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Mechanism of the selective catalytic reduction of NO in oxygen excess by propane on H–Cu–ZSM-5 Formation of isocyanide species via acrylonitrile intermediate

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Abstract

NO^+ nitrosonium species have been evidenced by in situ FTIR spectroscopy, on H–ZSM-5 and H–Cu–ZSM-5 zeolites under $NO+O_2$ flow (near reaction conditions) at 623 K. Propane introduction in the reaction stream leads to NO^+ disappearing and to acrylonitrile detection among reaction products on H–ZSM-5. In the presence of copper, acrylonitrile adsorbed on Cu^+ is rapidly decomposed into ethylene and cyanide Cu^+CN in these conditions. In a further step, cyanide isomerises into isocyanide Cu^+NC. A reaction pathway involving H^+ and Cu^+ zeolitic sites is proposed for isocyanide species formation from reactants. The transformation of isocyanide species into N_2 (already published) is recalled in order to define a complete mechanism for NO_x selective catalytic reduction. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: NO SCR; H–Cu–ZSM-5; Intermediates; Acrylonitrile; Isocyanide; Isocyanate

1. Introduction

Among the forecasted solutions to limit polluting waste emissions from diesel or lean-burn engines, the selective catalytic reduction (SCR) of NO_x by hydrocarbons is still a possible way, even if recently NO_x-trap has been preferred. Discovered in 1989 by Iwamoto [1,2] and Held et al. [3], it has the fundamental interest of reducing nitrogen oxides by hydrocarbons in oxygen-rich atmosphere. In the last 10 years, a big research effort has been devoted to this reaction mechanism, especially in the case of Cu–ZSM-5 zeolite catalysts. Two main reaction pathways are evoked:

- The first proposes the direct decomposition of NO on copper, the hydrocarbon playing the role of oxygen elimination [4–6]. But this mechanism cannot justify the influence of the hydrocarbon nature [7] nor the activity of H–ZSM-5 zeolites without copper [8]. This hypothesis seems nowadays rejected on copper, even if it is confirmed on other metals such as platinum [9].
- The second pathway involves a surface mechanism in which the hydrocarbon generates one or more intermediate species acting as reducing agents towards NO. The first step will be oxidation of NO to NO_2 or two surface nitrates, oxidising power increasing in the way $NO < O_2 < NO_2$ or nitrate. Nitrogen dioxide or nitrate should be the best species to oxidise the saturated hydrocarbon to give a $C_xH_yO_zN$ compound, which will react afterwards with a NO_x species to give N_2, CO_2 and H_2O. These intermediates have been characterised by IR spectroscopy: nitriles [10–12], acetonoxime [13,14], isocyanates [15–18], isocyanides [17,18] and ammonia [17–19].

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The studies carried on Cu–ZSM-5 zeolites generally do not take into account the presence of a strong acidity in this catalyst. The presence of this function will be responsible for the predominance of the second type of mechanism. In a previous paper [20], we have shown the formation of NO^+ species starting by NO and O_2 co-adsorption on H–ZSM-5 zeolite at room temperature, and we have suggested the possible role of this species in the SCR of NO_x by hydrocarbons. In FTIR study on the mechanism of the reaction between nitrogen dioxide and propene over acidic mordenites, Baerns and co-workers [12] have proposed NO^+ as intermediate in the acrylonitrile formation. In the present work, we report the formation and the role of acrylonitrile as a precursor of Cu^+NC isocyanide species. We have shown in a recent paper [18] that isocyanides are intermediate compounds in the SCR of NO_x by propane on H–Cu–ZSM-5.

2. Experimental

The H–Cu–ZSM-5 catalyst (Si/Al = 27) was prepared by ionic exchange with a $Cu(NO_3)_2$ solution giving a copper content of 1.47 wt.%. The design of the IR cell for in situ studies has already been reported [21]. It allows reactivity experiments combined with rapid collection of IR spectra of surface species using a Nicolet Magna 750 FTIR spectrometer. Gas products were analysed by FTIR in a gas micro-cell and by mass spectrometry (Balzers TCP121). The sample was pressed into a self-supporting disc (ca. $15\,mg\,cm^{-2}$), heated progressively to 623 K under 5% O_2 in helium and maintained for 3 h in these conditions. It was then exposed (flow rate $= 25\,cm^3\,min^{-1}$; GHSV $= 50\,000\,h^{-1}$) to different gas mixtures at 623 K. All the spectra of the adsorbed species were obtained by subtracting the spectrum of the activated wafer from the spectrum obtained after introduction of the reactants.

3. Results and discussion

3.1. Formation of NO^+ nitrosonium species

3.1.1. On H–ZSM-5

The activation of H–ZSM-5 zeolite is performed at 623 K under 20% O_2/He flow during 2 h, then under pure helium (1 h). In a second step, a flow of $25\,cm^3\,min^{-1}$ NO (2000 ppm) + O_2 (5%) in helium is introduced at 623 K. A steady-state is rapidly gained on the surface, as can be deduced from the difference spectrum represented in Fig. 1a. Negative bands are observed at 3739 and $3590\,cm^{-1}$, corresponding to Si–OH silanols and to SiOHAl-bridged hydroxyls, respectively. In the 2300–1500 cm^{-1} stretching region,

