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Potential reaction paths in NO_x reduction over Cu/ZSM-5

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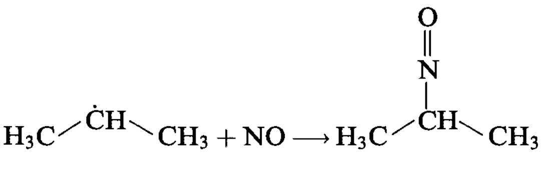
The reaction of NO with adsorbed acetone oxime has been studied over Cu/ZSM-5 employing FTIR and MS. It is found that $^{15}NO_{gas}$ reacts with ^{14}N labelled acetone oxime and/or its hydrolysis product, hydroxylamine, to form $^{14}N^{15}NO$ and $^{14}N^{15}N$ at 40°C. As acetone oxime is easily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

Keywords: NO_x reduction; Cu/ZSM-5 catalyst; adsorbed acetone oxime, IR spectra of; reaction with ^{15}NO; formation of $^{14}N^{15}N$; formation of $^{14}N^{15}NO$

1. Introduction

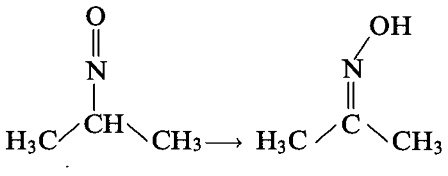
Reduction of NO_x by hydrocarbons in the emission from lean burn engines is catalyzed by zeolite supported transition metal ion catalysts among which Cu/ZSM-5, though not the most promising [1], is the most intensively studied representative [2–4]. The mechanism of this process is complicated; some suggestions 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 CH_4 and CD_4 of 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 N–N bond is formed by coupling of NO with an adsorbed, nitrogen-containing intermediate [8]. Beutel et al. report evidence that the H-abstraction is mediated by chemisorbed NO_y complexes [9]. The subsequent steps are not known in detail at the present time; the only certainty appears to be that the NO_y complexes are reduced to 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 NO to yield 2-nitrosopropane:



$$H_3C{-}\dot{C}H{-}CH_3 + NO \longrightarrow H_3C{-}CH(N{=}O){-}CH_3 \qquad (1)$$

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:



$$H_3C{-}CH(N{=}O){-}CH_3 \longrightarrow H_3C{-}C({=}N{-}OH){-}CH_3 \qquad (2)$$

This elementary chemistry motivated a study of the interaction of acetone oxime with NO, O_2 and H_2O 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

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O_2 (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 N_2 cooled MCT detector. Self-supporting wafers on ca. 10–15 mg/cm^2 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}. ^{15}NO (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 ^{15}NO 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 CH_3 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 ($\nu_{gas} = 3650$ 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 1706, 1586, 1487, 1443, 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 O_2 was tested. The spectrum at 100°C in O_2 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 Cu^+–CO adsorption complex [14].

The reactivity of acetone oxime towards ^{15}NO 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 ^{14}NO moiety in acetone oxime by ^{15}NO was observed. A treatment of Cu/Ox2/ZSM-5 with ^{15}NO at 80°C after a preceding O_2 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 (N_2O, CO_2) and 28 (N_2, CO, C_2H_4). Other masses found include 58 (acetone), 18 (H_2O) and 30 (NO). There are only traces of mass 45 and 29 at 160°C.

