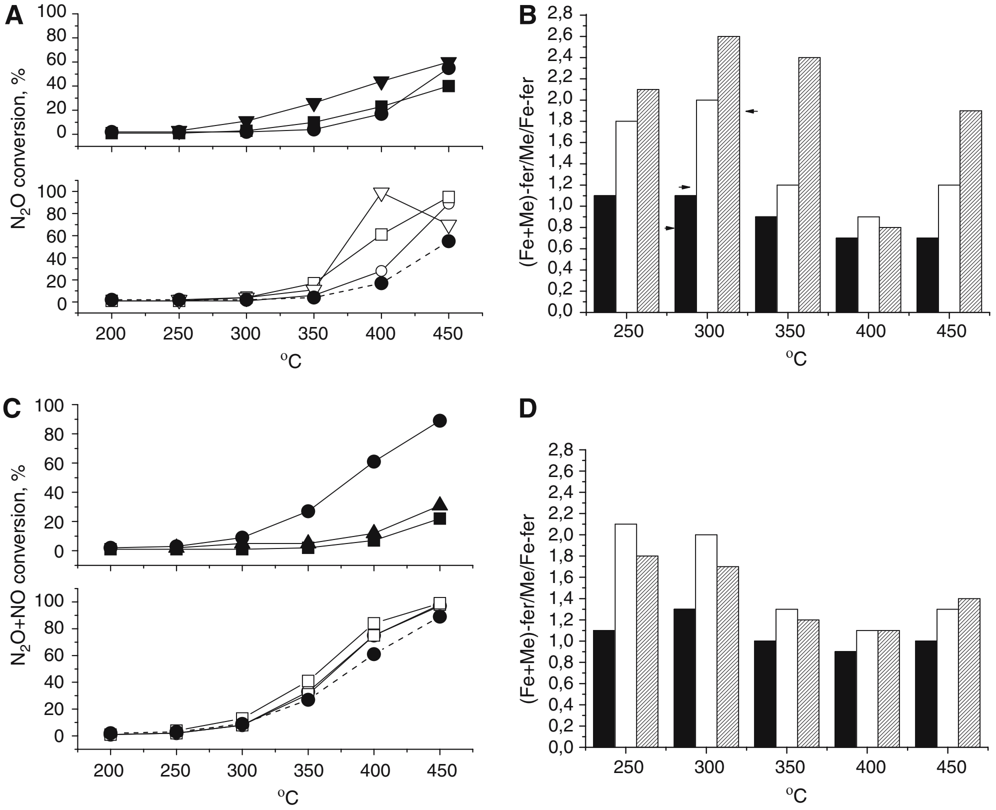

Figure 1. Temperature dependence of the conversion in N_2O decomposition over Fe-, Me- and Me/Fe-ferrierites (flow experiments). (A) Bottom: bimetallic ferrierites. Open symbols: circles for Pt/Fe-ferrieite, squares for Rh/Fe-ferrierite and triangles for Ru/Fe-ferrierite, dashed curve and solid circles for Fe-ferrierite. Top: monometallic ferrierites. Solid symbols: circles for Fe-ferrierite, squares for Rh-ferrierite and tringles for Ru-ferrierite. (B) Ratios of the N_2O conversion over sum of individual ferrierites to the respective bimetallic ferrierite. Solid column: Fe-ferrierite related to Pt/Fe-ferrierite, empty column: Rh-ferrierite + Fe-ferrierite to Rh/Fe-ferrierite. Stripped columns: Ru-ferrierite + Fe-ferrierite to Ru/Fe-ferrierite (arrows show the level of batch values for 280 °C). (C) Decomposition of N_2O 1000 ppm + NO 100 ppm. Arrangement and symbols are the same as in (A). (D) Ratios of the N_2O conversions in N_2O + NO mixture over sum of individual ferrierites to the respective bimetallic ferrierite. Solid column: Fe-ferrierite related toPt/Fe-ferrierite, empty column: Rh-ferrierite + Fe-ferrierite to Rh/Fe-ferrierite. Stripped columns: Ru-ferrierite + Fe-ferrierite to Ru/Fe-ferrierite.