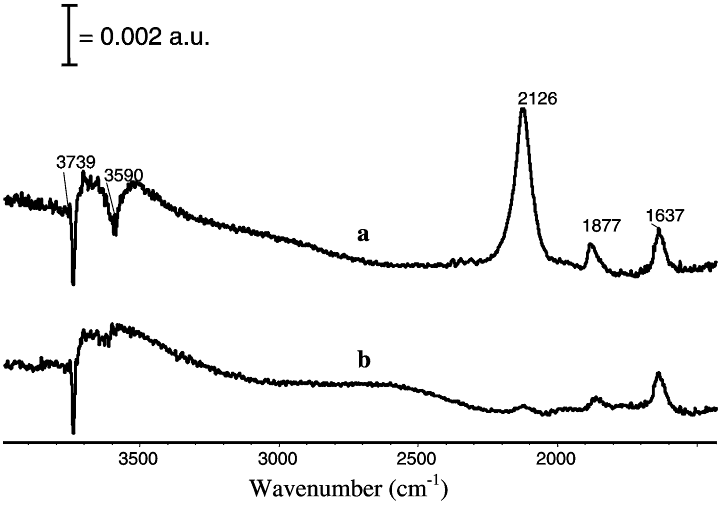


Fig. 1. FTIR spectra of species adsorbed on H–ZSM-5 under NO (2000 ppm) + O_2 (5%) + He flow at 350°C (a) and under further pure helium stream (b).

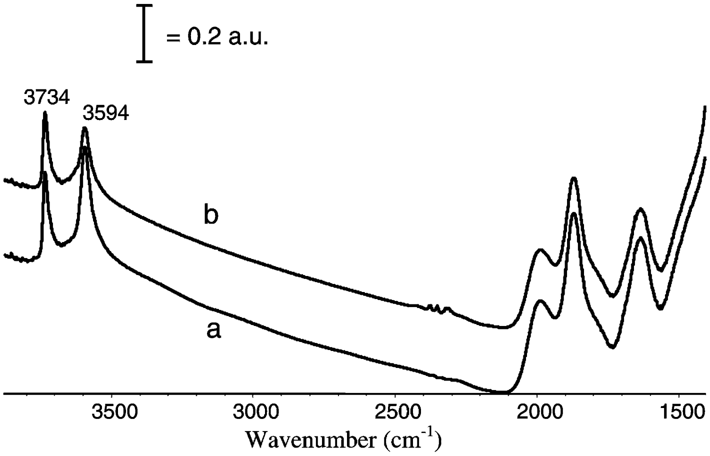


Fig. 2. FTIR spectra at 350°C of zeolites after activation: (a) H–ZSM-5; (b) H–Cu–ZSM-5.

three bands appear at 2126, 1877 and 1637 cm^{-1}. This spectrum is similar to that obtained by Hadjiivanov et al. [20] by NO and O_2 co-adsorption at room temperature in static conditions, on a H–ZSM-5 zeolite with a similar Si/Al ratio. This allows us to assign 2126 and 1637 cm^{-1} bands to NO^+ species in cationic position and to adsorbed H_2O, respectively. These water molecules belong to NO^+ species formation and to water traces in helium as well. The band at 1877 cm^{-1}, absent in the report of Hadjiivanov et al. [20], is assigned to NO species confined in the zeolitic channels ($\nu(NO) = 1875\,cm^{-1}$). NO suppression from the flow (Fig. 1b) produces a fast disappearing of bands at 2126 and 1877 cm^{-1} and the simultaneous recovering of the band at 3590 cm^{-1}. The formation process of NO^+ species is so identical to that evidenced in Ref. [20]. It can be resumed by the following reversible stoichiometric equation:

$$2NO + \tfrac{1}{2}O_2 + 2H^+ \rightleftarrows 2NO^+ + H_2O$$

3.1.2. *On H–Cu–ZSM-5*

In Fig. 2, FTIR spectra of H–ZSM-5 and H–Cu–ZSM-5 zeolites after activation are represented. SiOHAl-bridged hydroxyl stretching band at 3594 cm^{-1} is less intense, as awaited, for the exchanged zeolite. On the contrary, its intensity is greater than forecasted taking into account the introduced copper amount. The experimental ratio between bridged hydroxyl groups on exchanged zeolite and on the parent compound is 0.54, while with 1.47 wt.% Cu, the theoretical ratio should be 0.21 if copper is in the Cu^{2+} state, or 0.60 if copper is Cu^+. The consequent hypothesis that coppers might be mainly in the Cu^+ state in the exchanged zeolite is supported by in situ X-absorption experimental by Liu and Robota [22].

Under NO (2000 ppm) + O_2 (5%) stream, the spectrum recorded at the steady-state is shown in Fig. 3. Some remarkable differences with Fig. 1a (H–ZSM-5) appear. Now the main features are a sharp and intense band at 1625 cm^{-1}, with a shoulder at 1595 cm^{-1}, and a less intense peak at 1565 cm^{-1} (Fig. 3a). The study of the other regions of the spectrum at the absorbance scale of Fig. 1 puts in evidence several vibrations at 3231, 2593, 2122, 1939, 1866, 1817 and 1754 cm^{-1} together with a negative broad band at 3614 cm^{-1}.

Comparing both zeolite spectra allows to distinguish between species adsorbed on copper or on the zeolitic support. Among species bonded to the support, we find NO^+ characterised by the band at 2122 cm^{-1}, a little bit more intense than in absence of copper. The band at 1866 cm^{-1} is sometimes assigned to nitrosyl species on CuO [23] and preferentially to NO gas species confined in zeolitic channels. The other bands are considered as belonging to species co-ordinated to copper. The intense bands at 1625 and 1565 cm^{-1} are reported by many authors, but their assignment is controversial:

nitrite NO_2^- species [24–26];
N_2O_3 species [27,28];
nitrate NO_3^- species [13,23,25,29–31].

