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Role and importance of oxidized nitrogen oxide adspecies on the mechanism and dynamics of reaction over copper-based catalysts

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Abstract

The formation of nitrate and NO_2 adspecies over Cu/MFI and copper-on-alumina catalysts and their role in the mechanism of reaction is discussed on the basis of FT–IR results and catalytic tests in unsteady-state conditions. Three specific cases are discussed: (i) reduction of NO by propane/O_2 over Cu/MFI, (ii) conversion of NO by NH_3/O_2 over copper-on-alumina catalysts and (iii) oxygen-promoted reduction of NO in the absence of reductants over Cu/MFI. The formation of nitrate species leads to self-deactivation, but Cu^{2+}–NO_2 like adspecies are suggested to be a key intermediate in the reduction of NO to N_2 in all three cases examined.

Keywords: Cu/MFI catalysts; Cu–Al catalysts; Nitrate, formation of; NO_2 adspecies, formation of

1. Introduction

The chemistry of interaction and transformation of nitrogen oxides over copper-based catalysts has attracted considerable attention in recent years, due to the interesting properties of these catalysts (a) in the decomposition of NO or N_2O, (b) in the reduction of NO with hydrocarbons (propane, especially), (c) in the combined removal of NO and SO_2 from flue gas and (d) in the high-temperature reduction of NO with NH_3/O_2 [1]. Furthermore, the catalytic performances of copper-based catalysts is good in a wide range of reactions involving nitrogen oxides and copper ions are the key component of several enzymes involved in microbiological transformations of nitrogen oxides [1]. Copper-based catalysts are, thus, well suited for studies directed towards obtaining a better understanding of the fundamental aspects of the reaction mechanism in the conversion of NO. The small amount of data in the literature on this topic is quite contradictory. Particularly unclear is the role and importance of oxidized adspecies of nitrogen oxides (N_xO_y where $y > x$) in the overall reaction mechanism and catalytic behaviour. Various authors have proposed an initial step of oxidation of NO to NO_2 in its mechanism of reduction to N_2 in the presence of hydrocarbons/oxygen [2], but the possible role of analogous adspecies of nitrogen oxides in the reduction of NO in the presence of ammonia/oxygen or during its decomposition has not yet been clarified. Infrared evidence, however, has shown the formation of nitrite/nitrate species by anaerobic contact of NO with copper-based cat-

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alysts and suggest their possible role in the mechanism of decomposition of NO [3,4].

The objective of the research reported here was to study the role of oxidized adspecies of nitrogen oxides on the reactivity of both copper-zeolites and copper-on-oxides using IR spectroscopy and transient catalytic tests to obtain information on the dynamics of reaction and to determine the common features in the reaction mechanisms for the various copper-based catalysts and/or reductants.

2. Experimental

The Cu/MFI sample was prepared from the sodium form of the zeolite using a conventional room-temperature ion-exchange procedure described elsewhere [5,6]. The SiO_2/Al_2O_3 ratio for the MFI (ZSM-5) sample is 49 and the Cu/Al ratio 0.66. Copper-on-alumina samples were prepared by the incipient wet impregnation method on a 116 m^2/g γ-Al_2O_3 (Rhone–Poulenc 535) [7].

Unsteady-state catalytic tests were carried out in a quartz microreactor connected on-line with a mass quadrupole detector for fast and continuous analysis of the reaction products and inlet composition [7,8]. The data were elaborated to take into account possible multiple fragmentations. The same apparatus was employed for thermodesorption studies using a linear temperature ramp of 50°C/min. The tests were carried out using 0.5 g of grains with mean dimensions