280 °C are denoted by arrows for comparison with flow experiments in figure 1B. The effect of NO on the decomposition of nitrous oxide is negative over Rh-ferrierite and even inhibits the decomposition over Ru-ferrierite. In contrast, NO enhances the N_2O decomposition over Fe-ferrierite, Pt/Fe-ferrierite and Ru/Fe-ferrierite, while the effect tends to be negative over Rh/Fe-ferrierite. However, in accordance with the flow experiments, the decomposition of nitrous + nitric oxide does not differ greatly over Fe-ferrierite and bimetallic ferrierites.

The amount of zeolitic oxygens taking part in the decomposition is displayed in figure 3B (this is calculated from the degree of decomposition and the decrease in the ^{18}O concentration – for details see Refs. [8,9]. It follows that during the decomposition of nitrous oxide alone the number of participating oxygens exhibits the opposite behaviour to the N_2O decomposition, i.e. decreases in the presence of noble metals. However, NO considerably increases this amount except over Ru-ferrierite; the increase is considerably higher than that caused by ^{16}O added from nitric oxide.

Figure 3C shows the composition of individual dioxygen isotopomers: the presence of noble metals alone or in mixtures with iron enhances the formation of dioxygens enriched more in ^{18}O.

The composition of desorbed surface species during TPD from Fe-, Pt/Fe- and Rh/Fe-ferrierites is displayed in figure 4. The amount of NO_2 and of dioxygen is lower for bimetallic ferrierites than for Fe-ferririte. TPD from Rh-ferrrierite and Ru-ferrierite yields only a small amount of dioxygen and no NO_x species (not shown in the figure).

The ratio of dinitrogen to dioxide (see figure 5) released in the decomposition of nitrous oxide at 280 °C should be equal to 2 ($N_2O \rightarrow N_2 + 1/2O_2$), but the observed ratio is lower due to oxygen captured in the ferrierite during the decomposition of nitrous oxide. It can be seen that the amount of captured oxygen decreases in the sequence from Fe-ferrierite to Rh-ferrierite.

The equilibration of dioxygen isotopomers was measured at 280 °C to obtain information on the ability