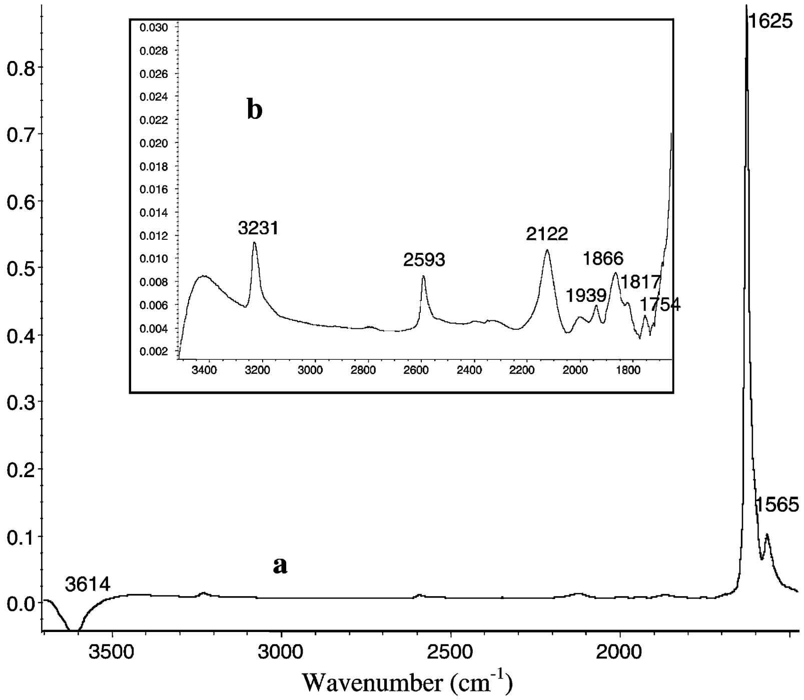


Fig. 3. FTIR spectrum of adsorbed species under NO (2000 ppm) + O_2 (5%) + He flow at 350°C on H–Cu–ZSM-5 (a) and zoom after intensity scale enhancement (b).

The assignment of these bands to a well-defined structure is difficult since the solid is not transparent in the range 1300–500 cm^{-1}. A correlation can nevertheless be found (varying NO concentration in the stream) concerning bands at 3231, 2593, 1625 and 1565 cm^{-1}. These four bands are characteristic of only one species since the intensity of the three less intense bands linearly vary with the intense feature at 1625 cm^{-1}. Starting from this result, it is possible to assign the band at 3231 cm^{-1} to the first overtone of 1625 cm^{-1} and that at 2593 cm^{-1} to a combination of the vibrational mode at 1625 cm^{-1} with another mode (undetectable) around 970 cm^{-1}. These spectroscopic results allow to discard the two first structures. Therefore, the two bands can likely be assigned to bidentate nitrates. The comparison with the IR spectrum of $Co(NO_3)_3$ which show two vibrations at 1619 and 963 cm^{-1} confirms this assignment [32]. The same result has been obtained by Hadjiivanov [33] in a recent paper.

The band at 1817 cm^{-1} is well known as a Cu^+NO species [34]. That at 1939 cm^{-1} (not reported in the literature for H–Cu–ZSM-5) cannot be due to $Cu^{2+}NO$ species in cationic position, which are normally located at 1911 cm^{-1}. It could be due to copper ions not belonging to the framework, such as $(Cu–O–Cu)^{2+}$ oxocations or CuO clusters [35].

3.2. Acrylonitrile species formation

3.2.1. NO + O_2 reaction with propane on H–ZSM-5

3.2.1.1. Study of the adsorbed phase. The zeolite activated as above is put under NO (2000 ppm) + 5% O_2 flow; it quickly reaches a steady-state identical to that presented in Fig. 1a. The introduction of 2000 ppm of propane in the stream leads to the immediate disappearing of NO^+ band, at 2122 cm^{-1} and to the rising of new bands (Fig. 4).

In the region 1750–1350 cm^{-1}, bands at 1694 cm^{-1} (after 2 min) then at 1668 cm^{-1} (between 6 and 15 min) temporarily appear. But in steady conditions, only three intense bands at 1641, 1542 and 1464 cm^{-1} and another, weaker, at 1386 cm^{-1} remain.

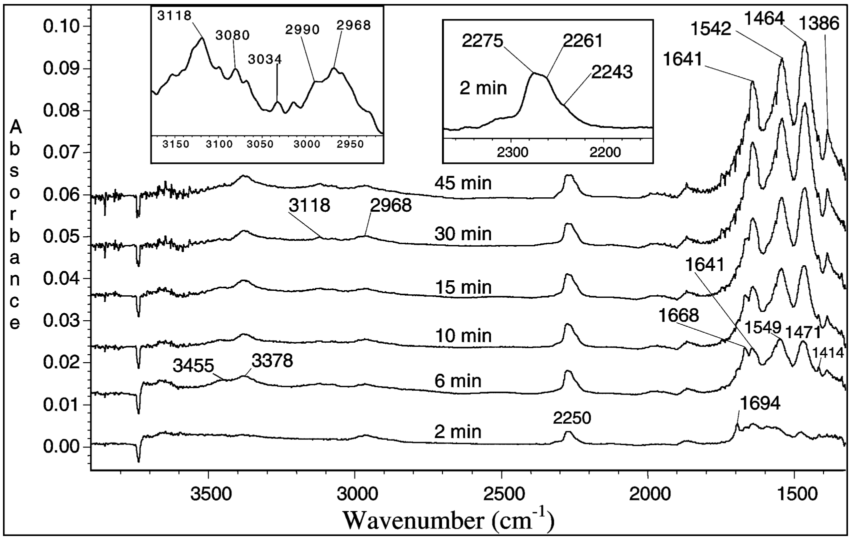


Fig. 4. FTIR spectra of adsorbed species on H–ZSM-5 under NO + C_3H_8 + O_2 stream at 350°C. Time $t = 0$ corresponds to propane in the flow.

