Potential reaction intermediates of NO_x reduction with propane over Cu/ZSM-5

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Received 13 January 1995; accepted 1 March 1995

Adsorption complexes that are formed by exposing Cu/ZSM-5 to nitric oxides have been identified by FTIR. Some of them are thermally decomposed below 200°C, but others, though much more stable thermally, are reduced at low temperature by chemical interaction with gaseous propane. The FTIR spectra suggest that the latter complexes are nitro and/or nitrate groups associated with Cu ions. Their formation and reduction when Cu/ZSM-5 is exposed to $NO + O_2 + C_3H_8$ seems consistent with the assumption that they are intermediates in catalytic NO_x reduction. Mass spectrometric analysis of the gases that are released when these complexes react with propane reveals formation of N_2, whereas thermal decomposition at higher temperatures only yields NO_2, NO, H_2O, traces of O_2, but no N_2. The results suggest that adsorbed NO_y groups ($y \geqslant 2$) are able to abstract H atoms from hydrocarbon molecules.

Keywords: NO_x reduction; Cu/ZSM-5 catalyst; adsorbed nitrate, IR spectra of; adsorbed nitro group, IR spectra of; adsorbed NO_x, reduction to N_2; adsorbed NO_x, H abstraction by; H abstraction from alkanes

1. Introduction

The harmful effects of NO emissions on the environment require abatement of these gases. Direct decomposition of NO to N_2 and O_2, though thermodynamically favorable, does not occur at low temperature in the absence of a catalyst [1,2]. Iwamoto et al. found that Cu supported on ZSM-5 is a unique catalyst for this process [3]; it is also quite active in NO_x reduction with hydrocarbons such as propane or propene [4]. Remarkably, this reduction is strongly enhanced by an excess of oxygen in the feed [5,6]. Three possible causes have been discussed for this effect of O_2 addition to mixtures containing NO and a hydrocarbon:

(1) Oxygen reacts swiftly with NO to form NO_2, which then interacts with the catalyst and reductant [7].

(2) The reductant reacts first with O_2, one of the intermediates of this process reacts with NO [8,9].

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(3) O_2 keeps the active sites clean by oxidation of coke deposits and their precursors [10].

These possibilities are not mutually exclusive. In our lab we compared feeds in which initially NO_x was either $NO_2 + O_2$ or $NO + O_2$; it was found that Cu/ZSM-5 catalyzes the formation of NO_2. Upon assuming that equilibrium between NO, O_2 and NO_2 is attained, the $NO_{2,eq}$ concentration prior to reduction could be calculated from the Bodenstein–Lindner relations [11]. When plotting the catalytic data of NO_x reduction versus the thus calculated $NO_{2,eq}$ values, the observed curves were identical for both feeds, indicating that the NO_2/NO equilibrium was indeed established for the temperatures and space velocities chosen, as has also been reported by other workers [12]. These results do, however, not exclude that over this catalyst NO_2 could be reduced back to NO before N_2 is formed [13].

Various authors have observed IR bands of surface complexes that are formed when Cu/ZSM-5 is exposed to NO_2 or to $NO + O_2$, although the assignment of the IR bands is still somewhat controversial. The key question addressed in the present paper then is: which of these surface complexes are potential reaction intermediates in NO_x reduction to N_2 with C_3 hydrocarbons? In the steady state of NO_x reduction, surface complexes will be formed from NO and O_2; these complexes are further referred to as NO_y with $y \geqslant 2$. Some of these NO_y complexes will interact with the hydrocarbon in a process ultimately resulting in N_2, while others will only be reduced back to NO or decompose thermally. In the present study the well-known strategy of unravelling chemical reaction networks is applied to investigate separately the formation and the consecutive reaction of putative reaction intermediates. For this purpose it was decided to:

(1) monitor the intensity decrease with increasing temperature of IR bands that were formed upon exposing Cu/ZSM-5 to NO_2 or $NO + O_2$ containing gas;

(2) compare such spectrokinetic data obtained in flowing He with those in a gas flow containing propane;

(3) analyse the gas released upon reduction or decomposition of the surface complexes.

Special attention has been focused on those IR bands which disappear at a lower temperature in propane than in helium and of which disappearance is accompanied by release of N_2. While NO and O_2 are crucial for the formation of NO_y complexes, the possibility that they could also interfere with the chemistry of NO_y reduction to N_2 by propane was checked in a separate experiment.