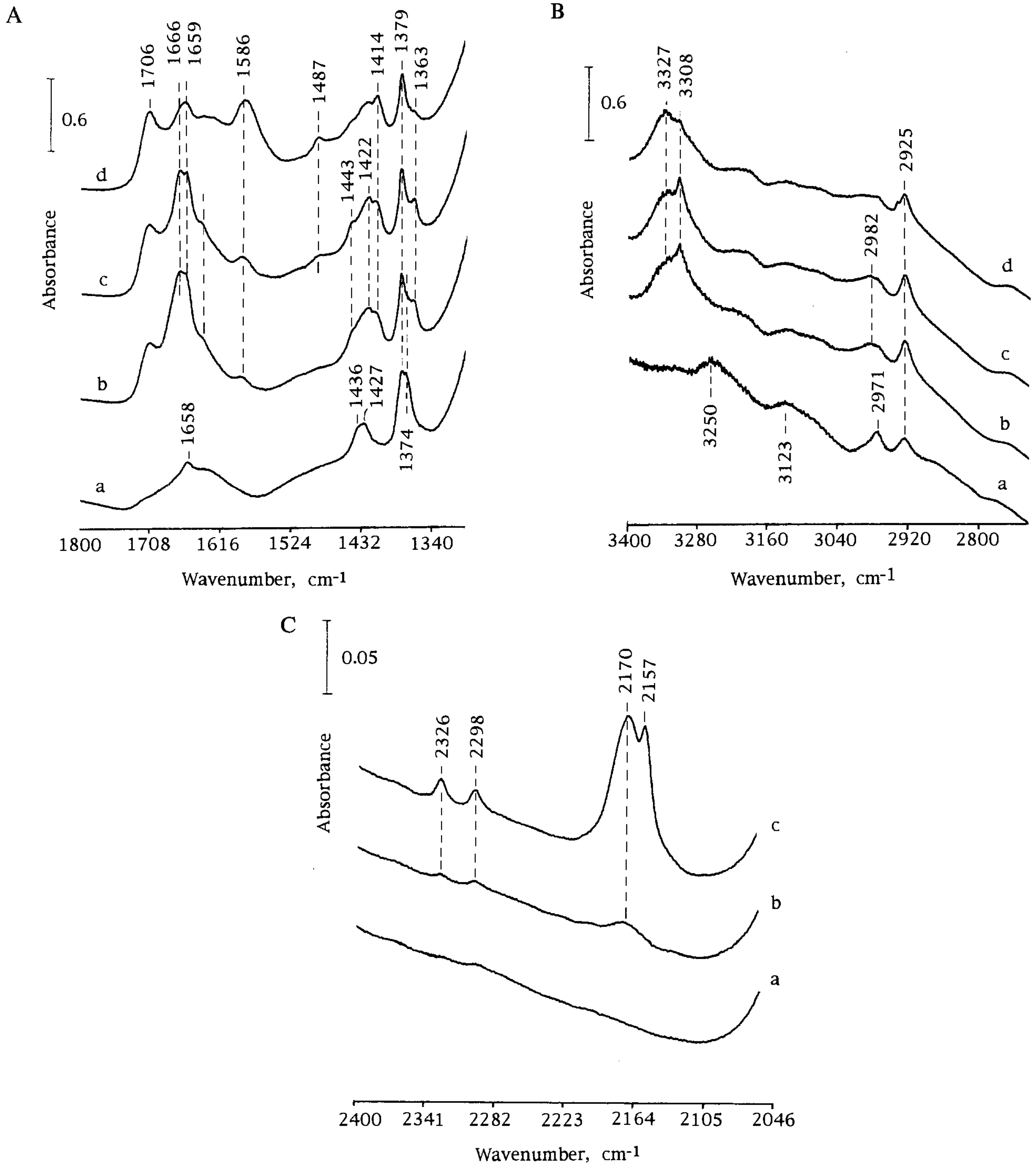


Fig. 1. FTIR spectra in the carbonyl and C–H deformation region (A), in the O–H and C–H stretching regime (B), and in the NCO stretching region (C) of Cu/OX2/ZSM-5 after 45 min in He at 60°C (a), 75 min in He at 80°C (b), 12 h in He at 100°C (c) and 50 min in O_2 at 150°C (d). Spectra are not background corrected.

3.2.2. *Reaction with* ^{15}NO

Fig. 3 shows the evolution of gases from Cu/OX1/ZSM-5 upon exposure to 5 mbar ^{15}NO. Spectra were taken after 60 min time of exposure at each temperature. A remarkable evolution of mass 45 and 29 is observed already at 40°C. Their signal intensities increase steeply upon heating to 80°C then level off. Masses 28 and 44 increase steadily with temperature. The evolution of these masses begins at 40°C in contrast to decomposition, which starts at 80°C. The results show that N_2O is formed when NO reacts with the adsorption complex and that the isotopically mixed $^{14}N^{15}NO$ and/or $^{15}N^{14}NO$ molecules predominate. The intensity of $m/z = 29$ significantly exceeds that of the N_2 fragment