The doublet at 2275 and 2261 cm^{-1} appears since the beginning of the reaction, increasing in intensity slowly but regularly with time.

In the region above 2800 cm^{-1}, other broad bands are detected in the first moments at 3455, 3378, 3118 and 2968 cm^{-1}; later three weak bands appear at 3080, 3034 and 2990 cm^{-1} (zoom in Fig. 4). The shoulder at 3455 cm^{-1} reaches its maximum intensity after 6 min under stream, then it progressively disappears with time (under flow). Vibrations at 3378 and 3118 cm^{-1} vary in the same way and reach a maximum intensity after ∼30 min of flow. The band at 2968 cm^{-1} (due to confined propane) is detected as soon as propane is introduced and it remains unchanged after 45 min of stream.

3.2.1.2. Study of the gas phase. The simultaneous analysis of the outlet gas from the reactor cell by online mass spectrometry has been first performed in analogical mode, i.e. recording all mass between 0 and 200 versus time. In these conditions, we can obtain a mass spectrum composed by several peaks that, compared with the reaction flow in absence of the catalysts, show the appearing of a quadruplet at $m/e = 50$, 51, 52 and 53 as soon as the reacting stream is sent inside the cell. The intensity of this massif is stable after about 10 min under flow (Fig. 5).

Mass 52 could be assigned to cyanogen (C_2N_2), but the mass spectrum of this compound does not show contributions to masses 50 and 51, whereas mass 53 is much weaker (∼3.5%). On the contrary, acrylonitrile ($CH_2{=}CHCN$) mass spectrum shows identical features for masses 50–53 (same relative intensity as the observed quadruplet — Fig. 5). At steady-state (after about 30 min), NO to N_2 conversion is 12%. Acrylonitrile concentration in the flow (evaluated by MS using a calibration curve for this compound) is around 20 ppm, corresponding to a conversion of about 1% of propane into acrylonitrile.

3.2.2. NO + O_2 *reaction with propene on H–ZSM-5*

3.2.2.1. Study of the adsorbed phase. The activated zeolite is flushed by NO (2000 ppm) + C_3H_6 (2000 ppm) + 5% O_2. In Fig. 6, infrared spectra of surface species recorded every 12 s are presented. This timing is necessary due to the rapid evolution of the surface. Spectrum obtained after 24 s under stream is equivalent to that recorded after 2 min with propane. As for propane, the first adsorbed species which appear are characterised by infrared bands around 2260 and 1696 cm^{-1}. After ∼1 min under flow, the latter band has almost disappeared, while other bands have risen, being partially equivalent to

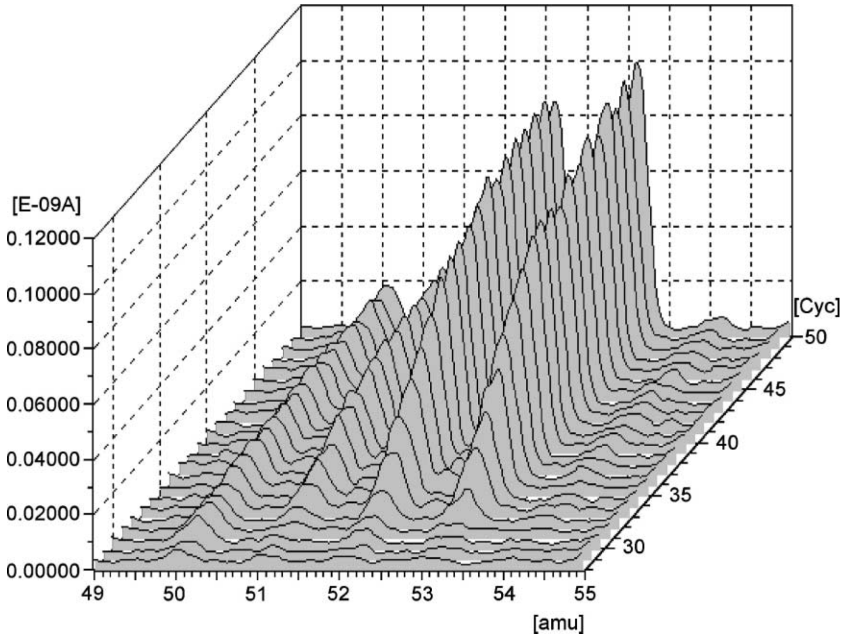


Fig. 5. Spectra of mass 49–55 under NO + C_3H_8 + O_2 flow on H–ZSM-5 at 350°C (1 cycle = 33.45 s).

those discussed in the case of propane: 3372, 2985, 2936, 2275, 2258, 1669, 1645, 1592, 1559, 1482 and 1416 cm^{-1}. For the rest, the two experiences differ: with propene steady-state is reached and the zeolite is rapidly deactivated by coke, as shown by the spectra recorded after 3, 15 and 30 min (Fig. 6b).

3.2.2.2. Study of the gas phase. The analysis of the gas products of the reaction reveals a much more important production of acrylonitrile from propene than from propane. NO to N_2 conversion is about 8%, but the fast deactivation of the catalyst impeaches evaluating if the initial amount is greater than in the case of propane. Deactivation also lowers acrylonitrile production down to 56 ppm at $t = 15$ min.