2. Experimental

2.1. CATALYST PREPARATION AND PRETREATMENT

Cu/ZSM-5 was prepared via ion exchange at room temperature (RT). A 0.15 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 = 0.665; Si/Al = 18; and Na/Al = 0.0. Prior to the IR and MS experiments the samples were calcined from 20 to 500°C at 0.67°C/min in O_2 flow (Linde, UHP), held for 2 h at 500°C, then cooled to room temperature in an O_2 flow.

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 of ca. 10–15 mg/cm^2 were prepared and inserted into a pyrex glass cell equipped with NaCl windows connected to a gas manifold. Spectra were taken in transmittance at RT with 50 scans accumulated at a spectral resolution of 1 cm^{-1}. After in situ calcination the sample was purged for 1 h at RT with 25 ml/min He (Linde, UHP). In the $NO + O_2 + He$ experiments, a stream of NO + He (Matheson) was diluted with O_2 (Linde, UHP) to obtain an NO_x concentration of 4500 ppm and an O_2 concentration of 750 000 ppm ($NO : O_2 = 1 : 167$). The total flow rate was 25 ml/min. The calculated equilibrium ratio at RT $(NO_2 : NO)_{eq.}$ is 154 : 1. After exposure to $NO + O_2 + He$ the samples were heated during 30 min to a specified temperature in 30 ml/min He (Linde, UHP) and held at this temperature for 30 min. Spectra were recorded at RT. In the reduction studies, samples were heated from 20 to 200°C at 6°C/min in flowing 2500 ppm C_3H_8 in He (Linde), total flow rate: 30 ml/min. After holding in the C_3H_8 + He flow for 15 min at 200°C, the cell was purged in UPH He for 10 min at 200°C and a spectrum was recorded at RT.

In situ high temperature FTIR measurements were carried out with another glass cell equipped with CaF_2 windows. The sample holder contained a heating filament embedded in a quartz tube. In the in situ high temperature measurements, the sample was saturated with NO_2 as described for the RT FTIR experiments. The sample was subsequently exposed to a stream of 3200 ppm NO, 3200 ppm propane and 8900 ppm O_2 at a total flow rate of 56 ml/min, and spectra were taken at increasing temperatures.

2.3. ANALYSIS OF RELEASED GASES

For on-line analysis of the released gases, a quartz reactor with a porous frit was charged with 400 mg Cu/ZSM-5. After calcination the sample was saturated with 2000 ppm NO_2 in He at RT. The reactor was then transferred to a recirculating manifold equipped with a Dycor quadrupole gas analyzer. The sample was heated in vacuo from 20 to 225°C and held at this temperature. For the reduction experiments, the recirculating manifold was filled with C_3H_8 + He. Computer monitoring of masses $m/e = 2$ through 46 began once the C_3H_8 signal was steady. A background spectrum was recorded for 2 min prior to exposing the sample to C_3H_8 + He. A mass spectrum was recorded every 30 s for 30 min.

A reduced Ni/SiO_2 trap was used to remove CO from the evolved gases, in order to eliminate CO contributions to $m/e = 28$. The efficiency of this "CO-getter" was verified in separate experiments.

3. Results

3.1. FTIR SPECTROSCOPY

Spectrum A in fig. 1 shows the NO stretching region of Cu/ZSM-5 which was exposed to $NO + O_2 + He$ at RT and purged 1 h with He at 200°C. Three bands were observed at 1628, 1594 and 1572 cm^{-1} which are ascribed to Cu^{2+} bonded

