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Synergy between metals in bimetallic zeolite supported catalyst for NO-promoted N_2O decomposition

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The detrimental effect of NO on N_2O decomposition over zeolite supported noble metal catalysts can be (partly) eliminated by combining noble metal with iron or cobalt. In the presence of NO, the total conversion of N_2O over these bimetallic-zeolites exceeds the sum of conversions over the monometallic analogues of the individual components. A synergistic effect between the metals is proposed to be responsible for this phenomenon. This synergistic effect gives superior N_2O decomposition activity under realistic conditions, i.e. in the presence of water and NO, at temperatures as low as 350 °C. The nature of the synergy is discussed in the light of some preliminary observations.

KEY WORDS: synergy, metals, bimetallic zeolite, N_2O decomposition

1. Introduction

Direct catalytic decomposition of N_2O in the tail gases of nitric acid plants has been identified as a cost efficient and safe method for N_2O abatement. However, in many plants tail gas temperatures are not high enough to promote decomposition of N_2O. The current state-of-the-art catalysts for N_2O decomposition operate only when the tail-gas temperature is higher than 400 °C [1,2,3]. The selective catalytic reduction (SCR) of N_2O with hydrocarbons works from temperatures of about 250 °C, which is about the lowest possible tail gas temperature of a nitric acid plant. In the past various studies have investigated SCR of N_2O using NH_3 [4], C_3 and C_4 [5,6,7] or methane [5,8] as a reducing agent. Combined NO_x and N_2O removal by means of HC-SCR was also investigated [9]. While SCR is feasible, the cost of the reducing agent makes it more expensive than other techniques [3,10]. Development of improved catalysts that convert N_2O at temperatures below 400 °C without reducing agent is therefore attractive.

Iron-zeolites, especially Fe-ZSM-5, are being studied for use as catalysts for N_2O decomposition [11–18]. NO_x, that is usually present in the off-gas, promotes N_2O decomposition over iron-zeolites [11]. Fe-FER [2,14] and Fe-BEA [18] perform particularly well. However, a temperature of 400 °C is still necessary with Fe-FER in the presence of H_2O and NO_x to achieve 75% N_2O conversion [2]. Noble metal catalysts have a higher intrinsic activity for N_2O decomposition in comparison to iron [19]. Unfortunately, N_2O decomposition reaction over noble metal catalysts is inhibited by NO, O_2 and H_2O [19,20]. This disfavours their use in the tail gas of nitric acid factories. This study shows, for the first time, how on zeolites a synergistic effect between iron or cobalt, and a noble metal, can improve N_2O decomposition tremendously if some NO is present. This effect also manifests itself in the presence of O_2 and H_2O. This synergy provides new opportunities for the use of noble metal to catalyse N_2O decomposition in exhaust gas at temperatures lower than currently reported.

2. Experimental

Co-MOR was prepared by impregnation of cobalt-nitrate on NH_4-MOR (Zeolyst CBV21a Si/Al = 10) (CoMOR). Rhodium-MOR was obtained by exchanging Rhodium-nitrate (10% Rh, J & M) at 80–85 °C for a period of 6 h while stirring at 500 rpm. Filtration and washing was carried out directly after the exchange (RhMOR). Subsequently, Rh-MOR was impregnated with cobalt-nitrate (CoRhMOR). The catalysts were calcined under flowing air with 3 °C/min toward 550 °C and kept there for 5 h.

Fe-FER was prepared by first exchanging Na/K-FER (Tosoh HSZ-720KOA, Si/Al = 9.2) three times with 0.1 M NH_4NO_3 to obtain NH_4-FER and subsequent impregnation of ironnitrate (FeFER). Ru-FER was obtained by exchanging $Ru(NH_4)_3Cl_6$ (1.5% Ru, J & M) with NH_4-FER at 80–85 °C for a period of 6 h while stirring at 500 rpm. Filtration and washing was carried out inbetween the exchange cycles. Calcination was carried out under flowing air with 3 °C/min toward 550 °C, maintained for 5 h, to obtain Ru-H-FER (RuFER). Fe-Ru-FER was obtained by incipient-wetness impregnation of Ru-NH_4-FER with ironnitrate