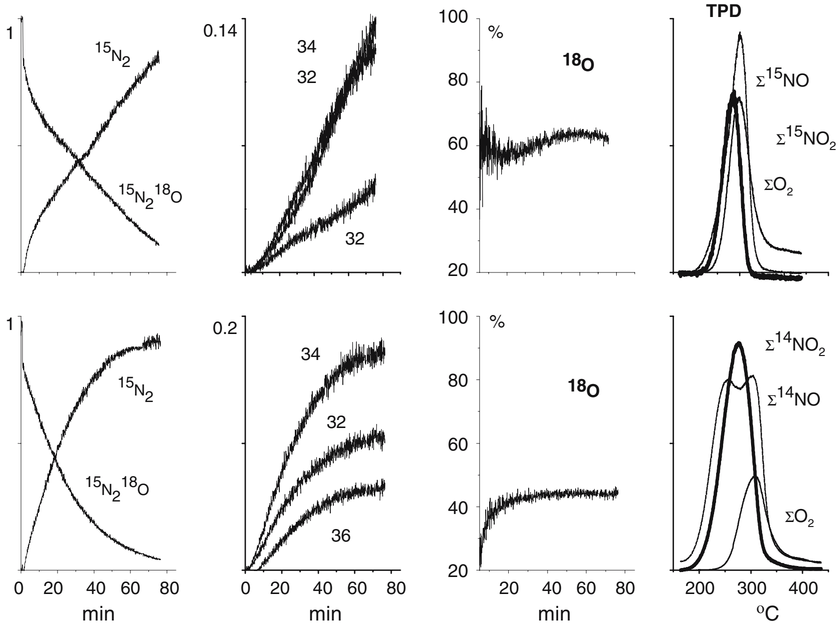

Figure 2. Decomposition of $^{15}N_2{}^{18}O$ without and with $^{14}N^{16}O$ over Pt/Fe-ferrierite, T = 280 °C (batch experiments). (A) 500 Pa $^{15}N_2{}^{18}O$; a, decomposition of $^{15}N_2{}^{18}O$ and formation of $^{15}N_2$; b, release of dioxygen isotopomers, 32 for $^{16}O_2$, 34 for $^{16}O^{18}O$ and 36 for $^{18}O_2$; c, ^{18}O % in dioxygen; d, TPD after the decomposition. (B) 500 Pa $^{15}N_2{}^{18}O$ + 50 Pa $^{14}N^{16}O$; e–h, the same as a–d.

to dissociate and recombine dioxygen molecules. It appeared that only very low equilibration proceeds over Fe-, Pt-, and Pt/Fe-ferrierites, a little higher rate was observed over Rh-ferrierite and a very rapid reaction proceeds over Rh/Fe-, Ru/Fe- and Ru-ferrierites.

4. Discussion

The enhancing effect of the presence of noble metals in Fe-ferrierite on the decomposition of nitrous oxide is the highest for Ru and Rh and the lowest for Pt (figure 1A, bottom). In monometallic ferrierites, virtually no decomposition proceeds over Pt-ferrierite, and that over Ru-ferrierite is higher than over Rh-ferrierite (except for the highest temperature also over Fe-ferrierite; see the top part of the figure 1A). The very low activity of Pt and high activity of Ru agree with the observations reported in Ref. [1]. The degree of decomposition is not equal to the simple sum of the values for Fe-ferrierite and Me/Fe-ferrierite, as follows from figure 1B. The increasing activity of bimetallic ferrierites compared to the sum of the monometallic ferrierites occurs at and above 350 °C especially above Pt/Fe-ferrierite, a lesser effect is found over Rh/Fe-ferrierite, and an effect over Ru/Fe-ferrrierite appears only at 400 °C.

The situation is changed when nitrous oxide is decomposed in the presence of NO. In this case, the decomposition over all the bimetallic ferrierites is very similar to that over Fe-ferrierite (cf. figure 1C). This is probably due to the alternative effect of NO on Rh- and Ru-ferrierite. Consequently, the sum of decompositions over monometallic ferrierites related to the respective bimetallic ferrierites is near to a value of 1 for all samples above 300 °C. A negative effect of NO on the decomposition of N_2O over Ru-ferrierite was reported by Pieterse *et al.* [10]; we have also found a similar effect for Rh. The simultaneous presence of these metals together with iron ions probably overwhelms the negative effect of NO over monometallic ferrierites.

The formation of dioxygen and its desorption from the Fe-zeolites is commonly assumed to be the rate-determining step in the decomposition of nitrous oxide. The use of $N_2{}^{18}O$ shows that the presence of noble metals enhances the recombination of oxygens from nitrous oxide (figure 3C, see the increased fraction of $^{18}O_2$) and thus partially decreases the participation of zeolite oxygens. This is most explicit over monometallic Rh- and Ru-ferrierites. The decomposition of N_2O practically does not proceed over Pt-ferrierite, but the presence of platinum in bimetallic Pt/Fe-ferrierite also increases the recombination of oxygen atoms from nitrous oxide. The higher recombination can be related to a lower fraction of captured oxygens – this decreases in the sequence Rh-ferrierite < Rh/Fe-ferrierite < Pt/Fe-ferrierite < Fe-ferrierite (see figure 5). In adition, the equilibration of dioxygen molecules – dissociation and recombination – proceeds very readily over Rh/Fe-, Ru/Fe- and Ru-ferrierite.