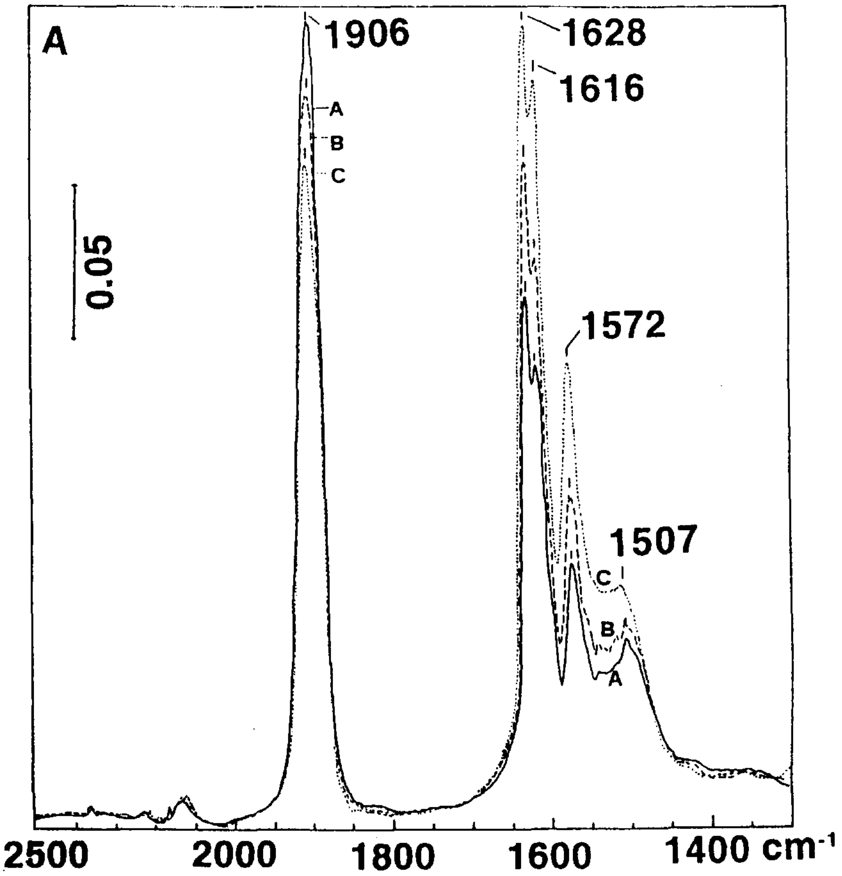

Fig. 1. IR spectra of adspecies of nitrogen oxides formed by putting 20 torr NO at rt in contact with Cu/MFI for 10, 20 and 60 min (curve a, b and c, respectively), followed by rt evacuation. The background spectrum of zeolite has been subtracted.

in the 0.1–0.2 mm range in order to minimize possible mass and heat transfer limitations.

Fourier-transform infrared (IR) measurements were recorded at rt in the transmission mode using self-supported disks and a conventional IR vacuum cell and gas-manipulation system which allows the sample to be treated in vacuum or in the presence of suitable pressures of gas up to 600°C [7].

3. Results and discussion

3.1. *Formation of Cu–nitrate species and their effect on the surface reactivity*

Reported in Fig. 1 are the IR spectra of adspecies of nitrogen oxides formed by anaerobic interaction of NO at rt for 10, 20 and 60 min over a Cu/MFI sample preactivated with O_2 at 500°C and then evacuated at rt to remove gaseous species. Two distinct types of species were detected: (i) a partially positively-charged mononitrosyl species adsorbed on isolated Cu^{2+} ions (band at 1906 cm^{-1}) and (ii) nitrate species [series of bands in the 1400–1650 cm^{-1} attributed to the stretching frequencies of various forms of nitrate species; tentatively, bridging nitrate interacting with copper ions and zeolite framework (bands at 1614 and 1628 cm^{-1}) and mono- and bi-dentate nitrate ions interacting with isolated copper ions only (bands at 1503 and 1572 cm^{-1})]. As the contact time with NO increases, the intensity of the bands of nitrate species progressively increases while that of mononitrosyl species decreases. Analogous spectra were recorded for NO contact at higher temperatures (up to 400°C), after consecutive contact with O_2 or in the presence of oxygen co-adsorption. Apart from a considerable increase in the intensity of nitrate species and a shortening of the time for their growth, no other significant differences were noted as regards the nature of adspecies of nitrogen oxides.

When NO was put in contact with copper-on-alumina samples with low copper loading (below 1 wt.-%), analogous species were detected, even though the spectra for nitrate species are less resolved. When the copper loading up to 10% was increased, however, the frequency for mononitrosyl species shifts to slightly lower frequencies (about 1890 cm^{-1}) and the more intense bands for nitrate species are detected at 1540, 1565 and 1588 cm^{-1}. Both changes are consistent with an increase in the formation of O-bridging copper–copper interactions which decrease the ionic character of the copper ions, change their reactivity towards NO and favour the formation of nitrate species bridging two copper ions [7].

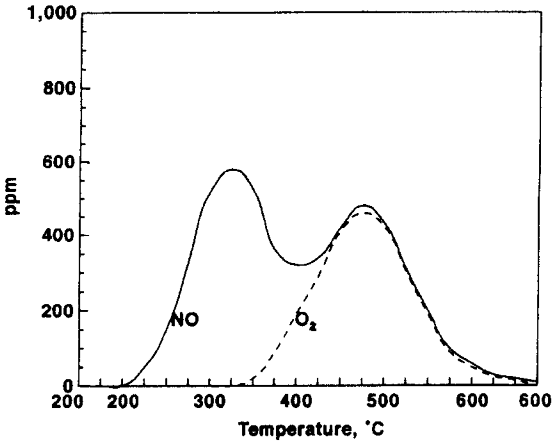

Fig. 2. Thermodesorption curves of NO and O_2 after preadsorption of NO and O_2 at 200°C over Cu/MFI followed by removal of gaseous species in a He flow.