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Table 1
Catalysts coding and chemical analysis

Catalyst	Elemental analysis						
	Si/Al[a]	Fe/Al	Fe (wt%)	Ru (wt%)	Co (wt%)	Co/Al	Rh (wt%)
FeFER	9	0.2	2.2				
RuFER	9			0.4			
FeRuFER	9	0.2	2.2	0.4			
CoMoR	9.5				2.2	0.2	
RhMoR	9.5						0.35
CoRhMOR	9.5				2.2	0.2	0.35

[a] Si/Al of the parent materials.

and subsequent calcination (FeRuFER). Table 1 lists the catalyst coding together with the results of chemical analysis. The parent zeolites used in this study were all crystalline as deduced from XRD analysis.

Activity measurements were carried out in a microflow reactor. Mass flow controllers supply the gases and water is fed using a liqui-flow controller (Bronkhorst Hi-Tec). The gas composition studied here, 1500 ppm N_2O, 0.5 vol% H_2O, 0 and 200 ppm NO, 2.5 % O_2 and bal. N_2, and is representative for a (larger) nitric acid plant [21,22]. All components are mixed in a controlled evaporator mixer and the lines are kept at approx. 120 °C to prevent condensation. Gas analysis was performed using FTIR, NO_x analyser and GC-TCD.

3. Results and discussion

Rhodium and cobalt supported by zeolite are both very active for N_2O decomposition in the absence of NO [19,20,23]. Figure 1 shows N_2O decomposition over CoMOR, RhMOR and CoRhMOR. The presence of NO boost N_2O decomposition activity over CoMOR while it has a strong negative effect on the performance of RhMOR. Combining cobalt and rhodium in CoRhMOR results in conversion somewhat higher than the sum of the individual monometallic analogues. 55% N_2O conversion was obtained with CoRhMOR at 350 °C (100% at 375 °C) in a feed of 1500 ppm N_2O, 200 ppm NO, 0.5% N_2O, 2.5% O_2 at a GHSV of 6000 h^{-1} during tests for over 600 h time-on-stream (figure 2).

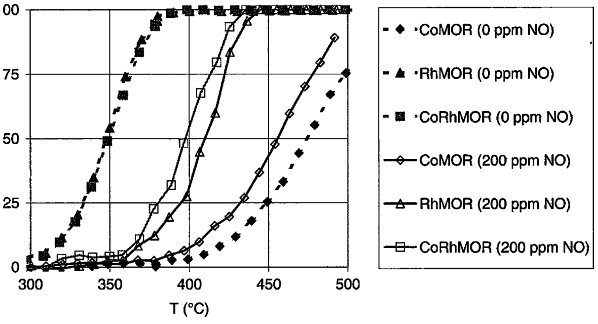

Figure 1. N_2O decomposition over CoRhMOR, CoMOR, RhMOR as function of the temperature:1500 ppm N_2O, 0 or 200 ppm NO, 0.5% H_2O, 2.5% O_2, W/F (STP) 11 g.s.mol^{-1}.

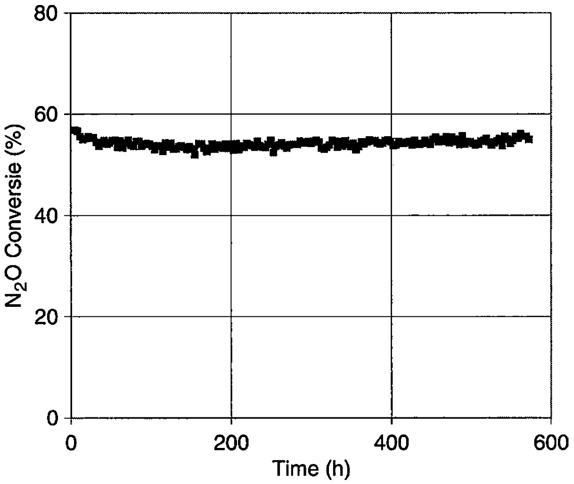

Figure 2. N_2O decomposition as function of the time on stream over CoRhMOR: 1500 ppm N_2O, 200 ppm NO, 0.5% H_2O, 2.5% O_2, GHSV ca. 6.000 h^{-1}.

