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Mechanism of NO decomposition over Cu-ZSM-5

W. Keith Hall * and Jozsef Valyon [1]

Department of Chemistry, Chevron Science Center, University of Pittsburgh,
Pittsburgh, PA 15260, USA

In the preceding Letter Shelef [1] has proposed a mechanism for NO decomposition involving coordinatively unsaturated Cu^{2+} sites on which NO molecules are chemisorbed in the gem-dinitrosyl form. At reaction temperature this complex is supposed to decompose into N_2 and O_2 without involving a redox process. That such a process is feasible has been pointed out by Moser [2]. Shelef cited several reasons in support of this view and others that have led him to think that a cyclic redox mechanism is not operative. These arguments are countered herein and some new data are presented showing the infrared spectra of surface species recorded under in situ reaction conditions.

Keywords: NO decomposition mechanism; redox catalysis-zeolites; Cu-ZSM-5; NO_x catalysis

It is generally conceded that when an overall process can be divided into two steps that can be carried out separately, they may be combined to form a catalytic reaction. For example, the reduced form of Cu-zeolites may be oxidized at room temperature with NO with the evolution of N_2 [3–5]. On completion of this step the catalyst may again be reduced with CO forming CO_2. Mixtures of CO and NO can thus be reacted to CO_2 and N_2. In the present instance it has been demonstrated [3,5] that the catalyst may also be *spontaneously* reduced by desorption of O_2 from the catalyst at temperatures above 623 K. This has been confirmed by EPR [3] as Cu^{2+} is converted to a lower valence state during this process. Indeed at elevated temperatures the catalyst was partially reduced by simply flushing the catalyst with helium. It is apparent, therefore, that reaction by a redox mechanism is feasible.

Li and Hall [3] studied the kinetics of the catalytic decomposition and found them consistent with a picture where a small equilibrium fraction of reduced sites is maintained in this way. These sites are converted to the oxidized form by reaction with NO. This small fraction of reduced sites is maintained in the steady state by a small but finite decomposition pressure of O_2 leading to a

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* To whom correspondence should be addressed.

[1] On leave from Central Research Institute for Chemistry, Hungarian Academy of Sciences, H-1525 Budapest, Hungary.

Langmuir-type inhibition term in $P_{O_2}^{1/2}$. Whereas, a mechanism can never be established by kinetics alone, still Shelef's ideas remain to be shown to be consistent with these observations.

The kinetic picture evolved is similar in some respects to that for the ammonia synthesis. In the latter the most abundant surface intermediate (MASI) is strongly held N atoms. These can only be removed by reduction with hydrogen, but a small fraction of vacancy sites is maintained by the formation and decomposition of NH_3. In the present case the MASI are O atoms. These will not desorb at an appreciable rate below about 623 K, but above that temperature a small fraction of reduced sites are made available by the spontaneous desorption of O_2 [5]. In the ammonia synthesis the rate is limited by the rate of dissociative adsorption of N_2; in the present case the rate of the reaction is limited by the rate of the reoxidation of the oxygen vacancies by NO and by the O_2 released. Since a template holding two NO molecules (or at least two nitrogen containing species) is a necessary requirement for the formation of the N–N bond, a gem-dinitrosyl species may function in the oxidation steps as suggested by Casewit and Rappe [6].

Shelef [1] has argued that the desorption of O_2 is not accompanied by reduction of the catalyst nor is Cu^{2+} reduced to Cu^{+}. This is in contradiction with the observations of Li and Hall [3] who showed that an equivalent loss of the EPR signal from Cu^{2+} was observed on desorption of oxygen equivalent to reduction of about 20% of the Cu^{2+} to Cu^{+}. It is also well documented that a catalyst so pretreated will react with NO to form N_2 at room temperature without releasing O_2 from the catalyst [4,5]. The equivalent O_2 can be released by raising the temperature above 623 K. Thus, there is firm evidence favoring a redox mechanism similar to that which is operative when a reducing agent is present [3], the only difference being the requirement for self-reduction, and this has been demonstrated experimentally. Finally the Langmuir inhibition term involving $P_{O_2}^{1/2}$ results naturally from the O_2 desorption–adsorption equilibrium.