The thermal stability of the nitrogen oxide adspecies can be determined by thermodesorption experiments. Reported in Fig. 2 is the evolution of NO and O_2 from Cu/MFI after a pretreatment at 200°C with a NO + O_2 flow followed by He treatment to remove gaseous species and the consecutive linear increase in catalyst temperature up to 600°C while maintaining the catalyst in the flow of helium. Two distinct NO desorption peaks can be seen, the first centred at 330°C and the second at about 480°C. The latter is associated with a parallel evolution of oxygen in a ratio of about 1 with respect to NO. This clearly indicates that the high temperature peak may be attributed to thermal decomposition of nitrate adspecies formed during the initial pretreatment at 200°C. The high temperature necessary for the decomposition of these nitrate species should be remarked. Apart for the case of decomposition of NO which is carried out at about 500°C on these Cu/MFI catalysts [6], the maximum in the reduction of NO to N_2 in the presence of hydrocarbons such as propane [6,8] or ammonia [9] occurs at about 300°C.

The formation and surface stability of nitrate species, however, also may have useful application, as shown by the new class of catalysts for the treatment of motor-vehicle emissions announced by researchers for Toyota, which is based on the concept of adsorption–storage of NO in the form of a surface nitrate-complex on an oxide matrix and the reduction of this complex by a second metallic element during periodic changes in O_2-content in the feed.

3.2. Nitrite or NO_2 adspecies as intermediate of reaction

The formation of nitrate species by oxidation of adsorbed NO gives rise to deactivation of the surface reactivity as discussed above, but the intermediate oxidation to nitrite or NO_2 adspecies leads to a promotion of the surface reactivity, since these species are involved in the mechanism of reduction up to formation of N_2 from NO or at least in one of the possible pathways [1]. Complex transient catalytic phenomena may thus be expected upon addition of oxygen to a feed containing NO and the reductant (hydrocarbon or ammonia).

Reported in Fig. 3 is the transient conversion of NO at 300°C when a step-change in the concentration of oxygen (shown also in the Figure) is made in a flow of 936 ppm NO + 1098 ppm NH_3 in helium over a copper-on-alumina catalyst containing 5 wt.-% CuO. Since NO itself is an oxidant, the base conversion in the absence of oxygen is different from zero, but immediately upon oxygen addition the conversion of NO rapidly rises. The formation of N_2, not reported here for sake of clarity, parallels the change in NO conversion, thus indicating that oxygen promotes the formation of N_2 from $NO + NH_3$ as expected. However, after about 1 min the conversion decreases reaching a steady-state value in about 3–4 min. The effect of oxygen in these tests is complex, because not only the nature of nitrogen oxides or ammonia adspecies varies upon its addition, but also their relative surface concentration. However, combining these data with IR, ESR and steady-state and unsteady-state catalytic data [7], it is possible to suggest that oxygen promotes a pathway of conversion of NO to N_2 involving the intermediate formation of an Cu^{2+}–NO_2 species which by reaction with neighbour ammonium ions gives rise to the formation of $N_2 + 2H_2O$. The further conversion of the NO_2 adspecies to a nitrite species competes with the above reaction and favours side reactions such as N_2O formation. The oxidation of NO to NO_2 and its consecutive conversion to the less reactive copper–nitrate species is responsible for the transient change in reactivity after the addition of oxygen shown in Fig. 3.

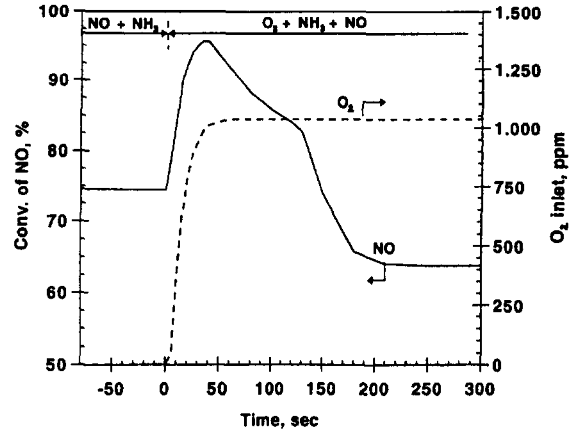

Fig. 3. Conversion of NO during a step change in the concentration of O_2 at 300°C over a CuO–Al_2O_3 catalyst (5 wt.-% CuO) in a flow of $He + NO + NH_3$.

