Infrared evidence for the existence of nitrate species on Cu-ZSM5 during isothermal rate oscillations in the decomposition of N_2O

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Isothermal oscillations in the rate of decomposition of N_2O were studied on an over-exchanged Cu-ZSM-5 catalyst by mass spectroscopy and *in situ* transient FTIR. Oscillations in the production of O_2 and N_2 were observed to occur in a temperature range of 410–490 °C at a total pressure of 1.0 Torr pure N_2O. FTIR has provided the first spectroscopic evidence that surface nitrate species are present under oscillatory conditions. This study confirmed a previously proposed model that predicts a slow build-up of surface nitrates, followed by a rapid nitrate decomposition coupled with an increase in the rate of N_2O decomposition. The IR signature of the surface nitrates suggests they are monodentate nitrate species bound to Cu^{2+} ions. Temperature-programmed desorption studies reveal a strong correlation between the stability of the surface nitrate species and the temperature range in which oscillations occur.

KEY WORDS: Cu-ZSM5; rate oscillations; N_2O decomposition; transient FTIR

1. Introduction

The decomposition of nitrous oxide (N_2O) has received a great deal of attention lately due to interest in reducing the emission of nitrogen oxides (NO_x) from various sources. In particular, N_2O is most commonly released by the production of adipic acid and from the combustion of coal in fluidized beds. The role of N_2O as a greenhouse gas is a particular concern [1,2].

Two independent research groups have recently reported isothermal rate oscillations in the decomposition of N_2O over Cu-ZSM5 catalysts. Oscillations were first observed by Linz and Turek [3] with 1000 ppm N_2O over Cu-ZSM5 with Si/Al $= 37$ and a Cu^{2+} exchange level of 160%. Oscillations were observed to occur between $T = 375$ and 450 °C with a corresponding period of 30–3 min [3]. Further kinetic and transient experiments led the to the conclusion that the oscillations were caused by the existence of a nitrate species bound to the exchanged copper [4–6]. However, no *in situ* spectroscopic evidence was presented to support this conclusion.

Ciambelli *et al.* [7,8] also reported oscillations over Cu-exchanged ZSM-5. In this case the starting zeolite had a Si/Al ratio of 80 and an exchange level of 640%. Oscillations were observed with 300 ppm of N_2O from $T = 324$ to 385 °C. The period of oscillation also decreased with increasing temperature from 80 to 10 min. The authors proposed a redox mechanism to describe the oscillations in which copper ions alternated between a reduced (Cu^+) and an oxidized (Cu^{2+}–O^{2-}–Cu^{2+}) state [8]. Both research groups were subsequently able to model the observed oscillations based on their proposed mechanisms [6,9,10].

The purpose of this study is to examine isothermal rate oscillations in the decomposition of N_2O on an over-exchanged Cu-ZSM5 catalyst. *In situ* transient FTIR spectroscopy was used in tandem with mass spectrometry (MS) in order to correlate surface species with gas phase products and further the understanding of the underlying mechanism driving these oscillations.

2. Experimental

The Cu-ZSM5 catalyst used in this study was prepared from Na-ZSM5 (Bayer Si/Al $= 37$) via ion exchange with aqueous copper acetate, as described previously [4,11]. The copper loading was found *via* atomic absorption spectroscopy (Perkin–Elmer atomic absorption spectrometer 3110) to be 1.75 wt% corresponding to a Cu^{2+} exchange level of 153%.