Shelef has argued that Cu^{+} centers cannot adsorb NO to form an NO^{-} species as suggested by Iwamoto et al. [4] or as $NO^{\delta-}$ as suggested by us [7]. Cu^{+} is a diamagnetic d_{10} species and thus has no way to accommodate the unpaired electron of the NO molecule which resides in an antibonding ($\pi 2p_x$) orbital. Strong bonds should be formed, however, with the paramagnetic d_9 Cu^{2+} ions. In fact everyone agrees that NO adsorbs on two different centers generating mononitrosyl IR bands in the 1900–1910 cm^{-1} region and at around 1810–1813 cm^{-1}. Shelef has suggested that in both cases these are Cu^{2+} centers at different lattice positions, whereas, Iwamoto et al. and ourselves have assigned the latter to NO adsorbed on Cu^{+} centers. This latter species is readily interconvertable with the dinitrosyls which can be formed on the adsorption of a second NO molecule. Decomposition of the dinitrosyl will lead to reoxidation of these sites [6]. The very recent work of Zecchina and co-workers [8] confirms this assignment; they prepared catalysts containing exclusively Cu^+ as base-exchanged cations and on adsorption of NO at 78 K obtained only the three bands in the 1730–1825 cm^{-1} region. On raising the temperature to 298 K the band near 1900 cm^{-1} slowly appeared as the catalyst was oxidized with the concomitant evolution of N_2. We independently made similar observations, albeit less convincingly, with the "reduced form" of our catalyst [7]. Therefore, the dinitrosyls are not formed on Cu^{2+} sites as supposed by Shelef and indeed lead to oxidation of the catalyst together with the formation of the 1900 cm^{-1} band in increasing intensity with time.

As pointed out by Shelef, Iwamoto et al. supposed that NO reacted with Cu^+ to form Cu^{2+}–NO^- (single, twin). Adjacent pairs were then supposed to react yielding N_2, O_2 and Cu^{2+}. Shelef has pointed out that this scheme is unlikely for high silica ZSM-5 zeolites where the sites are rather remote from each other. Yet Iwamoto's data [4] shows the catalytic activity per site increases with the Si/Al ratio. We, on the other hand, have suggested that the reaction occurs on single Cu^+ sites by forming first the mononitrosyl, then the gem-dinitrosyl which decomposes into N_2O leaving an oxygen atom behind. The N_2O is readily observed at lower temperatures [5], but it is preferentially consumed at higher ones. We have termed the species adsorbed on Cu^+ as $Cu–NO^{\delta-}$ for the following reason. The NO stretching frequency in the gas phase is at 1876 cm^{-1}. Because the HOMO of this molecule is antibonding, the donation of electron density from the molecule to the substrate would be expected to increase the stretching frequency as the bond is strengthened. This leads to the formation of the 1900 cm^{-1} band when the adsorption is on Cu^{2+}. When the NO is adsorbed on Cu^+ the vibrational frequency at 1810 cm^{-1} is lower than the gas phase frequency suggesting that back-bonding has put more electron density into the antibonding orbitals further weakening the NO bond. The nature of this bonding to Cu^+ ions is presently ill-defined, but we suppose that it is similar to that of CO bonded to transition metal ions. Conceivably the extra electron density present in the $Cu–NO^{\delta-}$ species is in some way functional in the formation of the dinitrosyl species as well as in the formation of the N–N bond. Clearly some theoretical work would be most helpful in this connection.

Assignment of a formal charge to an adsorbed species is a convenient fiction. Ordinarily it cannot be measured, but its sign may be inferred from physical measurements. What is important, and is measurable, is the result that occurs on the decomposition of the chemisorbed species. Thus NO is adsorbed on Cu^+ and this site is oxidized to Cu^{2+} on the decomposition of the intermediate.