The beneficial effect of even small amounts of NO on the decomposition of nitrous oxide is widely assumed to be due to the removal of oxygen atoms from Fe-zeolites leading to the restoration of the active sites. We have found that, in addition, NO also serves as a carrier of oxygens in the Fe-ferrierite lattice, increasing the

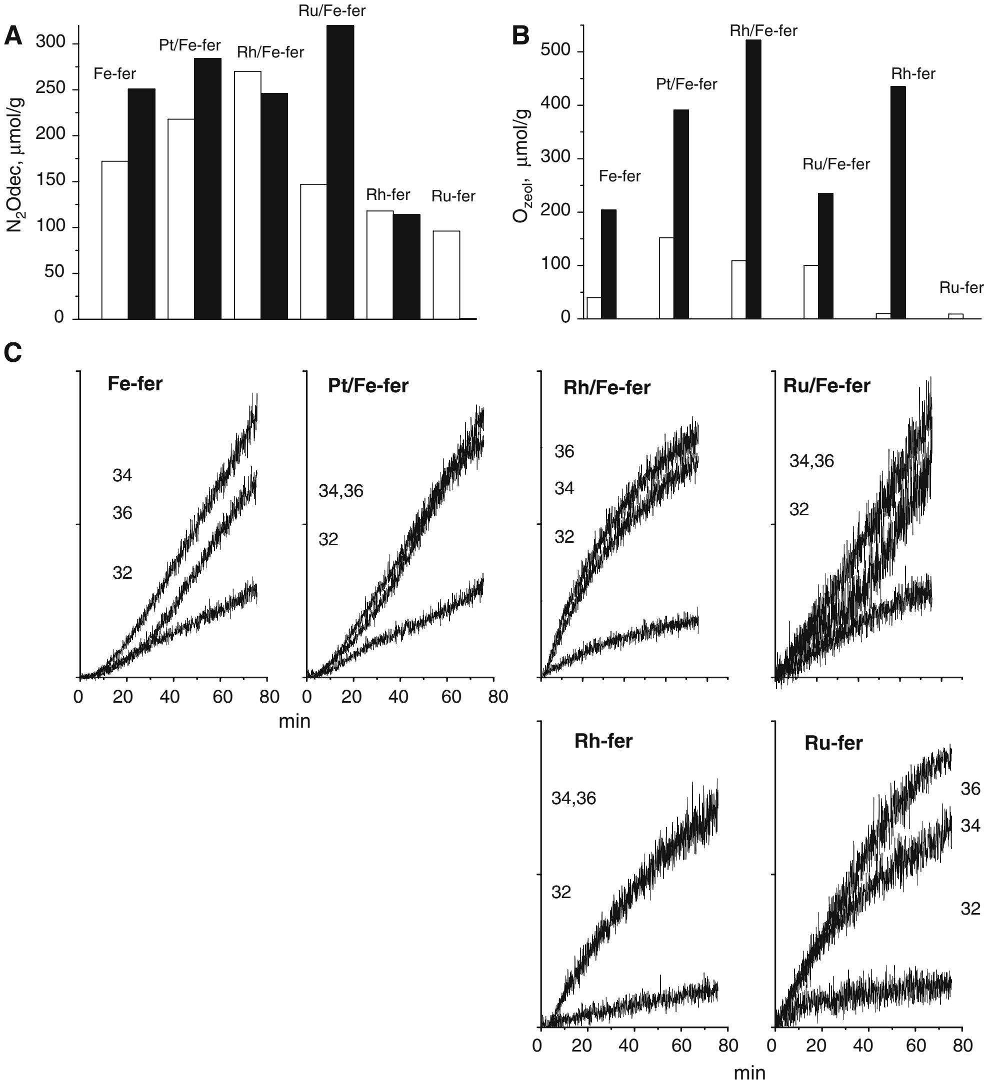

Figure 3. Comparison of $^{15}N_2{}^{18}O$ decomposition over individual ferrierites without and with $^{14}N^{16}O$, T = 280 °C (batch experiments). (A) $^{15}N_2{}^{18}O$ decomposed after 40 min, empty column without NO, solid columns with NO. (B) Amount of participating zeolite oxygens after 40 min. Decomposition of $^{15}N_2{}^{18}O$, T = 280 °C. Empty columns without NO, solid columns with NO. (C) Release of dioxygen isotopomers during the decomposition of $^{15}N_2{}^{18}O$.