For our experiments, the catalyst powder was pressed into an IR transparent wafer 14 mm in diameter. The wafer was then placed in a sample holder and inserted into a flow reactor built from a 2.75″ conflat five-way cross, as described previously [12,13]. The reactor was equipped with BaF_2 windows to allow for transmission infrared spectroscopy (Nicolet Protégé 460) and was connected to a mass spectrometer (Hiden HAL 201RC) *via* a variable conductance leak valve. The base pressure of the system was kept at 1×10^{-8} Torr by a turbomolecular pump (Leybold). A 60 mg wafer was placed in the sample holder along with a 40 mg partial wafer. The partial wafer only occupied half the cross-sectional area of the sample holder. This allowed the total mass of catalyst to be 100 mg without increasing the thickness of the entire cross-section. Oscillations were not ob-

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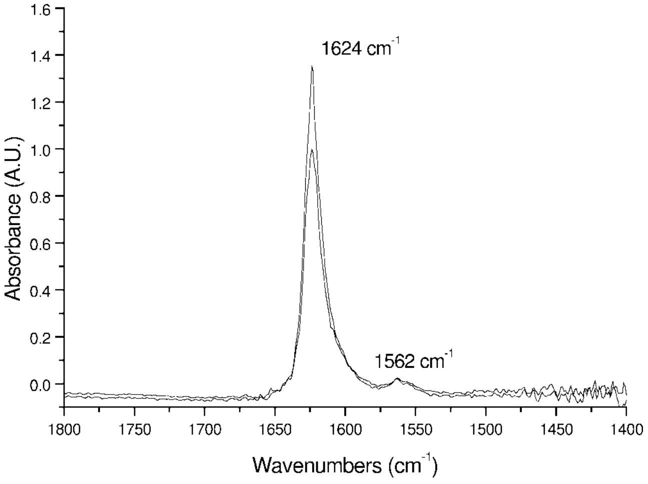


Figure 1. IR spectra collected under oscillatory conditions ($T = 460\,^{\circ}$C, $P = 1.0$ Torr, N_2O flow rate = 5.0 sccm). The two spectra shown are during the high and low reaction portions of the oscillations.

served and the conversion of N_2O was low if the total catalyst weight did not exceed 90 mg.

Once a catalyst pellet was inserted into the reactor, the system was pumped down to 1×10^{-8} Torr for 8 h. Prior to each experiment, the catalyst was heated in a linear ramp to 400 °C in flowing helium (20 ml(STP)/min, $P = 100$ mTorr) over 30 min and then held at 400 °C for 30 additional minutes. The temperature of the reactor was then adjusted to the reaction temperature (350–500 °C), and N_2O was passed over the catalyst at 5–10 ml(STP)/min at a total pressure of 1.0–2.0 Torr. Gas phase species (N_2O, O_2, N_2, and NO) were monitored by MS at a rate of 12 points per second, while surface species were measured using transient FTIR at a spectral resolution of 2 cm^{-1}. In transient mode, 32 spectra were co-added at a rate of 6 spectra per minute. Due to the fact that mass 30 is also a significant fragment of N_2O, a portion of the N_2O signal was subtracted from the NO signal in order to compensate for this overlap. The portion subtracted (31.1%) was based on the tabulated fragmentation pattern of N_2O.

Post reaction temperature-programmed desorption of surface species was also performed. The system was kept at the reaction temperature for 30 min in flowing N_2O to allow the catalyst to equilibrate. The system was then cooled to room temperature in flowing N_2O. This procedure ensured the surface nitrate species remained stable while the system cooled. The reactor was evacuated and subsequently heated to 525 °C at 10 °/min. Desorbing species were monitored using MS.

3. Results

Figure 1 shows an example of FTIR spectra obtained during the oscillations. The only peaks present are an intense absorption band centered at 1624 cm^{-1} and a smaller peak centered at 1562 cm^{-1}. The assignment of these bands in the literature is somewhat ambiguous. Absorption peaks in this range on Cu-ZSM5 catalysts are typically assigned to some form of NO_x species and are typically observed when NO_2 is adsorbed or NO is passed over the catalyst in the presence of O_2 [14–23]. Table 1 gives a summary of previously assigned IR peaks in this range. It should also be noted that the peaks observed in this system are virtually identical to two peaks observed when N_2O is passed over Fe-ZSM5 at a 200 °C. Oscillations were also observed over the iron catalyst, but only in the presence of water vapor [24].

