Potential reaction paths in \( \text{NO}_x \) reduction over Cu/ZSM-5

T. Beutel, B. Adelman and W.M.H. Sachtler

V. N. Ipatieff Laboratory, Center for Catalysis and Surface Science, Department of Chemistry, Northwestern University, Evanston, IL 60208, USA

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The reaction of \( \text{NO} \) with adsorbed acetone oxime has been studied over Cu/ZSM-5 employing FTIR and MS. It is found that \( ^{15}\text{NO} \) gas reacts with \( ^{14}\text{N} \) labelled acetone oxime and/or its hydrolysis product, hydroxylamine, to form \( ^{14}\text{N}^{15}\text{NO} \) and \( ^{14}\text{N}^{13}\text{N} \) at 40°C. As acetone oxime is easily formed from alkyl radicals and \( \text{NO} \) via alkylnitroso compounds, the results indicate possible reaction paths for the SCR of \( \text{NO}_x \) by hydrocarbons over zeolite based catalysts. The isotopic data suggest predominant formation of \( \text{N}-\text{N} \) bonds occurs via interaction of gaseous \( \text{NO} \) with a nitrogen containing adsorbed complex.

Keywords: \( \text{NO}_x \) reduction; Cu/ZSM-5 catalyst; adsorbed acetone oxime, IR spectra of; reaction with \( ^{15}\text{NO} \); formation of \( ^{14}\text{N}^{13}\text{N} \); formation of \( ^{14}\text{N}^{15}\text{NO} \)

1. Introduction

Reduction of \( \text{NO}_x \) by hydrocarbons in the emission from lean burn engines is catalyzed by zeolite supported transition metal ion catalysts among which Cu/ZSM-5, though not the most promising [1], is the most intensively studied representative [2-4]. The mechanism of this process is complicated; some suggestions made on the basis of known chemistry were recently reviewed by Smits and Iwasawa [5]. The kinetic isotope effect measured by Cowan et al. in SCR with \( \text{CH}_4 \) and \( \text{CD}_4 \) of \( \text{NO}_x \) over Co/ZSM-5 [6] suggests that abstraction of a hydrogen atom from the hydrocarbon is likely to be the rate limiting step. Hall and coworkers suggest that free radicals are formed in this process [7], but the \( \text{N}-\text{N} \) bond is formed by coupling of \( \text{NO} \) with an adsorbed, nitrogen-containing intermediate [8]. Beutel et al. report evidence that the H-abstraction is mediated by chemisorbed \( \text{NO}_y \) complexes [9]. The subsequent steps are not known in detail at the present time; the only certainty appears to be that the \( \text{NO}_x \) complexes are reduced to \( \text{N}_2 \) in this process [10,11].

H-abstraction from propene is known to preferentially lead to an allyl radical; from propane it is most favorable at the secondary C-atom. It appears reasonable to assume that the secondary propyl radical will react with \( \text{NO} \) to yield 2-nitrosopropane:

\[
\text{H}_3\text{C} = \text{CH} - \text{CH}_3 + \text{NO} \rightarrow \text{H}_3\text{C} - \text{CH} = \text{CH}_3
\]

Secondary and primary nitrosocompounds are known to undergo spontaneous isomerization to their respective oximes. With 2-nitrosopropane as a reactant this reaction leads to the formation of acetone oxime as described by:

\[
\text{H}_3\text{C} - \text{CH} - \text{CH}_3 \rightarrow \text{H}_3\text{C} - \text{C} - \text{CH}_3
\]

This elementary chemistry motivated a study of the interaction of acetone oxime with \( \text{NO} \), \( \text{O}_2 \) and \( \text{H}_2\text{O} \) at the surface of Cu/ZSM-5. The results of this study, using isotopic labelling, FTIR and gas phase mass spectrometry are reported in the present paper.

2. Experimental

2.1. Catalyst preparation and pretreatment

Cu/ZSM-5 was prepared via ion exchange at room temperature (r.t.). A 0.015 M Cu(OAc)\(_2\) solution was added drop-wise to a Na/ZSM-5 (UOP lot #13923-60) slurry. The slurry was stirred for 24 h before being vacuum filtered. The product was washed with doubly deionized water, then air dried. This process was repeated twice. The powder was crushed to > 60 mesh. Elemental analysis, via inductively coupled plasma atomic emission spectroscopy, gave the following data: Cu/Al = 0.51; Si/Al = 18, and Na/Al = 0.05. Prior to the isotope exchange and MS experiment the samples were calcined from 20 to 500°C, then cooled to r.t. in an
O₂ (UHP) flow. Calcined Cu/ZSM-5 and Na/ZSM-5 samples were impregnated ex situ with an aqueous acetone oxime solution. Samples with oxime/copper ratios of 1 : 1, 2 : 1 and 8 : 1 were prepared: they will be referred to as Cu/OX1/ZSM-5, Cu/OX2/ZSM-5, and Cu/OX8/ZSM-5, respectively. A Na/OX/ZSM-5 sample was also prepared with a similar weight load to the Cu/OX2/ZSM-5. Another sample was prepared by impregnation of hydroxylamine hydrochloride (HA) on calcined Cu/ZSM-5 with a HA/Cu ratio of 2/1 designated as Cu/HA/ZSM-5.