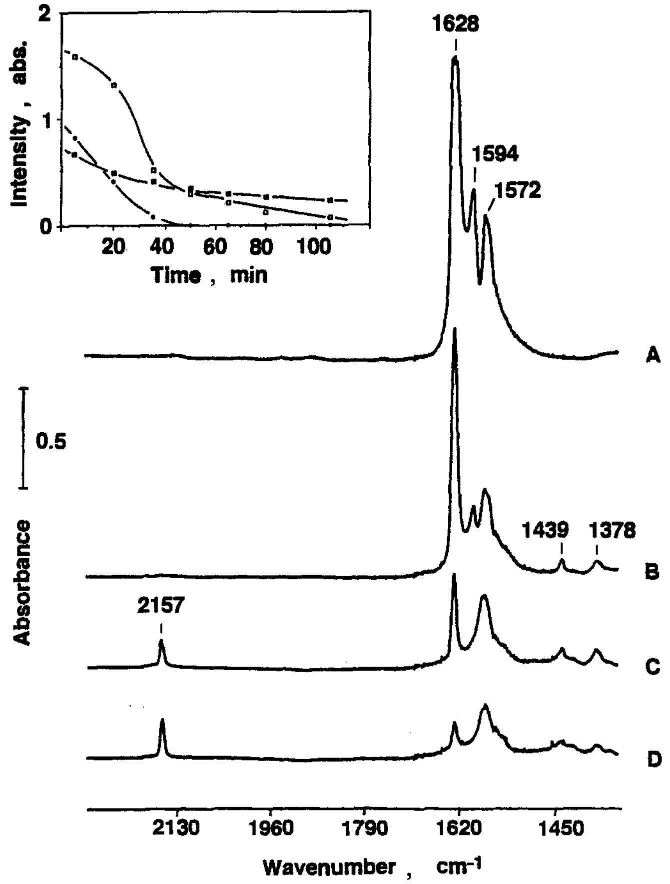

Fig. 1. FTIR spectra of Cu/ZSM-5, calcined, saturated with $NO + O_2 + He$ and purged 1 h with He at 200°C (A), followed by exposure to a stream of $C_3H_8 + He$ at 200°C for 20 min (B), 35 min (C) and 65 min (D). The insert depicts a plot of the band intensities at 1628 cm^{-1} (□), 1594 cm^{-1} (◆) and 1572 cm^{-1} (■) of adsorbed NO_y in flowing $C_3H_8 + He$ at 200°C as a function of time.

NO_y adsorbates, presumably *nitro* and/or *nitrate* groups [14]. A detailed discussion of the band assignment is beyond the scope of this paper and will be addressed in a forthcoming publication.

Fig. 2 shows the concentration of these groups in flowing He while the temperature is raised. All band intensities remain unchanged even upon thermal treatment at 200°C for 14 h. The bands at 1594 and 1572 cm^{-1} decline above 200°C, but the band at 1628 cm^{-1} is depleted only at 300°C.

The reactivity of NO_2 containing adsorbates towards propane is illustrated in spectra B–D of fig. 1. It is evident that the adsorbed NO_y species react at 200°C with propane. The complex absorbing at 1594 cm^{-1} reacts much faster; it disappears within 35 min of C_3H_8 exposure. Since the ratio of any two bands changes with time, it follows that these three bands belong to three different species. Oxidation products detected by IR are carbonates (bands at 1439 and 1378 cm^{-1}) and CO adsorbed on Cu^+ (2157 cm^{-1}).

Exposing a sample to a flow of $NO + O_2 + C_3H_8$ in the high temperature cell, and increasing the temperature results in the spectra shown in fig. 3. Bands at 1594 and 1572 cm^{-1} persist under these conditions up to 250°C; the nitro band at 1628 cm^{-1} is detected at 300°C but disappears at 350°C. Upon stopping the hydrocarbon flow, the bands at 1628 and 1594 cm^{-1} are restored but the low frequency band is not. These results show that propane does not interfere with the formation of the NO_y complexes; these entities show the behavior expected for steady state intermediates.

In another experiment the band characteristic of Cu^+–CO was recorded while propane reacted at 250°C with NO_y groups adsorbed on Cu/ZSM-5. Fig. 4 shows the surface concentration of CO versus time of C_3H_8 exposure. After recalcination

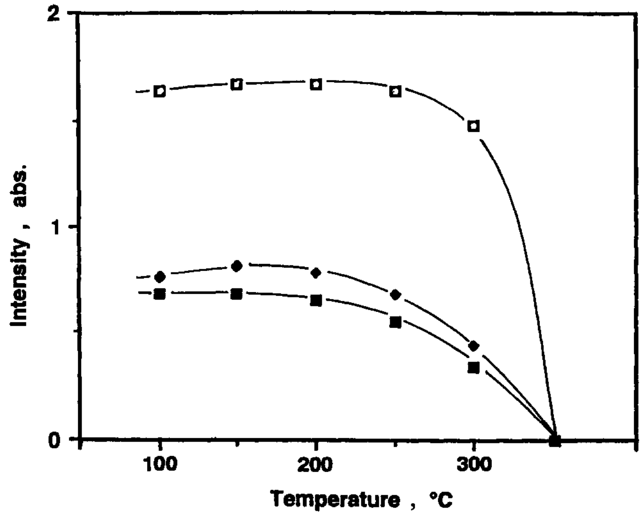

Fig. 2. Temperature dependence of the concentration of sorbed NO_y as measured by the absorbance at 1628 cm^{-1} (□), 1594 cm^{-1} (◆) and 1572 cm^{-1} (■).