Table 1
Previous assigments of IR absorption of NO_x type species on Cu-ZSM5.

Peak position (cm^{-1})	Assignment	Reference
1572–1576	Monodentate nitrate	[14,20,22,23]
1576	NO^- stretch of Cu^{2+}–$(NO_2)(NO^-)$	[18,21]
1620–1630	Cu^{2+}–NO_2	[14,16,21]
1630	Monodentate nitrate	[17]
1611	NO_2^-	[20]
1614, 1628	Bridging nitrates	[22]
1631	Bidentate nitrate on Cu^{2+}–O–Cu^{2+}	[23]

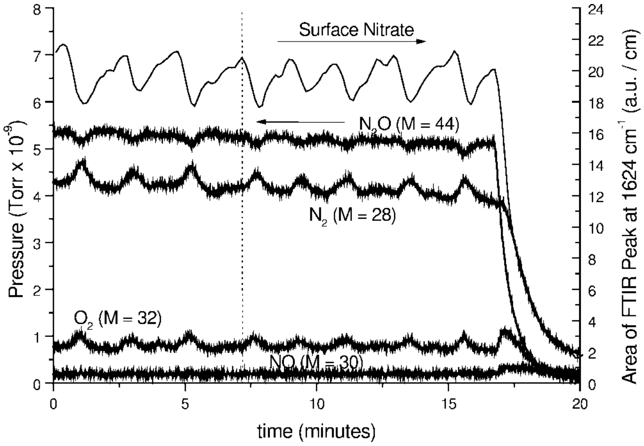


Figure 2. Isothermal rate oscillations in the decomposition of N_2O as monitored by both FTIR and MS. Reaction conditions are $T = 460\,^{\circ}$C, $P = 1.0$ Torr, and N_2O flow rate = 5.0 sccm(STP).

Figure 2 shows the oscillations observed on the Cu-ZSM5 sample at $T = 460\,^{\circ}$C, $P = 1.0$ Torr, and a flow rate of 5 ml/min of N_2O. In accordance with previous studies on this system and at this temperature [5,6], the period of the oscillations was 2–3 min. An increase in the production of N_2 and O_2 corresponded to a decrease in the concentration of N_2O in the reactor. In addition to the MS data, figure 2 also shows the integrated peak area of the nitrate species as a function of time. The surface nitrate concentration is seen to oscillate in a saw-toothed manner. A slow increase in surface nitrates is followed by an abrupt decrease in nitrate concentration concurrent with a release of oxygen and nitrogen.

This observation provides spectroscopic evidence to support the nitrate mechanism proposed previously [5,6]. In fact, the saw-toothed behavior of the surface nitrate peak is precisely the behavior predicted by Ochs and Turek in the analysis of their transient experiments (see figure 2, [6]). A slow buildup of surface nitrates and surface oxygen was

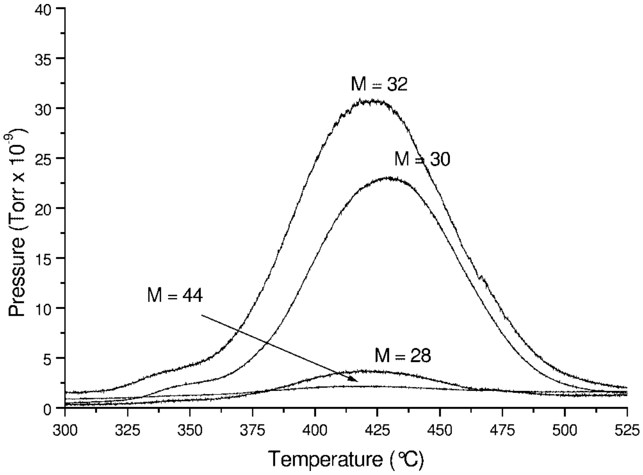


Figure 3. TPD of the Cu-ZSM5 catalyst after cooling in N_2O from the reaction temperature ($T = 450\,^\circ$C). The heating rate used was 10°/min.

predicted, followed by a release of both surface species concurrent with a release of N_2, O_2, and a small amount of NO. Ochs and Turek also observed a significant release of O_2 and NO when the inlet gas was switched to pure helium. As can be seen from figure 2, when the reactor is evacuated at the reaction temperature, a significant amount of O_2 and a small amount NO is released.