3.2.3. Acrylonitrile adsorption

At room temperature in static conditions (in order to avoid any reaction), the IR spectrum of adsorbed acrylonitrile on H–ZSM-5 (not shown here) is characterised by several bands in the region of ν(=CH) and ν(=CH_2) vibrations (3120, 3077, 3034 and 2989 cm^{-1}), by an intense vibration ν(CN) at 2261 cm^{-1} and by a sharp band at 1415 cm^{-1} (δ(=CH_2)). The appearing of these species corresponds to the disappearing of SiOHAl acid-bridged hydroxyls and to the formation of a broad band with an Evans' window [36] typical for a strong hydrogen bond.

The main adsorbed species is thus a species bound to the surface via the interaction of the nitrile function nitrogen atom with an acid hydroxyl group of the zeolite.

Sending a flow of 2000 ppm of acrylonitrile in helium at 623 K on the H–ZSM-5 zeolite shows the fast evolution of this compound.

The spectrum recorded after 2 min shows (Fig. 7):

- two bands near 3460 and 3364 cm^{-1};
- three bands at 3121, 3075 and 3031 cm^{-1};
- a massif of two unresolved bands at 2273 and 2258 cm^{-1};
- a series of more or less intense bands at 1668 (strong), 1630, 1551, 1478 and 1416 cm^{-1}.

Only the bands in the regions 3500–3200 and 1700–1350 cm^{-1} increase in intensity with time. Those at 3121, 3075, 3031, 2272, 2254 and 1416 cm^{-1}, assignable to acrylonitrile, remain constant (except for the intensity inversion of bands at 2272 and

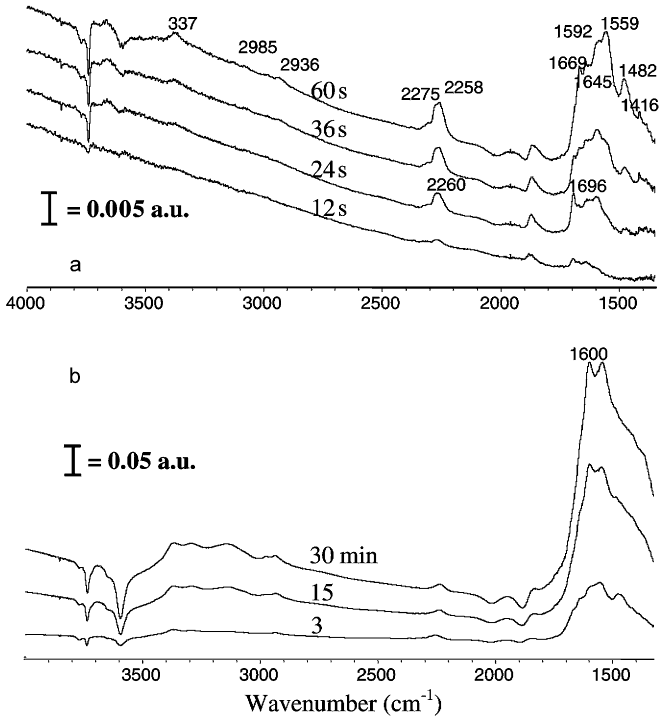


Fig. 6. FTIR spectra of adsorbed species on H–ZSM-5 under NO + C_3H_8 + O_2 flow at 350°C: (a) spectra recorded during the first minute of reaction; (b) spectra recorded during the following 30 min.

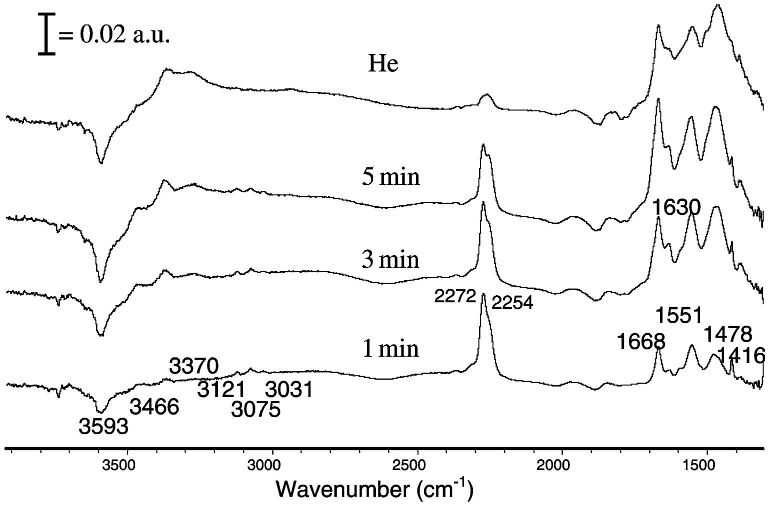


Fig. 7. FTIR spectra of adsorbed species on H–ZSM-5 under acrylonitrile (2000 ppm in helium) at 350°C.

2254 cm^{-1}). Stopping acrylonitrile in the flow mainly leads to the disappearing of these bands; on the catalyst only bands at 3466, 3361, 3283, 2272, 2254, 1666, 1631, 1551, 1465 and 1387 cm^{-1} remain.