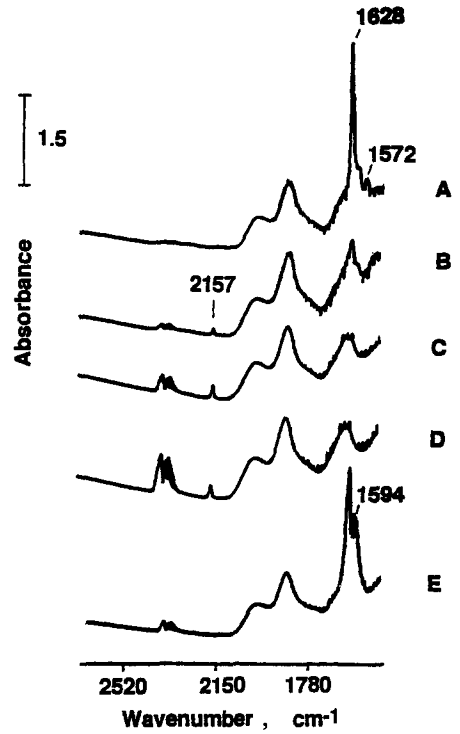

Fig. 3. In situ FTIR spectra of Cu/ZSM-5 in a flow of $NO + O_2 + C_3H_8$ at 250°C (A), 300°C (B), 350°C (C) and 400°C (D) and in $NO + O_2$ at 400°C (E). The background and gas phase contributions have not been subtracted.

in O_2 at 450°C and exposing to $C_3H_8 + He$ at 250°C this band is significantly weaker.

In order to discriminate between CuO particles and oxocations such as $[Cu–O–Cu]^{2+}$, use is made of the technique described in ref.[15] to selectively decompose the $[Cu–O–Cu]^{2+}$ ion pairs to Cu^+ ions by calcination and purging in He at 450°C. The formation of CO over such samples, shown in curve C, has thus to be ascribed solely to the oxidation of propane by CuO particles.

3.2. ANALYSIS OF RELEASED GASES

Fig. 5 shows the evolution of N_2, CO_2, and H_2O while propane is circulated at 225°C over a Cu/ZSM-5 sample that was previously exposed to NO_2 at RT and evacuated at 225°C. As N_2, C_3H_8, CO and CO_2 all contribute to mass 28, the determination of N_2 is not trivial. CO was removed by the pre-reduced Ni/SiO_2 "getter". The contribution from the fragmentation of C_3H_8 was calculated from mass 29 and a calibration factor that was determined from the spectrum of C_3H_8. Likewise, the contribution to mass 28 from the fragmentation of CO_2 was determined by calibration as a fraction of the $m/e = 44$ peak and subtracted from the $m/e = 28$

