On the mechanism of nitric oxide decomposition over Cu-ZSM-5

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Cu-ZSM-5, a copper-containing zeolite, catalytically decomposes NO at temperatures below those of other catalysts. A mechanism is proposed which is based on active sites consisting of coordinatively unsaturated cupric (Cu^{2+}) ions in a square planar configuration. These sites are posited to chemisorb NO molecules in the gem-dinitrosyl form. The pair of adsorbed NO molecules desorbs as N_2 and O_2. This mechanism accounts for the experimental behavior in chemisorption and decomposition without invoking a cyclical oxyreduction of the surface sites.

Keywords: NO decomposition; copper zeolite

1. Introduction

In the past decade Iwamoto and co-workers [1,2] have explored in detail NO decomposition over Cu-exchanged zeolites, in particular over Cu-ZSM-5. Recently, Iwamoto and Hamada [3] have again summarized their work. It is the purpose of this note to clarify some points in the proposed mechanism of NO decomposition.

In the most recent communication [3] it is conceded that the "new" decomposition catalysts do not have sufficient activity for practical implementation, notwithstanding that they begin to decompose nitric oxide at temperatures below those of the "old", conventional decomposition catalysts. There is little indication as well that the needed improvement in activity by one to two orders of magnitude can be achieved, because the usual practical stratagem of temperature increase is not feasible: with the increase of the temperature above 600°C the rate of the reaction decreases. The mechanism of the decomposition is nevertheless worth clarifying.

2. Salient characteristics of NO decomposition on Cu-ZSM-5

The following are the main features described in refs. [1–3]:

(1) The reaction is a true decomposition and under controlled conditions a good material balance is achieved [4–5].

(2) The decomposition passes through a reversible maximum with rising temperature, at 500–600°C.

(3) The reaction order in NO is 1.2 [1] or 1.0 [5]; it may change with NO concentration.

(4) Oxygen inhibits the reaction but the inhibition decreases with temperature [5].

(5) Excess Cu loading in zeolite (i.e. more than one Cu ion per two Na^+ ions, or protons) enhances the activity.

(6) The specific decomposition rate per exchanged copper ion decreases with the increase of the aluminum content of the zeolite structure.

(7) Sulfur compounds in the gas phase suppress the decomposition.

3. Mechanism

The mechanism proposed to account for these observations is given as a cyclical process [1–3]:

$$\begin{tikzcd}
2Cu^{2+} \arrow[r, "\text{elevated temp.}", "-O^{2-}"'] & 2Cu^{+} \arrow[r, "+2NO"] & 2Cu^{2+}\text{-}NO^{-}. \arrow[l, bend left, "-N_2,\ -O_2"]
\end{tikzcd}$$

To render this mechanism in words:

(1) A pair of cupric ions loses a doubly charged oxygen ion upon heating, which can be considered an activation step. A pair of cuprous ions is formed due to the electrons the doubly charged oxygen ion left behind.

(2) The pair of cuprous ions adsorbs a pair of NO molecules. The adsorption is such that the cuprous ions reduce the nitric oxide molecules to produce an adsorbed pair of anions.

(3) The pair of anions decomposes into a molecule of dioxygen and a molecule of dinitrogen, restoring the pair of the cuprous adsorption sites.

The cuprous ions are not poisoned by the oxygen, either formed by the decomposition or present in the gas stream, because they are deemed to be stable in the zeolite at the elevated temperatures of the process. Neither is the cuprous ion easily reduced to the metal.

The stable activity is also due, according to Iwamoto [2], to the absence of copper particle growth within the ZSM-5 structure under the conditions of use. The supporting evidence is adduced from IR spectra of NO chemisorption on Cu-ZSM-5 at room temperature and EPR spectra.

The IR spectrum [1,6] shows a large band assigned to NO^+ (nitrosonium) at 1906 cm^{-1}, and smaller bands, NO^- (nitrosyl) at 1813 and a doublet due to a negative pair of nitrosyls $(NO)_2^-$ at 1827 and 1734 cm^{-1}. The negatively charged bands are less stable and decrease with time at room temperature. The dominant band at 1906 cm^{-1} grows at their expense. The negatively charged species are said to be adsorbed on Cu^+ since their formation required treatment at high temperatures and is blocked out by CO, known to adsorb preferentially on cuprous ion sites. Because the room temperature decay in the IR absorbance peaks, ascribed to negatively charged adsorbed nitrosyls, was fit to a second order plot, it was concluded that this process (at room temperature) is the basis for the mechanism given above (at reaction temperature) [6].

The EPR evidence shows that the adsorption–desorption cycle of NO corresponds to a decrease–increase of the intensity of the Cu^{2+} EPR signal, which is the outcome of NO donating its antibonding electron to the cupric ion [6].

4. Questions about the mechanism

Since the decomposition of nitric oxide requires pairing of the molecules, it is plausible that the adsorbed geminal dinitrosyls are important. But the evidence presented is not compelling that they adsorb on the cuprous ions and are negatively charged upon chemisorption. Pairing of nitrogens by the interaction of two NO species, each one adsorbed on a different copper site does not seem probable because in high-silica zeolites the copper ions are spaced too far apart.