This experiment shows that the main bands in the 3500–3300 and 1700–1400 cm^{-1} regions are due to the reaction of acrylonitrile on the catalyst, probably its hydrolysis by water traces in the flow. Moreover, it seems that the bands at 3460 and 3364 cm^{-1} can be correlated to the strong band at 1669 cm^{-1}. In fact those bands only decrease after stopping acrylonitrile in the flow. The adsorbed species characterised by the bands at 3460, 3364 and 1669 cm^{-1} can be assigned to acrylamide formation. These values differ from acrylamide spectrum when diluted in KBr, but it is accepted that IR spectra of amides are extremely difficult to assign, –CO and –NH_2 functions being sensitive to molecular association by hydrogen-bridging bonds [37].

The doublet in 2300–2240 cm^{-1} region likely corresponds to ν(CN) vibrations (due to its positions). We can a priori discard vibrations corresponding to SiCN (2218 cm^{-1}) or SiNC (2100 cm^{-1}) species, which could be formed by the reaction of nitrile with silanols [38]. The ν(CN) vibration of pure acrylonitrile (liquid phase) is located at 2230 cm^{-1}. The adsorption of this compound on a H–ZSM-5 zeolite can give rise at such a temperature to species protonated by very strongly acidic Si(OH)Al hydroxyls [39] (ν(CN) estimated near 2274 cm^{-1} by comparison with acetonitrile) and to species bonded to Si(OH)Al by strong hydrogen bond ($\nu(\mathrm{CN}) = 2262$ cm^{-1}).

The species characterised by the bands at 1634, 1550, 1465 and 1386 cm^{-1} can be partially assigned to the formation of acrylate species produced by the hydrolysis of acrylamide adsorbed species hydrolysis. The adsorption of acrylic acid on V_2O_5/TiO_2 [40] has been characterised by acrylate species features at 1635, 1495, 1440 and 1375 cm^{-1}.

3.2.4. Tentative assignment of the catalyst spectrum in working conditions

The IR spectrum of the adsorbed species on H–ZSM-5 zeolite under $NO + C_3H_8$ (or C_3H_6) $+ O_2$ flow is relatively complex, nevertheless acrylonitrile detection in the gas phase allows a good interpretation of the IR spectrum of the catalyst surface at the beginning of the reaction. We can thus assign spectral bands in Fig. 4:

- 3118, 3080, 3034, 2775 or 2261 and 1414 cm^{-1} to two types of acrylonitrile species: protonated and bonded by strong hydrogen bond to hydroxyl groups, showing bands at 2275 and 2261 cm^{-1}, respectively.
- 3455, 3378 and 1668 cm^{-1} to acrylamide species.
- 1694 cm^{-1} to acetamide species: contrary to previous bands, the latter is not evidenced during acrylonitrile reaction on H–ZSM-5 zeolite at 350°C. In a study performed in our laboratory, Thibault-Starzyk et al. [41] has shown that direct hydrolysis of acetonitrile on the same zeolite gives rise to two bands at 1692 and 1667 cm^{-1}, together with two pairs of bands at 3299 and 3220 cm^{-1} and 3464 and 3383 cm^{-1}, respectively. Those two series of vibrations can in fact correspond to two acetamide species adsorbed in different ways. The lacking of acetonitrile species (easily characterised by a couple of bands at 2308 and 2282 cm^{-1}) on H–ZSM-5 catalyst in working conditions can be explained by a faster hydrolysis of acetonitrile species. These bands appear in the spectrum at the beginning of the reaction, before that steady-state condition can be reached, when the initial water vapour pressure is too weak for the fast hydrolysis of these amides.
- 1641, 1542, 1464 and 1386 cm^{-1} to acrylate and acetate species: acetate species being characterised by a doublet of intense bands at around 1540 and 1450 cm^{-1} [40]. The initially non-simultaneous evolution of these two species explains the correlated evolution of the above-mentioned bands. Furthermore, acetate and acrylate species stability justifies the persistence in the time of the IR bands observed at 1631, 1546, 1465 and 1386 cm^{-1}.

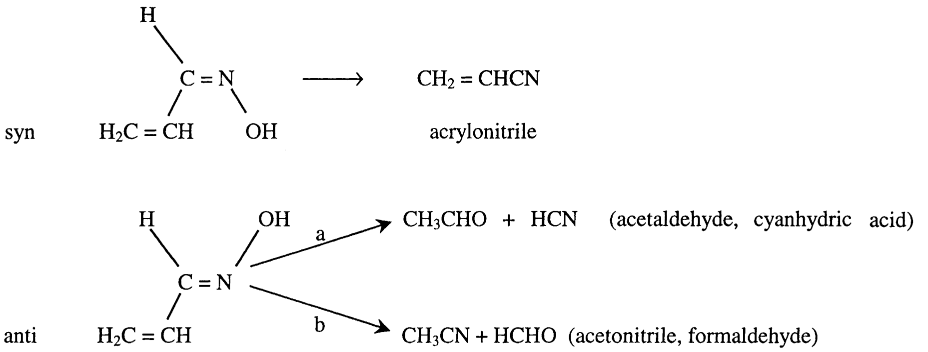
3.2.5. Acrylonitrile formation proposed mechanism

Acrylonitrile formation can be explained by a mechanism similar to that of propene ammoxidation proposed by Kokes and reported by Menon [42]. NO produced by NH_3 oxidation would react with propene; the author justifies this mechanism by the presence of reaction by-products. This mechanism, criticised in the case of ammoxidation [43], is in any case reliable for NO + propene direct reactions on NiO/Al_2O_3 [44] or Ag_2O/SiO_2 [45].