Unlike the study by Ochs and Turek [6], this work showed no release of nitric oxide during the oscillations. In addition, the shape of the oxygen transient during the oscillations is symmetric in this study while Ochs and Turek observed a complex transient with a sharp initial release followed by a broad shoulder. These subtle differences in the reaction behavior are most likely due to the lower conversion observed in this system as compared to that of Ochs and Turek. In our IR cell reactor, conversion is limited by the small amount of catalyst and significant bypassing of the catalyst wafer by the reactant gas flow.

Additional evidence to support the role of surface nitrate in the onset of oscillations is found in the TPD spectrum of the adsorbed species. Figure 3 shows the TPD spectrum of the Cu-ZSM5 catalyst after being cooled to room temperature from 450 °C in flowing N_2O and then evacuated. The nitrate species are seen to desorb as approximately equal portions of O_2 and NO with a small amount of N_2. In addition, the desorption peak occurs between $T = 350$ and 500 °C, which is comparable to the parameter space for oscillations observed by Lintz and Turek for this reaction ($T = 375$–$450\,^\circ$C) [3]. Figure 3 also shows that the maximum in the oxygen desorption peak occurs at a slightly lower temperature than does the nitric oxide peak ($T = 423\,^\circ$C compared to 430 °C). This difference in the desorption temperatures suggests O_2 is released first when the nitrate species decomposes.

4. Discussion

Based on the results of this study, it is possible to assign the IR peak at 1624 cm^{-1} to the anti-symmetric NO_2 stretch of monodentate nitrate bonded to a Cu^{2+} ion. This assignment is based on that of Komatsu *et al.* [17] who have also proposed that NO can react with the Cu^{2+}–O–Cu^{2+} dimer and chemisorbed oxygen to form a surface nitrate. Komatsu *et al.* were able to rule out adsorbed NO_2 as the surface species, and specify the nitrate geometry as monodentate based on adsorption experiments with ^{15}NO and $^{18}O_2$. This assignment would also be consistent with our TPD experiment (figure 3) if nitrate decomposition is initiated by O_2 release and subsequent desorption of the remaining NO. The peak at 1562 cm^{-1} is most likely due to the NO_2 symmetric stretch of the monodentate nitrate species. It also appears in the work of Komatsu *et al.*, and in our study it always appears in the same ratio to the peak at 1624 cm^{-1}, as shown in figure 5. The relatively small intensity of the 1562 cm^{-1} band compared to the 1624 cm^{-1} may imply that the angle between the two free oxygen atoms is large. This would enhance the change in the dipole moment of the anti-symmetric stretch while diminishing the change in dipole moment of the symmetric stretch.

If the concentration of nitrate species is high and the band at 1624 cm^{-1} is very intense (typically > 2.0 absorbance units), a weak band is observed at 2590 cm^{-1}. This peak is most likely a combination band formed by the simultaneous excitation of the anti-symmetric NO_2 vibration of the nitrate at 1624 cm^{-1} and a third vibration at approximately 960 cm^{-1}. This third vibration is most likely due to the N–O stretch of the portion of the nitrate complex bonded to the copper ion [25,26], and verifies that the adsorbed complexes observed in this system are nitrate (NO_3^-) and not nitro (NO_2) type species.