The beneficial effect of combining metals for N_2O decomposition in the presence of NO becomes particularly clear upon combining ruthenium with iron. Figure 3 shows the effect of NO on RuFER, FeFER and FeRuFER. Without NO in the feed RuFER is more active than FeFER and FeRuFER. This is in agreement with the generally observed very high activity of zeolite supported noble metal catalysts, especially rhodium and ruthenium, in the decomposition of N_2O [19]. FeRuFER shows somewhat lower activity in comparison to RuFER:iron may partially block (access to) Ru and lowers the number of Ru sites available for reaction. However, in the presence of 200 ppm NO the FeRu combination catalyst is by far the most active. Combining iron and ruthenium in FeRuFER results in conversion much higher than the sum of the individual monometallic analogues, i.e. FeFER and RuFER. Clearly, a synergy exists between the metals. It is tempting to explain this synergy by the mechanisms known for the monometallic analogues.

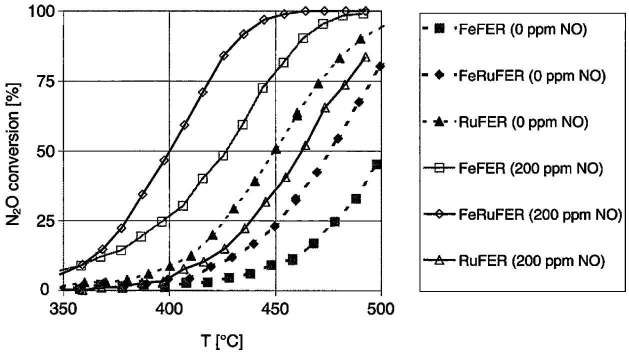

Figure 3. N_2O decomposition as function of the temperature over FeRuFER, RuFER FeFER: 1500 ppm N_2O, 0 or 200 ppm NO, 0.5% H_2O, 2.5% O_2, W/F (STP) 11 g.s.mol^{-1}.

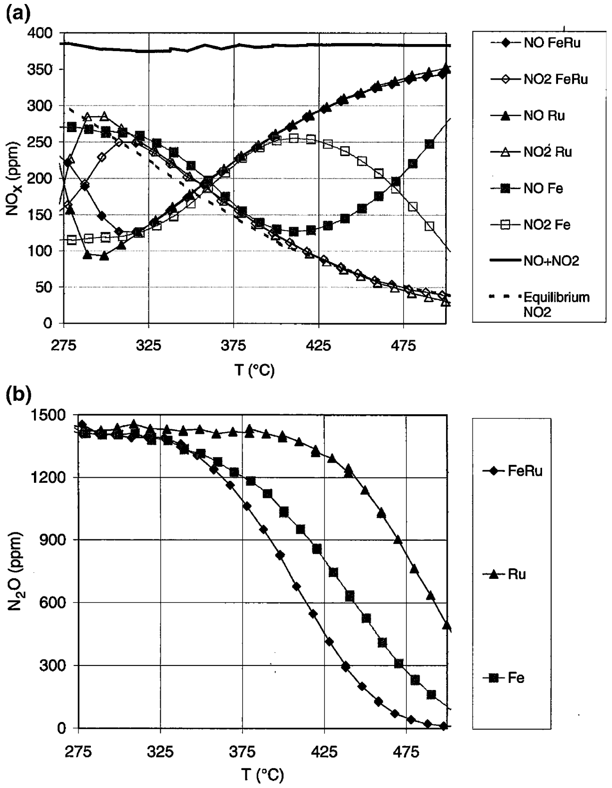

Figure 4. FeRuFER, RuFER, FeFER (a) upper scheme, NO–NO_2 concentration versus temperature, (b) lower scheme, N_2O concentration versus temperature: 1500 ppm N_2O, 400 ppm NO, 2% O_2, W/F (STP) 11 g.s.mol^{-1}.