It considers several organic intermediates having different functions, that lead to the formation of the triple bond C≡N via oxime modification; only the starting steps will be different, taking into account that we start from propane and that NO^+ species formation on the surface has been put in evidence, these species being reactive. The hydrocarbon must be activated to perform nitration NO^+ being far less-reactive than $NO_2{}^+$ [46]. The first step needs thus propene formation:

$$\begin{aligned} CH_3\text{–}CH_2\text{–}CH_3 &\xrightarrow{-H_2} CH_2{=}CH\text{–}CH_3 \\ &\xrightarrow[+NO^+]{-H^+} CH_2{=}CH\text{–}CH_2\text{–}NO \\ &\rightarrow \underset{\text{allyl oxime}}{CH_2{=}CH\text{–}CH{=}N\text{–}OH} \end{aligned} \tag{1}$$

Zeolite acidity can justify $C_3H_8 \rightarrow C_3H_6$ transformation, and the formation of propene from propane on H–ZSM-5 has already been reported [47]. Propene, by reacting with NO^+, forms nitrosopropene, unstable, which isomerises into allylic oxime. Depending on oxime configuration (syn or anti), it is possible to obtain acrylonitrile via trans-elimination, acetaldehyde via acid decomposition, or acetonitrile via Beckman rearrangement; this transformation generally takes place in acid medium. Nitriles can react in the presence of water traces to give the amide species detected on the surface.



(1)

The parallel formation of acrylonitrile and acetamide (and probably of acetonitrile – reaction 1) shows that the two oxime forms are present as intermediates even if the “anti” configuration of the oxime is thermodynamically more stable. This supports the hypothesis of a mechanism similar to that of abovementioned propene ammoxidation.

The reaction using propene as reductor on HMFI confirms this result. We observe an immediate and greater production of acrylonitrile in the gas phase, that infers a reaction pathway close to that of propene ammoxidation. Cocking or pore filling by propene oligomerisation impeaches to verify that NO → N_2 conversion in the case of propene is greater, as awaited.

3.3. *Formation of copper isocyanide species* Cu^+NC

3.3.1. NO + O_2 *reaction with propane over H–Cu–ZSM-5*

3.3.1.1. Adsorbed phase study. The species formed on the catalyst under NO + O_2 flow have been described in Section 1. We recall nitrosonium band present at 2123 cm^{-1} and two strong bands at 1626 and 1565 cm^{-1} assigned to a bidentate nitrate species. Propane introduction progressively provokes these three bands disappearing, giving rapidly rise to a steady-state which presents a simple surface spectrum (Fig. 8). It is constituted by:

- A broad band around 3600 cm^{-1} due to water formation during propane combustion. The negative peak near 3600 cm^{-1}, present under NO + O_2 oxidising flow, is eliminated after propane arrival. This shows that the catalyst is partially reduced in presence of propane, with a concomitant formation of bridged SiOHAl hydroxyls at 3600 cm^{-1}.
- A weak carbonyl bands Cu^+CO at 2157 cm^{-1}.
- Three bands at 1621, 1543 and 1435 cm^{-1} corresponding to carboxylate species due to simple propane combustion; in fact they exist in the

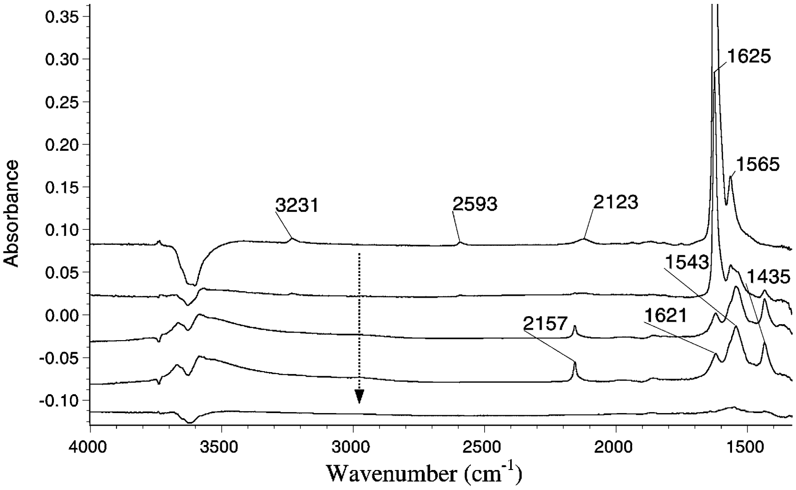


Fig. 8. Effect of C_3H_8 introduction on adsorbed species obtained under NO (2000 ppm) + O_2 (5%) flow at 350°C on H–Cu–ZSM-5: time evolution.

absence of NO in the reacting flow. They differ from those obtained on the zeolite without copper in the same conditions.

NO introduction in $C_3H_8 + O_2$ flow or the $C_3H_8 + NO + O_2$ flow itself gives two identical infrared spectra of the surface. After reacting species stop, under pure helium, the surface quickly recovers its initial spectrum.

3.3.1.2. Gas phase study. Concerning NO reduction activity, we observe that the steady-state is reached few minutes after the introduction of the third reactant (NO or C_3H_6). NO conversion is thus fixed at 65% (with a N_2 selectivity close to 100%) and propane conversion at 70%. Reaction products are in any case composed by N_2, CO_2, H_2O and unconverted compounds. Acrylonitrile or other species are not detected.

In these reaction conditions, H–Cu–ZSM-5 zeolite is too active to allow intermediate species detection. On the contrary, it is well known that this reaction does not take place in the absence of oxygen, therefore the ratio of this component represents a parameter which can slow down kinetics and allows intermediate molecule detection.