Ochs and Turek [6] proposed a model to describe the oscillations in this system involving the following six steps:

$$N_2O + 2\square \rightarrow O_s + N_2 \qquad (1)$$

$$2O_s \rightarrow O_2 + 4\square \qquad (2)$$

$$N_2O + O_s \rightarrow 2NO + 2\square \qquad (3)$$

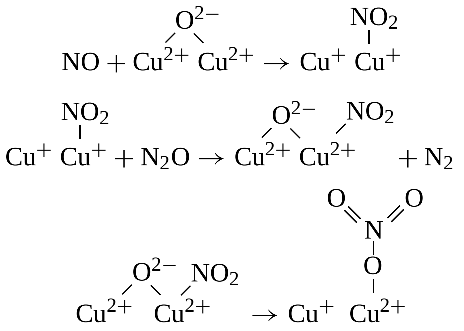
$$NO + 2O_s \rightarrow NO_{3,s} + 3\square \qquad (4)$$

$$NO_{3,s} \rightarrow NO + O_2 + \square \qquad (5)$$

$$N_2O + O_s \rightarrow O_2 + N_2 + 2\square \qquad (6)$$

where $\square$ designates an active site [6]. It was assumed that the active site in this mechanism is Cu^+ and that the surface oxygen is exclusively in the form of Cu^{2+}–O–Cu^{2+}. This explains the need for two active sites for each adsorbed oxygen atom. (1) and (4) have high corresponding rate constants while (2), (3), and (6) have much lower rate constants. The rate constant of (5) is intermediate but the reaction is assumed to be inhibited by the presence of surface oxygen. The rate of (5) is taken to be zero until the surface concentration of oxygen drops below a critical value ($\theta = 0.34$) [6].

According to this mechanism, nitrate species are formed *via* (3) and (4). Nitric oxide is first formed in (3) from N_2O and a bridged oxygen atom. This reaction is essentially identical to the reverse of a reaction proposed by Lei *et al.* over



$$\mathrm{NO} + \overset{O^{2-}}{Cu^{2+}\;Cu^{2+}} \rightarrow \overset{NO_2}{Cu^{+}\;Cu^{+}} \qquad (4a)$$

$$\overset{NO_2}{Cu^{+}\;Cu^{+}} + N_2O \rightarrow \overset{O^{2-}\;\;NO_2}{Cu^{2+}\;Cu^{2+}} + N_2 \qquad (4b)$$

$$\overset{O^{2-}\;\;NO_2}{Cu^{2+}\;\;Cu^{2+}} \rightarrow Cu^{+}\;\;\overset{O-NO_2}{Cu^{2+}} \qquad (4c)$$

Figure 4. Proposed reaction mechanism for the formation of nitrate species on the surface of Cu-ZSM5.

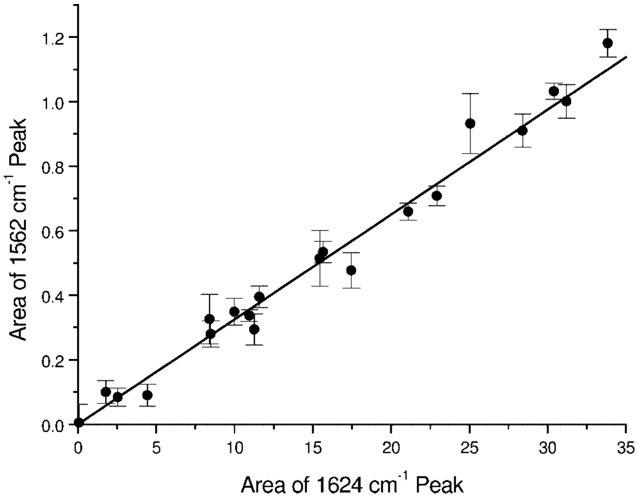


Figure 5. Comparison of the area of the FTIR peak at 1624 and at 1562 cm^{-1}. The peaks always appear at the same ratio and are therefore most likely different vibrations of the same surface species.