In studies of NO chemisorption on copper-on-alumina, it was established that nitric oxide chemisorbs overwhelmingly on cupric ions forming the surface $(NO)^+$ nitrosonium ion [7]. However, IR studies of NO chemisorption on transition metal ions [8] show that the assignment of the absorption peak of a negatively charged surface nitrosyl should be in the frequency range below 1700 cm^{-1}. The review of Kung and Kung [9] gives only three examples of such low absorption peak frequency in 70 recorded IR spectra of chemisorbed NO and only these are assigned to negatively charged species. Such assignments also agree with organometallic nitrosyls in solution, where IR peaks of NO^+ are shifted upwards of NO in the gas and NO^- very far downwards [10].

The reason for the low absorption peak frequency of negatively charged (anionic) surface nitrosyls is straightforward. The donated electron goes into the available antibonding orbital ($\pi^* 2p_x$) of the NO molecule. This results in a weakened nitrogen to oxygen bond, i.e. is a vibrator with a less stiff spring. The formation of this anion is (in most cases) a thermodynamically uphill process and the anionic surface species is unlikely to be stable at the catalyst operating temperatures. Whether negatively charged, adsorbed nitrosyls exist at all, even at room temperature, has been questioned [10].

Conversely, the donating of the electron located in the antibonding orbital of the NO molecule is favored, but requires an accepting orbital in the chemisorption site. Therefore, NO adsorbs prevalently on $Cu^{2+}(d^9)$ ions and not on $Cu^{+}(d^{10})$ ions. For which reason solutions of cupric ions are used to absorb nitric oxide present in gas streams [11]. Hence, it is more plausible that the antisymmetric and symmetric vibrations of the gem-dinitrosyl on Cu-ZSM-5 observed at 1827 and 1734 cm^{-1} are associated with neutral surface species chemisorbed coordinatively through their lone pairs [8]. Refs. [9,12] afford a summary of gem-dinitrosyls on several ionic adsorbents, including zeolites, showing that their IR absorption peaks all appear in the frequency range consistent with an assignment to a non-ionized surface species. There are over 30 examples listed in refs. [9,12].

If this is so, the cyclic mechanism of oxyreduction proposed by Iwamoto, for which such a charge transfer is a necessary condition, cannot be justified.

There exists evidence that the isolated cupric ions in ZSM-5 are quite resistant to reduction. The desorption of the oxygen upon heating from isolated cupric ions in Cu-ZSM-5 has been shown not to be associated with their reduction [13]. These ions are coordinatively unsaturated and therefore adsorb at room temperature even non-polar molecules such as xenon and hexane [14]. This tendency to adsorb virtually any gaseous species explains the observation that evacuated catalysts adsorb CO, presumably not very strongly. Furthermore, owing to their structure the isolated Cu^{2+} ions are also resistant to reduction by CO below 400°C [13].

5. Another alternative

The mechanism proposed below posits that the decomposition of nitric oxide does not require the oxyreduction of the surface which usually prevails when both oxidizing species and reducing species from the gas phase alternately donate and remove an oxygen ion from the surface. It is more plausible to assume that cupric (Cu^{2+}) ions are the active sites. More precisely, only those cupric ions which adsorb the gem-dinitrosyls. Then, there is no need to postulate an oxyreduction cycle of the surface, which is highly improbable in the absence of a reducing species in the gas phase. The pair of nitrosyls adsorbed in a proximity of molecular dimensions on a single site rearranges itself so as to desorb as the thermodynamically favored O_2 and N_2 molecules.

The obvious requirement is that these adsorption sites remain stable during reaction conditions and be resistant to chemisorption of oxygen. Any event that will eliminate or block these sites either transiently or permanently will result in reversible or permanent deactivation of the catalyst. There is evidence that Cu-ZSM-5 contains such required sites. The structure of Cu-ZSM-5 has been studied in the aforementioned work of Kucherov et al. [13]. This solid contains two types of isolated Cu^{2+} cations: one in a four-coordinated square planar configuration, the other is five coordinated. Thus both species are coordinatively unsaturated. The square planar site appears in particular to be the proper locus for the gem-dinitrosyl adsorption. The density of both kinds of sites is related to the Al/Si ratio of the host zeolite. At low loadings of copper, the five-coordinated Cu^{2+} species prevails; with the increase of Cu loading the relative importance of the square planar increases [14]. All this is in conformance with the experimentally observed NO decomposition behavior.

The reversible passage of the NO decomposition on Cu-ZSM-5 over a maximum with rising temperature is most likely associated with the temperature sensitive adsorption equilibrium:

$$Cu^{2+}:NO + NO_g \rightleftharpoons Cu^{2+}(\text{gem-dinitrosyl})\ [12],$$

which shifts to the left at higher temperatures. As noted, both mono- and di-nitrosyls, with IR absorption peaks in the same range, co-exist.

Furthermore, the coordinatively unsaturated copper sites in ZSM-5 are catalytically stable up to 600°C [15] and the four-coordinated species are active in the oxidation of methane [15] and ethane [16]. Prolonged calcination at 800°C virtually kills irreversibly this activity [15].

The issue of the resistance of the coordinatively unsaturated sites to deactivation by oxygen is touched briefly upon by Kucherov et al. [13]. In EPR studies they noticed a broadening of the signal from the isolated Cu species in O_2 at 400°C but no evidence of bond formation was apparent.

Whether the mechanism proposed here will be confirmed by more detailed work is obviously open to question, but it offers a more convincing picture than the cyclical one. Again, whether the same coordinatively unsaturated sites and dinitrosyl adsorption are implicated in the selective reduction of nitric oxide on Cu-ZSM-5 [2] is a question for the future. A recent patent [17] claims that the Cu^{2+} ions in square planar configuration are the active sites in the selective reduction of nitric oxide.

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