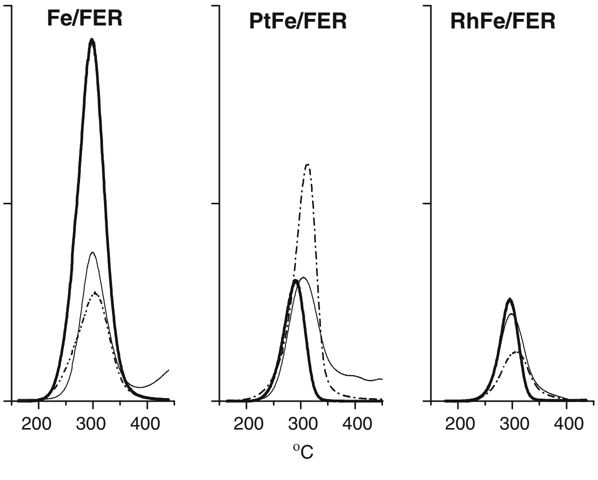

Figure 4. TPD of surface species after the decomposition of N_2O at 280 °C. Bold, NO_2; dot-dashed, NO; thin, O_2.

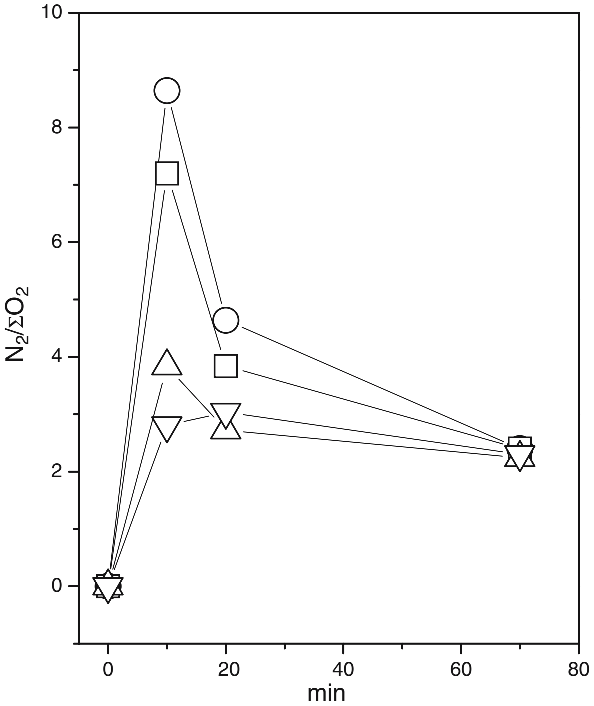

Figure 5. N_2/O_2 ratios during the decomposition of $^{15}N_2{}^{18}O$, T = 280 °C. Circles, Fe-ferrierite; squares, Pt/Fe-ferrierite; up triangles, Rh/Fe-ferrierite; down triangles, Rh-ferrierite.

mobility of zeolite oxygens and their involvement in the formation (and desorption) of dioxygen. The same enhancing role is played by surface NO_x species created during the decomposition of nitrous oxide alone [9]. It follows from figure 4 that the amount of surface species desorbed during TPD decreases in the sequence: Fe-ferrierite > Pt/Fe-ferrierite > Rh/Fe-ferrierite, i.e. in the increasing role of recombination of oxygen atoms from N_2O (figure 3C) and decreasing amount of the participating zeolite oxygens (figure 3B). The addition of NO increases the N_2O decomposition especially over Fe- and Pt/Fe-ferrierites. This supports the above conclusions related to a change in the mechanism from enhancement by NO_x (added and/or created during the decomposition of nitrous oxide alone) to increased recombination of oxygen atoms in the presence of Rh and Ru.

5. Conclusions

A synergic effect in the decomposition of nitrous oxide between Fe-ferrierite and bimetallic Me/Fe-ferrierites is tentatively ascribed to the mechanism passing from that enhanced by the presence of NO_x species and prevailing recombination of oxygen atoms with the zeolite oxygens (characteristic for Fe-ferrierite) to a mechanism of enhanced recombination of oxygen atoms from nitrous oxide (inherent with noble metals).

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