All samples were dried at r.t. to avoid decomposition and outgassed in situ for 2–6 h at 40°C.

2.2. FTIR measurements

Spectra were collected on a Nicolet 60SX FTIR spectrometer equipped with a liquid N₂ cooled MCT detector. Self-supporting wafers on ca. 10–15 mg/cm² were prepared and inserted into a pyrex glass cell equipped with NaCl windows connected to a glass manifold. Spectra were taken in transmittance at r.t. with 50 scans accumulated at a spectral resolution of 1 cm⁻¹. ¹⁵NO (Cambridge, 98%+) was pulsed into flowing carrier gas.

2.3. Mass spectrometry

On-line analysis of the released gases was carried out in a recirculating manifold equipped with a Dycor quadrupole gas analyzer. A pyrex reactor with a porous frit was charged with 400 mg of sample then attached to a recirculation manifold equipped with an on-line quadrupole mass spectrometer. The samples were heated in vacuo to 40°C prior to ¹⁵NO exposure. Signal intensities were normalized using the double ion peak of Ar (m/z = 20) as an internal standard.

3. Results

3.1. FTIR spectroscopy

Figs. 1A, 1B and 1C show the IR spectra of acetone oxime impregnated on Cu/ZSM-5 after heating to 60°C in He. Bands at 1436 and 1427 cm⁻¹ and bands at 1379 and 1374 cm⁻¹ in spectrum a of fig. 1A can be ascribed to the C–H deformation vibrations of adsorbed acetone oxime where the former two bands are due to the antisymmetric and the latter two are due to the symmetric deformation vibrations of the CH₃ groups. For the crystalline state band pairs at 1437/1424 cm⁻¹ and 1377/1368 cm⁻¹ have been reported for the antisymmetric and symmetric deformation vibrations while a band at 1661 cm⁻¹ was found for the C=N stretching vibration [12]. The weak absorption at 1658 cm⁻¹ in spectrum a of fig. 1A must be ascribed to the C=N stretching vibration. The C–H stretching vibrations are located at 2971 and 2925 cm⁻¹ in spectrum a of fig. 1B. O–H stretching vibrations of acetone oxime are observed at 3250 and 3123 cm⁻¹. The frequency shift of these bands as compared to the O–H stretching frequency of the free molecule (ν_gas = 3650 cm⁻¹) is evidence of H-bonding. The occurrence of two bands at 3130 and 3290 cm⁻¹ has been reported by Califano and Lüttke [13] and ascribed to self-associated trimers of acetone oxime. A spectrum taken at 40°C (not shown) looks identical to that at 60°C.

At 80°C, a dramatic increase in band intensity is observed in the region of C≡X double bonds (X = N, O) at 1666 and 1659 cm⁻¹ and new bands appear at 1586, 1487, 1422, 1414 and 1363 cm⁻¹ (spectrum b of fig. 1A). In the range of X–H stretching vibrations new bands occur at 3227 and 3308 cm⁻¹ (spectrum b of fig. 1B), which are characteristic of N–H stretching vibrations. Band intensities at 3250, 3123 and 2971 cm⁻¹ are depleted. The C–H band at 2925 cm⁻¹ is enhanced and a new C–H stretching vibration at 2982 cm⁻¹ appeared. Further increase of temperature to 100°C does not change the spectrum.

The reactivity of acetone oxime towards O₂ was tested. The spectrum at 100°C in O₂ is similar to the spectrum in He at the same temperature. Heating to 150°C causes a decrease in band intensity at 1666, 1659 and 1363 cm⁻¹ and an increase in intensity at 1586 and 1487 cm⁻¹. The appearance of bands at 2157, 2170, 2326 and 2298 cm⁻¹ is observed at 150°C as seen in spectrum c of fig. 1C. This is interesting since the band at 2157 cm⁻¹ has been assigned to a Cu³⁺–CO adsorption complex [14].

The reactivity of acetone oxime towards ¹⁵NO was tested at 40°C. Bands characteristic of the oxime decrease and new bands at 1531, 1564, 1582 and 1677 cm⁻¹ appeared. No exchange of the ¹⁴NO moiety in acetone oxime by ¹⁵NO was observed. A treatment of Cu/OX2/ZSM-5 with ¹⁵NO at 80°C after a preceding O₂ exposure at the same temperature yielded also bands at 1535 and 1567 cm⁻¹.

3.2. Mass spectrometric gas analysis

3.2.1. Cu/OX8/ZSM-5 decomposition

Fig. 2 shows the normalized signal intensities of gaseous products while Cu/OX8/ZSM-5 is heated stepwise from 40 to 160°C. Data collection started after 15 min at each temperature. No gaseous products could be detected below 80°C. The most prominent masses are 44 (N₂O, CO₂) and 28 (N₂, CO, C₂H₄). Other masses found include 58 (acetone), 18 (H₂O) and 30 (NO). There are only traces of mass 45 and 29 at 160°C.