A transient change in the surface reactivity due to oxygen is also observed in the reduction of NO to N_2 in the presence of C_3H_8/O_2 over Cu/MFI (ZSM-5). Reported in Fig. 4 is the conversion of NO in transient catalytic step-

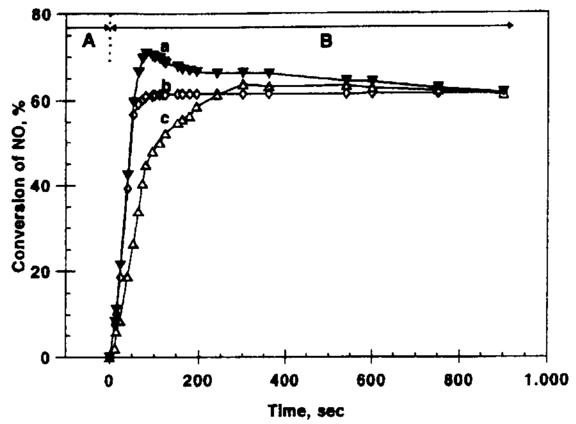

Fig. 4. Conversion of NO in step-change experiments at 300°C over Cu/MFI (see text).

change experiments at 300°C over Cu/MFI when (a) a change in NO + C_3H_8 concentration is made over the catalyst maintained in a flow of O_2 in helium, (b) a change in C_3H_8 concentration is made over the catalyst maintained in a flow of NO + O_2 in helium and (c) a change in NO concentration is made over the catalyst maintained in a flow of O_2 + C_3H_8 in helium. When NO and propane are fed together over the oxidized catalyst (curve a), NO conversion rapidly reaches the stationary conditions, but when only propane or NO is added to feed of the other two components an initial overshoot (curve b) or a delay (curve c) in reaching stationary condition is observed. Combining these data with other results on the stationary and unsteady-state behaviour [8] it is possible to suggest that also in this case a relevant pathway of reaction involves the intermediate formation of a active NO_2–hydrocarbon complex intermediate to N_2 formation. However, also in this case consecutive oxidation to form a nitrate species competes with the selective pathways and leads to a partial inhibition of the surface activity. Furthermore, direct consecutive oxidation of activated hydrocarbon also competes with the formation of the active intermediate. These competitive reactions explain the transient change in the surface reactivity towards NO conversion shown in Fig. 4.

3.3. Low-temperature promotion of the reduction of NO by O_2 in absence of reductants

While oxygen deactivates NO conversion to N_2 or N_2O at temperatures above 350–400°C, it can promote the reduction of NO at low reaction temperatures (250°C) in the absence of any reducing agent. This is especially evident in transient catalytic experiments (Fig. 5) when a step-change in the concentration of oxygen is made over the catalyst maintained in a flow of NO in helium. Data of Fig. 5 refer to a Cu/MFI catalyst, but analogous results were observed also for copper-on-alumina [7]. Immediately upon addition of oxygen, the clear formation of both N_2 and N_2O is observed (Fig. 5). In about 5 min the activity declines, but a not negligible formation of N_2 and N_2O is still observed in stationary conditions, even though low. It is reasonable also in this case to suggests the formation of a Cu^{2+}–NO_2 species which react with NO to form a Cu^{2+}–N_2O_3 like complex intermediate to N_2O and N_2. This is consistent with old IR and ESR evidences on the chemistry of disproportionation of NO at rt over zeolites [10]. Consecutive oxidation to a nitrate species competes also in this case, but the competition is clearly more severe than when ammonia or hydrocarbons are present due to the

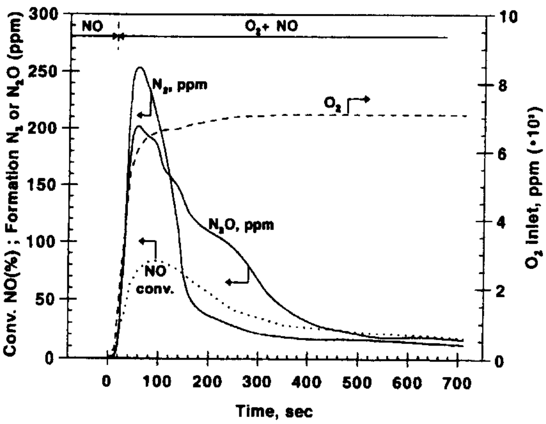

Fig. 5. O_2 step-change experiments at 250°C over Cu/MFI in a flow of NO in helium.

lower rate of transformation of Cu^{2+}–N_2O_3 like complex.

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