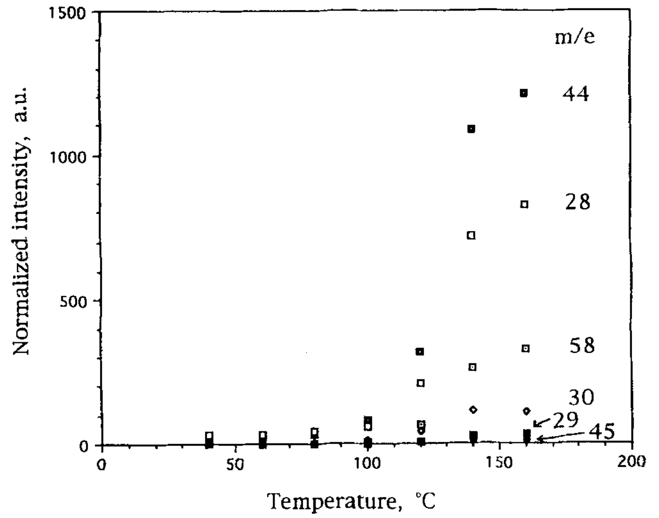


Fig. 2. MS analysis of gases evolved during thermal decomposition of Cu/OX8/ZSM-5 plotted versus temperature. Spectra were taken after 15 min exposure to each temperature; $m/z = 44$: CO_2, N_2O; $m/z = 28$: CO, N_2; $m/z = 58$: acetone; $m/z = 30$: NO, N_2.

of N_2O [15] showing that $^{14}N^{15}N$ is a true product of this reaction. A rough estimate leads to a $^{14}N^{15}NO/^{14}N^{15}N$ ratio of 1.6 ± 0.2.

The reactivity of Cu/OX2/ZSM-5 was also tested in a mixture of $^{15}NO + O_2$ at a ratio $O_2/^{15}NO = 1.7$. $^{14}N^{15}NO$ was detected, but in smaller quantities than in the absence of O_2. As a blank experiment, Na/OX/ZSM-5 was exposed to ^{15}NO. After reaction at 80°C, the amount of $^{14}N^{15}NO$ formed relative to the oxime loading was six times smaller than when Cu/OX1/ZSM-5 was used.

In order to check the reactivity of hydroxylamine, the hydrolysis product of acetone oxime, Cu/HA/ZSM-5 was prepared and exposed to ^{15}NO. The evolution of $^{14}N^{15}NO$ was registered.

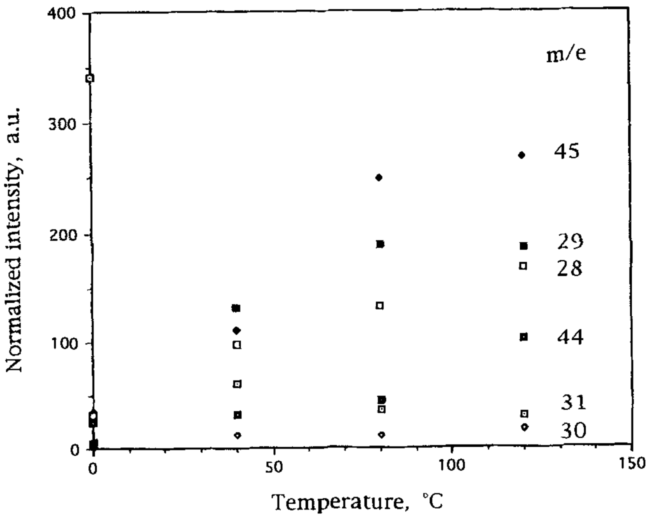
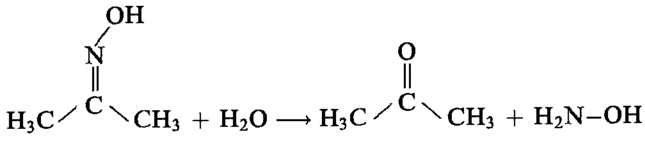


Fig. 3. MS analysis of gases evolved during reaction of 5 mbar ^{15}NO with Cu/OX1/ZSM-5 as a function of temperature. Spectra were recorded after 60 min exposure to each temperature; $m/z = 45$: $^{14}N^{15}NO$; $m/z = 29$: $^{14}N^{15}N$; $m/z = 31$: ^{15}NO.