The usual procedure for obtaining IR spectra of adsorbed NO is to prepare a spectroscopic platelet, treat it with O_2 to remove impurities, and then in a flow of an inert gas at the pretreatment temperature (usually 773 K) for several hours. In the present case the catalyst becomes partly reduced in the last step. It is then exposed to NO, usually at room temperature and the spectrum is recorded. In our work the IR cell used was a modified version of that of Basu et

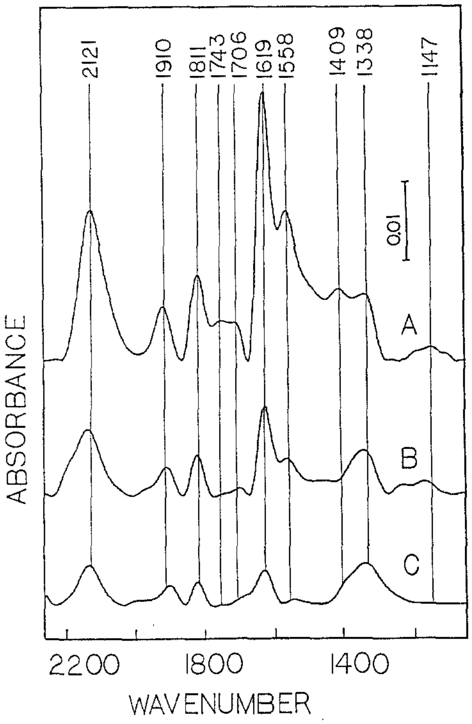

Fig. 1. IR spectra of the surface species taken under steady-state reaction conditions over Cu-ZSM-5 (Si/Al = 14, Cu/Al = 0.57) catalyst at (A) 623 K, (B) 673 K, (C) 723 K. The corresponding NO decomposition rates to N_2 (measured separately) were (A) 0.66×10^{-4}, (B) 1.17×10^{-4} and (C) 4.5×10^{-4} mol NO/g min, respectively. A platelet of about 17 mg/cm^2 thickness was pretreated in flowing He at 723 K for 3 h. It was then contacted with a flow of 4% NO in He at the indicated temperature for 30 min prior to recording the spectra. Then 200 scans were accumulated both in the He and the NO flow. Spectra shown were obtained by computer subtraction of the recorded spectra. The adsorbate could be completely desorbed at these temperatures by simply flushing with He and this was done between A and B, and between B and C.

al. [9]. It permitted the spectrum to be taken at any temperature in the range $100 < T < 773$ K in a flow of pure He containing zero or 4% NO. The temperature was recorded with a thermocouple in contact with the catalyst. In our previous work [7] we were able to obtain useful spectra up to about 573 K where the bands became too weak to be useful. Thus, the highest temperature data was taken just below that where the catalytic reaction sets in (where the oxygen desorption rate becomes significant). Through improvements in technique, we have now been able to raise the temperature into the catalytic regime. Some of these results are presented in fig. 1. where several significant features appear, viz. bands corresponding to the $NO^{\delta+}$ and $NO^{\delta-}$ species (in the 1895–1910 cm^{-1} and 1810–1815 cm^{-1} regions, respectively) are clearly evident. The dinitrosyl bands, if present at all, were too weak to characterize. Spectator species are also present (most particularly the band in the 2120–2130 cm^{-1} region corresponding to chemisorbed NO_2). The possible significance of the remaining bands at 1335–1340 cm^{-1}, 1409 cm^{-1}, 1540–1558 cm^{-1} and at 1619–1623 cm^{-1} cannot as yet be assessed. They are thought to correspond to rather stable mono- and bimolecular complexes of NO_2 and NO with NO_2. They are probably spectator species and have no major effect on the redox properties of the catalyst and they may even inhibit the reaction. On the other hand these species conceivably could be the true reaction intermediates and in this event Shelef may be correct. Redox chemistry may not be involved. This possibility is now open for investigation.

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