Cu-ZSM5 in which NO adsorbed on a pair of Cu ions reacts to form N_2O and a bridged oxygen [27]. The formation of NO from N_2O in this manner has also been reported to occur over Fe-ZSM5 catalysts [24]. Once NO is formed from (3), it immediately is reacted in (4) to form nitrate. Thus NO is critical in this system as an intermediate in the formation of nitrate species. However, it should be noted that at no time during the experiments were IR absorption bands visible in the 1800–1900 cm^{-1} region, which would correspond to adsorbed NO.

The advantage of the Ochs and Turek model over that of Ciambelli [10] is that it accounts for the release of NO during the highly reactive phase through (5). It also can account for the observation that NO quenches the oscillations and drives the reaction into the high state of reactivity [4,5]. In this case, the rate of (4) is increased by the increased concentration of NO. This then limits the amount of surface oxygen and thus allows (5) to never be inhibited.

Several aspects of the above reaction mechanism, however, remain unclear. First, in order for (2) to occur, two pairs of Cu ions would have to exist in very close proximity, which seems unlikely in a zeolite with a $Si/Al > 30$. However, isotope experiments have shown that lattice oxygen is also involved in the release of O_2 from Cu-ZSM5 [28], thus two pairs may not be necessary.

Second, the details of (4) are also unclear. Again, two pairs of Cu ions are needed for the reaction. Figure 4 shows an alternate pathway for (4) in which only one pair of Cu ions is necessary. In this pathway, adsorbed NO_2 is formed first from gas phase NO and a bridged oxygen atom. An additional molecule of N_2O then reacts with the Cu^+ pair to reform the bridge. It is also possible that the NO_2 desorbs and reacts with a bridged oxygen atom at a different location. In (4c), the bridged oxygen combines with the adsorbed NO_2 to form a monodentate nitrate species. It is assumed that (4b) and (4c) proceed rapidly and that the concentration of adsorbed NO_2 remains low during the reaction. Experiments with $^{18}O_2$ suggest that the bridged oxygen species becomes the atom that links the copper ion to the nitrogen atom in the monodentate nitrate complex [17]. This sequential formation of nitrate through NO and NO_2 has also been proposed in the Fe-ZSM5 system [24]. Based on this mechanism, in a situation where the concentration of N_2O decreased, one would expect a small amount of NO_2 to desorb from the catalyst. This desorption of NO_2 has been observed when the catalyst is in the high state of reactivity [5].

Finally, it is unclear why and how the critical concentration of surface oxygen affects the stability of the adsorbed nitrate species. (4c) of figure 4 shows a proposed reaction leading to the formation of the monodentate nitrate species. If it is assumed that a nearby bare Cu^+ ion is necessary for the decomposition of the nitrate to occur, an adsorbed oxygen atom on the Cu^+ ion could inhibit this reaction. Due to the charge on the Cu ion bonded to the nitrate species, this Cu ion pair is no longer able to react with N_2O and reform the oxygen bridge as it can in (4b). Thus, some other mechanism would have to exist to transport an oxygen atom to the Cu^+ ion. Dandekar and Vannice [1] have suggested that isolated Cu^+ are capable of reacting with N_2O to form N_2 and Cu^{2+}–O^- or Cu^{2+}–$(OH)^-$ species. In addition, other authors have proposed that lattice and extra-lattice oxygen are, in general, very mobile and that Cu^+ and Cu^{2+}–O sites can act as "portholes" for oxygen into and out of the zeolite structure [28]. It is conceivable that one of these processes is able to transport oxygen to the Cu^+ ions adjacent to the nitrate species, thus inhibiting nitrate decomposition. When the overall concentration of "surface" oxygen is depleted, bare Cu^+ ions then catalyze the decomposition of nitrate into NO and O_2. This process then becomes autocatalytic as NO can then attach other surface oxygen sites *via* (4). Furthermore, this type of mobile oxygen may also be involved in the formation of O_2 (2) and in the formation of nitrate from adsorbed NO_2 (4b).