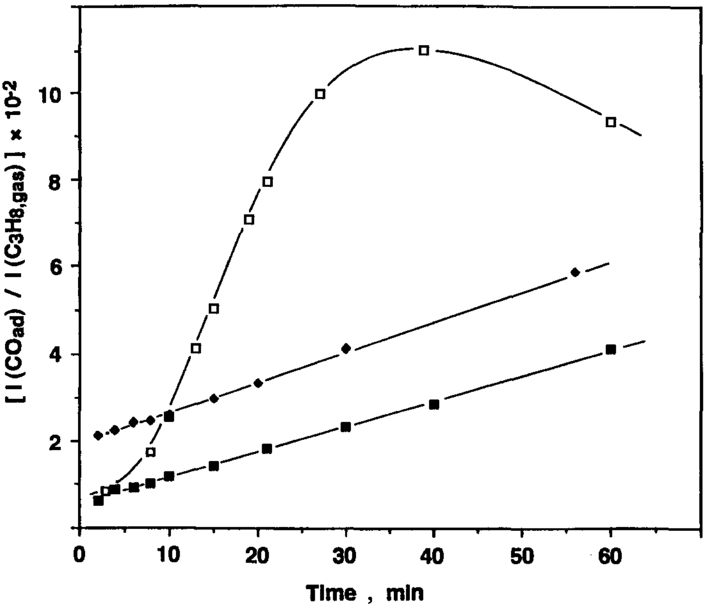

Fig. 4. Integrated band intensity at 2157 cm^{-1}, normalized by the integrated intensity of gas phase C_3H_8, measured under in situ conditions during the reaction of NO_2 precovered Cu/ZSM-5 with propane at 250°C (□), after recalcination at 450°C in O_2 and He purge at 20°C (◆) and after calcination at 450°C in O_2 and subsequent He purge at 450°C (■).

peak. With these corrections the quantity of N_2 was analyzed and found to be significant. Little H_2O evolution was detected. In the absence of the Ni/SiO_2 trap, NO ($m/e = 30$) was detected in the gas phase, and the intensities of m/e peaks at 28 and 44 were higher.

In the absence of a reductant, the sorbed NO_y complexes were stable and did not decompose at 225°C within 30 min. Upon heating to 500°C at 8°/min, the gas phase was analyzed and condensable products trapped in a liquid nitrogen cooled trap. No N_2 could be detected in the product of thermal decomposition of adsorbed NO_y. Upon removing the trap, the condensed compounds were analyzed and the following found prevalent: NO ($m/e = 30$), NO_2 ($m/e = 30$ and 46), and H_2O ($m/e = 18$). Modest amounts of O_2 ($m/e = 32$) and N_2O ($m/e = 44$) were also detected. No appreciable increase in $m/e = 28$ was detected after removal of the trap.

4. Discussion

Since the light-off temperature for homogeneous combustion of hydrocarbons in NO_2 is above 700°C, whereas NO_x reduction over Cu/ZSM-5 occurs below 500°C, the rate limiting step for the catalytic process does not appear to take place

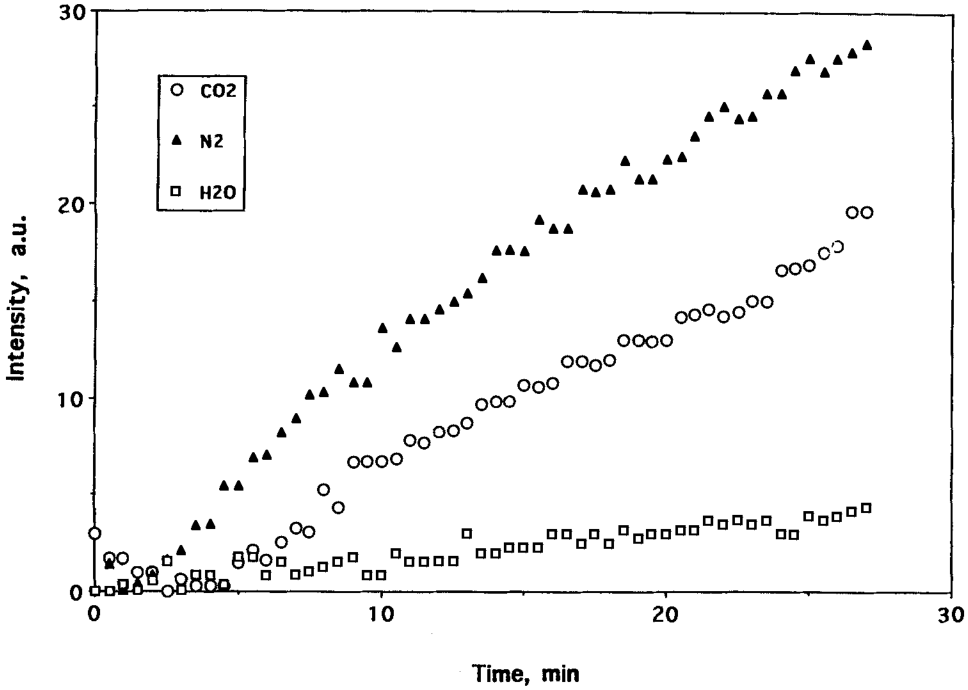

Fig. 5. Evolution of N_2 (▲), CO_2 (○), and H_2O (□) upon exposure to C_3H_8 at 225°C as detected by mass spectroscopy. The Cu/ZSM-5 sample was presaturated with NO_2 at RT and evacuated at 225°C. A pre-reduced Ni/SiO_2 trap was used to remove CO from the evolved gases.

in the gas phase. The present *FTIR* results show that sorbed NO_y species, which we tentatively identify as nitro and/or nitrate groups, are thermally stable at 200°C. The present results suggest that these groups are potential reaction intermediates, as has been reported by others [16].