NO promotes the N_2O decomposition activity over iron-zeolite by accelerating (rate determining) oxygen desorption:adsorbed NO accommodates oxygen from N_2O and the formed adsorbed NO_2 can react with a second oxygen from the neighbouring site, thus accelerating the recombination of oxygen from N_2O and its subsequent desorption [12]. Oxygen desorption is also the rate determining step over Ru-zeolites [24]. Nevertheless, with ruthenium, N_2O decomposition activity is lower in the presence of NO. As the effect of NO is reversible, poisoning of N_2O sorption sites by NO is likely the reason for the lower activity. For iron it is reported that the adsorption sites for NO (NO_2) and N_2O (alpha-oxygen) are different [12]. Therefore, the synergy of the metals may be explained by the presence of strong NO adsorption sites on iron in FeRuFER leaving ruthenium sites free for reaction of N_2O, i.e. iron is trapping NO. This NO-trap is regenerated by either spill-over of NO toward α-oxygen and subsequent recombinative desorption or oxidation with gasphase oxygen. The increase in the activity of Fe-Ru-FER in comparison with Fe-FER and Ru-FER in the presence of NO would than be explained by (1) less NO molecules to inhibit N_2O decomposition over Ru sites and (2) NO-assisted N_2O decomposition on iron sites as known for Fe-FER is also preserved for FE-RuFER. However, the NO-NO_2 profiles for Fe, Ru and FeRu supported by FER do not fully support this explanation. NO-NO_2 concentration variations as a function of the temperature were used before with Fe-ZSM-5 to gain insight in the role of NO in N_2O decomposition [12]. In figure 4 we have carried out a similar study that shows N_2O depletion (b) and NO_2 formation (a) as a function of the temperature in a feed comprising N_2O, NO, O_2 and N_2. From figure 4a it follows that the formation of NO_2 over Fe-FER increases as a function of temperature, reaching a maximum at 410–430 °C. This temperature coincides with the inflection point of the N_2O decomposition conversion curve (figure 4b). The amount of NO_2 produced is far beyond the thermodynamic equilibrium concentration NO_2 ($2NO + O_2 \Longleftrightarrow 2NO_2$) displayed by the dashed line in Figure 4a. At higher temperatures NO_2 concentration is lowered again. The total NO_x conversion is constant indicating that NO_x is not converted to N_2 or N_2O. These observations are in line with the ones previously reported by Perez-ramirez on Fe-ZSM-5 [12] and were ascribed to the oxidation of NO with N_2O as being an essential part of the mechanism of NO-assisted N_2O decomposition. In the case of Ru-FER, no such excessive NO_2 formation is observed in agreement with the general observation that NO does not promote N_2O decomposition over Ru-zeolite. Strikingly, the NO–NO_2 behaviour of Fe-Ru-FER does not show any behaviour characteristic to Fe-FER:NO_2 formation beyond thermodynamic equilibrium concentrations at temperatures over 350 °C is not observed. Therefore, no indications for NO-assisted N_2O decomposition over iron sites in Fe-Ru-FER can be found. These observations show that the catalytic nature of the bimetallic catalysts is not a sum of intrinsic properties of the monometallic analogues. Close inspection of the NO–NO_2 profiles of both Ru-FER and FeRu-FER shows that the NO oxidation reaction on Fe-Ru is somewhat suppressed as compared to Ru-FER at low temperature. Therefore, the presence of iron in Fe-Ru-FER seems to decrease the affinity of Ru for NO and, consequently, the inhibitory power of NO. On the other hand, NO-assisted N_2O decomposition on the iron sites in Fe-Ru-FER is not observed.

However, acknowledging the enormous difference in the conversion levels of Fe-Ru-FER and Ru-FER it is clear that the synergy deserves much more investigation. Currently, research is ongoing to further clarify the synergy to optimise bimetallic catalysts for N_2O decomposition.

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