4. Discussion

4.1. Reactions of adsorbed acetone oxime in the absence of NO_x

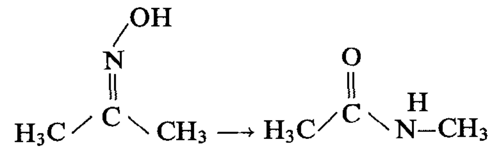
The significant changes in the IR spectrum during heating of Cu/OX2/ZSM-5 from 60 to 80°C indicate the onset of thermal decomposition of acetone oxime. Emerging strong absorption bands at 1666 and 1659 cm^{-1} are ascribed to C=O double bonds. The significant intensity increase in the C=X (X = N, O) stretching region can be attributed to the higher extinction coefficient of the carbonyl group in comparison to the C=N group of the original oxime. The band at 1666 cm^{-1} is assigned to acetone together with characteristic bands at 1412 and 1363 cm^{-1} for the antisymmetric and symmetric CH_3 deformation vibrations. This assignment is confirmed in separate experiments of acetone adsorption on Cu/ZSM-5 which yielded bands at 1667, 1418 and 1365 cm^{-1}, respectively. Acetone is also observed mass spectrometrically by the peak at $m/z = 58$. It is known that acetone is formed by hydrolysis of acetone oxime according to



$$(CH_3)_2C{=}N{-}OH + H_2O \longrightarrow (CH_3)_2C{=}O + H_2N{-}OH \quad (3)$$

Hydroxylamine, the coproduct of reaction (3), is also detected by its narrow band at 3308 cm^{-1} which is most likely caused by unperturbed N–H stretching vibrations of the H_2NOH molecule. A band at 3297 cm^{-1} has been reported by Giguère and Liu [16] for gaseous hydroxylamine. Following their band assignment, the shoulders at 1641 and 1443 cm^{-1} in spectra b and c of fig. 1A may be ascribed to the NH_2 and OH bending vibrations of hydroxylamine, respectively.

Another reaction of oximes is the Beckmann rearrangement which leads to the formation of N-methylacetamide:



$$(CH_3)_2C{=}N{-}OH \longrightarrow H_3C{-}C({=}O){-}NH{-}CH_3 \quad (4)$$

An indication that this reaction occurs indeed on Cu/ZSM-5 is found in spectrum b of fig. 1A, as N-methylacetamide displays a C=O stretching vibration at

1658 cm^{-1} [17], which is close to the carbonyl frequency at 1659 cm^{-1} measured in spectrum b. Bands at 1422 and 1379 cm^{-1} in this spectrum are ascribed to the antisymmetric and symmetric CH_3 deformation vibrations of the amide. The broad band at 3327 cm^{-1} in spectrum b of fig. 1B is attributed mainly to the N–H stretching vibration of N-methylacetamide, but may also contain contributions from O–H stretching vibrations of H_2NOH, perturbed by H-bonding, and other secondary products, such as methylamine. Molten N-methylacetamide displays a band at 3297 cm^{-1} [17].

N-methylacetamide is known to easily undergo hydrolysis to acetic acid and methylamine. There are indications that this reaction takes place: the weak bands at 1586 and 1487 cm^{-1}, which are found to emerge upon heating the sample to 80°C, are typical for acetates [18]. Their intensity increases as the sample is heated to 150°C; simultaneously, the amounts of acetone and amide on the surface decrease significantly and carbon dioxide forms in the gas phase, leading to an intense peak at $m/z = 44$. However, the intensity of the band at 1379 cm^{-1} remains constant. It is therefore reasonable to assume that this band contains contributions from another species, most likely a carbonate ion. The formation of methylamine as a co-product of hydrolysis of N-methylacetamide could not be detected by MS. Possibly adsorbed amine moieties may be masked by the broad N–H stretching vibration band, observed in spectra b to d of fig. 1B. At 1439 cm^{-1}, a second band grows in as the temperature is increased to 150°C. Bands at 1439 and 1379 cm^{-1} are tentatively assigned to monodentate carbonate ions. Interestingly, these bands also appear when propane is combusted in NO and O_2 at 200°C (not shown).