These complexes are found to be highly reactive towards hydrocarbons, as is manifest by the rapid decrease of their band intensities in the presence of C_3H_8. This clearly occurs below the temperature of their thermal decomposition. As Bethke et al. did not detect NO_2 in the exit gas from ZrO_2 and ZSM-5 supported Cu catalysts exposed to a feed of $NO + O_2 + C_3H_6$ [13], the reduction of NO_2 appears to be faster than the re-oxidation of NO.

Results of our attempts to simulate the steady state of the catalytic reaction show that in the presence of $NO + O_2 + C_3H_8$, the nitro and nitrate groups can be detected on the catalyst surface at temperatures as high as 250°C; the nitro group is even observed at 300°C. These bands are absent at 400°C, yet two bands reappear upon elimination of C_3H_8 from the feed. The nitro and nitrate bands begin to disappear at temperatures where NO_x reduction occurs and can be restored at temperatures where the thermodynamic equilibrium is shifted towards NO_2 decomposition to NO and O_2. This strongly suggests that NO_x reduction occurs at the surface or is at least initiated at the surface.

While the *infrared* results clearly discriminate between the thermal decomposition of a surface group and its chemical reaction with a hydrocarbon, gas phase analysis is crucial to decide which reduction/decomposition process of an adsorbed entity leads to NO and which to N_2. The mass spectrometric data of the present study demonstrate that destruction of surface nitro and nitrate groups leads to N_2 *only in the presence of a reductant.* In contrast, thermal decomposition results in evolution of NO, NO_2 and H_2O. It follows that formation and reduction of NO_2/NO_3^- groups are instrumental steps in the reaction mechanism of SCR.

Witzel et al. [17] stress the similarity between NO_x reduction over Co/ZSM-5 and the homogeneous reaction of a cold flame [18]. In both cases, H abstraction from a hydrocarbon molecule is a critical step. They propose that gas phase free radicals are involved; the concept that radicals are formed at the surface of heterogeneous catalysts was proposed earlier by Voevodskii et al. [19] and found to be valid for methane oxidation by Lunsford et al. [20].

As it is known that with methane as the reductant Cu/ZSM-5 differs vastly from Co/ZSM-5, it appears that a catalyst-specific entity is involved in the hydrogen abstraction step. Accordingly, the present results would be consistent with a mechanism in which the rate limiting step is a reaction of the type:

$$NO_{y,ads} + C_3H_8 \rightarrow HNO_{y,ads} + \cdot C_3H_7 \qquad (1)$$

The hydrocarbon radical may react further with NO_{gas} or another $NO_{y,ads}$ to form organic nitroso or nitro compounds which ultimately result in formation of N_2.

Another noteworthy result of the present work is that formation of CO_{ads} was found more pronounced on the pre-saturated samples than on the fully oxidized or thermally reduced samples. This suggests that the copper nitro and/or nitrate groups have a greater ability to activate the hydrocarbon than copper oxocations such as $[Cu–O–Cu]^{2+}$, or CuO particles or the zeolite.

5. Conclusion

The reduction in C_3H_8 of copper nitro and nitrate groups, characterized by FTIR, occurs at temperatures where their thermal decomposition is negligible. Reduction products are N_2, CO_x and H_2O besides NO. Copper nitro and/or nitrate groups are likely intermediates of NO_x reduction. They seem to be able to abstract H atoms from hydrocarbon molecules; the radicals formed in this way will react further as proposed by others [16].

Acknowledgement

A seed grant by the Northwestern Center for Catalysis and Surface Science and a grant-in-aid by the Ford Motor Corporation are gratefully acknowledged. TB thanks the Deutsche Forschungsgemeinschaft for a stipend enabling him to join the V.N. Ipatieff Laboratory.

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