5. Summary

This letter has provided spectroscopic evidence that the kinetic rate oscillations previously observed in the decomposition of N_2O over Cu-ZSM5 are related to the levels of monodentate nitrate surface species on Cu^{2+}–O–Cu^{2+} dimers. Transient FTIR data supports the previous reaction mechanism to describe oscillations proposed by Ochs and Turek [6]. The additional information provided by FTIR allows for a refinement of the previously proposed model. In addition, the thermal stability of surface nitrate species as measured by TPD corresponds to the temperature range in which oscillations occur, providing further evidence for the role of surface nitrates in this reaction.

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References

[1] A. Dandekar and M.A. Vannice, Appl. Catal. B 22 (1999)179.
[2] C. Kroeze, Sci. Total Environ. 152 (1994) 189.
[3] H.G. Lintz and T. Turek, Catal. Lett. 30 (1995) 313.
[4] T. Turek, Appl. Catal. B 9 (1996) 201.
[5] T. Turek, J. Catal. 174 (1998) 98.
[6] T. Ochs and T. Turek, Chem. Eng. Sci. 54 (1999) 4513.
[7] P. Ciambelli, E. Garufi, R. Pirone, G. Russo and F. Santagata, Appl. Catal. B 8 (1996) 333.
[8] P. Ciambelli, A. Di Benedetto, E. Garufi, R. Pirone and G. Russo, J. Catal. 175 (1998) 161.
[9] P. Ciambelli, A. Di Benedetto, R. Pirone and G. Russo, Chem. Eng. Sci. 54 (1999) 4521.
[10] P. Ciambelli, A. Di Benedetto, R. Pirone and G. Russo, Chem. Eng. Sci. 54 (1999) 2555.
[11] Y. Li and J.N. Armor, Appl. Catal. 76 (1991) L1.
[12] P. Fanson, W.N. Delgass and J. Lauterbach, J. Catal. (2001), submitted.
[13] J. Lauterbach, G. Bonilla and T. Pletcher, Chem. Eng. Sci. 54 (1999) 4501.
[14] T. Beutel, B.J. Adelman and W.M.H. Sachtler, Appl. Catal. B 9 (1996) L1.
[15] K. Hadjiivanov, D. Klissurski, G. Ramis and G. Busca, Appl. Catal. B 7 (1996) 251.
[16] T. Cheung, S.K. Bhargava, M. Hobday and K. Foger, J. Catal. 158 (1996) 301.
[17] T. Komatsu, T. Ogawa and T. Yashima, J. Phys. Chem. 99 (1995) 13053.
[18] J. Valyon and W.K. Hall, J. Phys. Chem. 97 (1993) 1204.
[19] A.W. Aylor, S.C. Larsen, J. Reimer and A.T. Bell, J. Catal. 157 (1995) 592.
[20] T.E. Hoost, K.A. Laframboise and K. Otto, Catal. Lett. 33 (1995) 105.
[21] S.-K. Park, V. Kurshev, Z. Luan, C.W. Lee and L. Kevan, Micropor. Mesopor. Mater. 38 (2000) 255.
[22] G. Centi and S. Perathoner, Catal. Today 29 (1996) 117.
[23] B. Ganemi, E. Bjornbom and J. Paul, Appl. Catal. B 17 (1998) 293.
[24] E.-M. El-Malki, R.A. van Santen and W.M.H. Sachtler, Micropor. Mesopor. Mater. 35–36 (2000) 235.
[25] K. Nakamoto, *Infrared and Raman Spectra of Inorganic and Coordination Compounds* (Wiley–Interscience, New York, 1976).
[26] P.M. Castro and P.W. Jagodzinski, J. Phys. Chem. 96 (1992) 5296.
[27] G.D. Lei, B.J. Adelman, J. Sarkany and W.M.H. Sachtler, Appl. Catal. B 5 (1995) 245.
[28] J. Valyon, W.S. Millman and W.K. Hall, Catal. Lett. 24 (1994) 215.