Another degradation product which is formed at 150°C in O_2 is CO. Its presence is detected by the characteristic CO stretching frequency of Cu^+–CO complexes and the peak at $m/z = 28$ in the mass spectrum of the gas phase. This peak must be due mainly to CO. Hydrocarbon molecules – such as C_2H_4 and fragments of C_2H_6 or higher hydrocarbons – should give satellite peaks at $m/z = 27$, which are, however, virtually absent. A contribution of N_2 to peak $m/z = 28$ cannot be ruled out. Together with the formation of CO, IR bands at 2298 and 2170 cm^{-1} are detected. The former band can be assigned to a Si^{4+} bonded NCO complex in good agreement with literature data [19,20]. The assignment of the band at 2170 cm^{-1} is less straightforward. It falls in the range of CN^- or NCO^- ions bonded to Cu^{2+} ions as reported by Li et al. [21] but is 10 cm^{-1} lower than that reported by Solymosi and Bánsági [20]. However, interpretation of the band at 2170 cm^{-1} as an organoisonitrile cannot be excluded from the present data [22].

In order to check whether the generation of the species absorbing at 2170 cm^{-1} proceeds via the Beckmann rearrangement of acetone oxime, N-methylacetamide was impregnated on Cu/ZSM-5. Interestingly, decomposition of the amide did not yield this band, but resulted in the formation of Cu^+–CO. Additionally, to identify the band at 2170 cm^{-1}, Cu/ZSM-5 has been impregnated with an aqueous solution of NaOCN. When this sample was treated in He to 100°C, a band at 2271 cm^{-1} with shoulders at 2227 and 2220 cm^{-1} was observed. The main band is ascribed to Na^+–NCO, whereas the bands at 2227 and 2220 cm^{-1} are close to the 2225 cm^{-1} band which Solymosi and Bánsági ascribe to Cu^0–NCO [20,23]. Upon heating the sample to 175°C, the band intensity at 2271 cm^{-1} decreased strongly and a band at 2188 cm^{-1} was formed. The latter band is indicative of Cu^{2+}–NCO complexes [20]. However, the absence of an absorption at 2170 cm^{-1} rather suggests that the latter band might be due to an organoisonitrile molecule.

4.2. *Reactions of adsorbed acetone oxime with NO_x*

In view of the mechanism of the catalytic reduction of NO_x, the most interesting observation of this study is the formation of significant amounts of $^{14}N^{15}NO$ ($m/z = 45$) and $^{14}N^{15}N$ ($m/z = 29$) upon heating Cu/OX1/ZSM-5 at 40°C in the presence of ^{15}NO (fig. 3). This result shows that the predominant formation of N–N bonds occurs between impinging ^{15}NO molecules and ^{14}N containing surface complexes. The latter could be acetone oxime or one of its isomers or decomposition products. The high preponderance of isotopically mixed N_2O ($^{14}N^{15}NO$ or $^{15}N^{14}NO$) over $^{14}N_2O$ argues against any alternative mechanism which assumes decomposition of acetone oxime to ^{14}NO, followed by reaction of two NO molecules with each other. Additionally, decomposition of ^{15}NO has been ruled out as evidenced by the small signal intensity at $m/z = 46$.

After eliminating ^{14}NO as a plausible reaction partner of ^{15}NO to produce N_2 and/or N_2O with mixed N isotopes, other products originating from acetone oxime have to be considered. One obvious candidate is hydroxylamine, the N-containing product of reaction (3). In order to check this possibility, the formation of $^{15}N^{14}NO$ was studied from NO and Cu/ZSM-5 that had been impregnated with hydroxylamine hydrochloride from aqueous solution. When this material, Cu/HA/ZSM-5, was heated to 80°C and exposed to ^{15}NO, formation of mixed labelled nitrous oxide was indeed observed. Upon normalizing the amount of $^{15}N^{14}NO$ with respect to that of the ^{14}N containing precursors, the quantity of $^{15}N^{14}NO$ formed over Cu/HA/ZSM-5 was about 50% of that produced over Cu/OX1/ZSM-5 after reaction at 80°C.

Additional data show that mixed labelled nitrous oxide is also formed with ^{15}NO in the presence of O_2 over Cu/OX2/ZSM-5. However, oxygen appears to lower the production of this molecule. For instance, with $O_2/^{15}NO = 1.7$ the $^{14}N^{15}NO/OX$ ratio is found 3.6 times lower than in the absence of O_2.

It was also found that in the absence of copper the reaction of $^{15}NO_{gas}$ with Na-ZSM-5 supported acetone oxime, Na/OX/ZSM-5, yielded $^{14}N^{15}NO$, but that the $^{14}N^{15}NO$/OX ratio was six times lower than in the presence of copper. Evidently Cu sites are beneficial but not crucial for this particular reaction. This observation agrees with the known fact that NO_x reduction, although promoted by transition metal catalysts, proceeds also over H/ZSM-5 or Na/ZSM-5 [3].

Mass spectrometry does not distinguish between $^{14}N^{15}NO$ and $^{15}N^{14}NO$. NMR spectroscopy may be employed in the future.

In summary, the present data suggest that $^{15}NO_{gas}$ reacts with adsorbed nitrosopropane or its isomeric acetone oxime or hydroxylamine (hydrolysis product of acetone oxime) to form $^{14}N^{15}N$ and $^{14}N^{15}NO$.

5. Conclusion

One possible reaction path for the reduction of NO_x with propane over Cu/ZSM-5 that is consistent with the experimental results of the present study and previous papers, could consist of the following steps:

(1) formation of NO_y chemisorption complexes, in particular nitrate ions ligated to Cu^{2+} ions;

(2) interaction of C_3H_8 with NO_y complexes yields sec-propyl radicals;

(3) sec-propyl radicals react with NO forming nitrosopropane;

(4) nitrosopropane, or its isomer, acetone oxime, or their hydrolysis product, hydroxylamine, react with NO to N_2, possibly via N_2O.

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References

[1] Y. Li and J.N. Armor, Appl. Catal. B 2 (1993) 239.
[2] M. Iwamoto, H. Yashiro, K. Tanda, N. Mizuno, Y. Mine and S. Kagawa, J. Phys. Chem. 95 (1991) 3727.
[3] M. Iwamoto, in: *Zeolites and Related Microporous Materials: State of the Art 1994*, Proc. 10th Int. Zeolite Conf., Part B, Garmisch-Partenkirchen, July 1994, eds. J. Weitkamp, H.G. Karge, H. Pfeifer and W. Hölderich (Elsevier, Amsterdam, 1994) pp. 1395–1410.
[4] J. Valyon and W.K. Hall, Catal. Lett. 19 (1993) 109.
[5] R.H.H. Smits and Y. Iwasawa, Appl. Catal. B 6 (1995) L201.
[6] A.D. Cowan, R. Dümpelmann and N.W. Cant, J. Catal. 151 (1995) 356.
[7] F. Witzel, G.A. Sill and W.K. Hall, J. Catal. 149 (1994) 229.
[8] D.B. Lukyanov, G. Sill, J. d'Itri and W.K. Hall, J. Catal. 153 (1995) 265.
[9] T. Beutel, B.J. Adelman, G.D. Lei and W.M.H. Sachtler, Catal. Lett. 32 (1995) 83.
[10] Y. Li, T.L. Slager and J.N. Armor, J. Catal. 150 (1992) 241.
[11] B.J. Adelman, T. Beutel, G.-D. Lei and W.M.H. Sachtler, J. Catal., in press.
[12] S. Califano and W. Lütke, Z. Phys. Chem. NF 6 (1956) 83.
[13] S. Califano and W. Lütke, Z. Phys. Chem. NF 5 (1955) 240.
[14] J. Sárkány and W.M.H. Sachtler, Zeolites 14 (1994) 7.
[15] A. Corna and R. Massot, in: *Compilation of Mass Spectroscopy Data* (Heyden, London, 1966).
[16] P.A. Giguère and J.D. Liu, Can. J. Chem. 30 (1952) 948.
[17] C.J. Pouchert, *The Aldrich Library of FT-IR Spectra*, 1st Ed., 1 (1985) 754.
[18] H. Krietendrink and H. Knözinger, Z. Phys. Chem. NF 102 (1976) 43.
[19] V.A. Matyshak and O.V. Krylov, Catal. Today 25 (1995) 26.
[20] F. Solymosi and T.J. Bánsági, J. Catal. 156 (1995) 75.
[21] C. Li, K.A. Bethke, H.H. Kung and M.C. Kung, Chem. Commun. 121 (1995) 594.
[22] K. Nakamoto, in: *Infrared and Raman Spectra of Inorganic Coordination Compounds* (Wiley, Chichester, 1978).
[23] V.A. Bell, J.S. Feeley, M. Deeba and R.J. Farrauto, Catal. Lett. 29 (1994) 15.