3.3.2. Oxygen amount influence

The oxygen amount has some influence and between 0 and 1% O_2, new species are formed on the surface, being characterised by bands at (Fig. 9):

- 3088 and 3023 cm^{-1} in the region of ethylic ν(CH);
- 2965 and 2940 cm^{-1} in the region of aliphatic ν(CH);
- 2157 and 2047 cm^{-1} in the region of triple bonds or double cumulated bonds;
- a series of bands in the carboxylate region modified respect to the steady-state.

Concerning reactivity, we have represented NO and C_3H_8 conversions versus oxygen amount in the stream (Fig. 10). We observe that the maximum in NO conversion is situated near 1.5% O_2 in the flow, while propane oxidation continuously grows up with oxygen concentration.

A maximum in the NO SCR activity by propane versus oxygen ratio has already been reported by several authors [48,49]. The interesting result of this experiment is that these new species are evidenced when the catalyst is at maximum activity. It is also possible to observe in Fig. 10 that at ca. 0.5% O_2, one C_3H_8 molecule is able to reduce two NO molecules, i.e. the double of what we obtain usually with 5% of oxygen (we will come back later on this topics).

These new bands in Fig. 9 cannot be assigned without additional information. Acrylonitrile over Cu–zeolite reaction will give us these information.

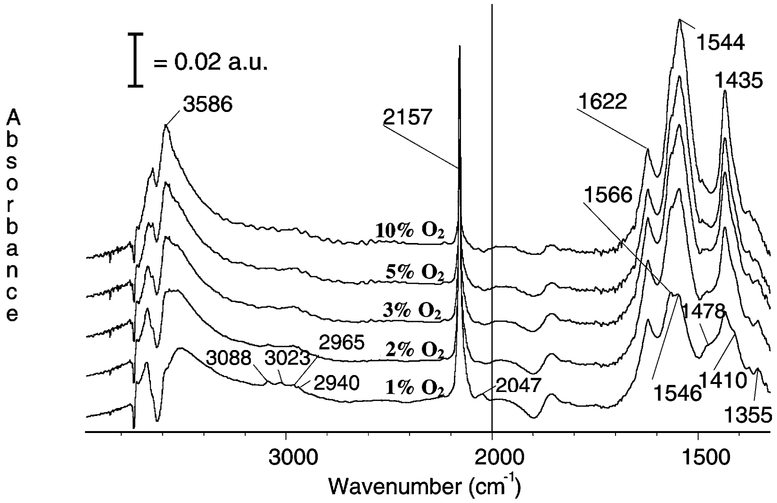


Fig. 9. Adsorbed species on H–Cu–ZSM-5 under NO (2000 ppm) + C_3H_8 (2000 ppm) + O_2 flow in steady-state conditions at 350°C.

3.3.3. CH_2=CHCN acrylonitrile adsorption

In Section 3.2.1, we have seen that H–ZSM-5 zeolites present a high activity in NO_x SCR by propane. During this study, we have given evidence of the presence of acrylonitrile on the catalyst surface and in the output gas. With H–Cu–ZSM-5 catalysts acrylonitrile presence is detected on the surface (carbonyl species adsorption hides these species in Fig. 9), but no traces of it can be found in the effluents. Therefore, it seems that this compound is formed on the catalysts which keep an important protonic acidity. But in the presence of copper acrylonitrile seems reacting faster to give species which could have a role into NO SCR.

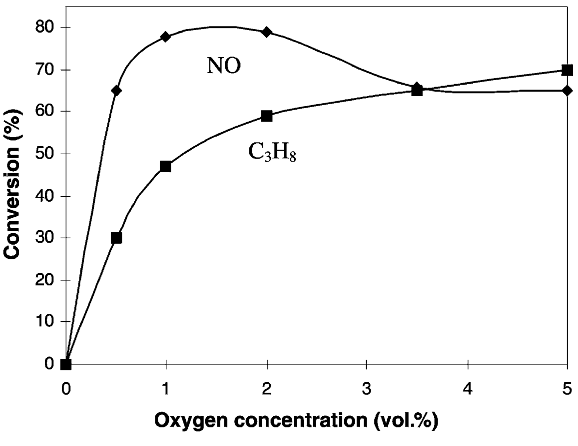


Fig. 10. Influence of oxygen amount on NO and C_3H_8 conversion on H–Cu–ZSM-5 under NO (2000 ppm) + C_3H_8 (2000 ppm) + O_2 flow in steady-state at 350°C.

Acrylonitrile can generate various adsorbed species on an HMFI zeolite (Section 3.3.3) as well. In order to characterise these species in detail in the case of a partially copper-exchanged zeolite, we have started by adsorbing this compound in static conditions at room temperature. This acrylonitrile adsorption on a H–Cu–ZSM-5 catalyst leads (Fig. 11a) to partial SiOHAl hydroxyls disappearing and to the appearing of:

- ethylic ν(CH) bands at 3121, 3078, 3035 and 2989 cm^{-1};
- two broad and intense bands at 2800 and 2400 cm^{-1};
- two ν(C≡N) sharp and intense bands at 2279 and 2262 cm^{-1};
- a sharp ν(C=C) band at 1607 cm^{-1} (1646 cm^{-1} is a component due to water);
- a sharp and very intense δ(=CH_2) band at 1414 cm^{-1}.

After heating at 150°C under O_2 (Fig. 11b), the spectrum presents the following evolution: the two broad bands at 2800 and 2400 cm^{-1} as well as the band at 2262 cm^{-1} disappear, while the intensity of the band at 2279 cm^{-1} increases. The intensity of the other features remains unchanged, except for SiOHAl hydroxyl band, which becomes less negative.

This experiment allows assigning the two forms of acrylonitrile adsorption on H–Cu–ZSM-5 zeolite. The

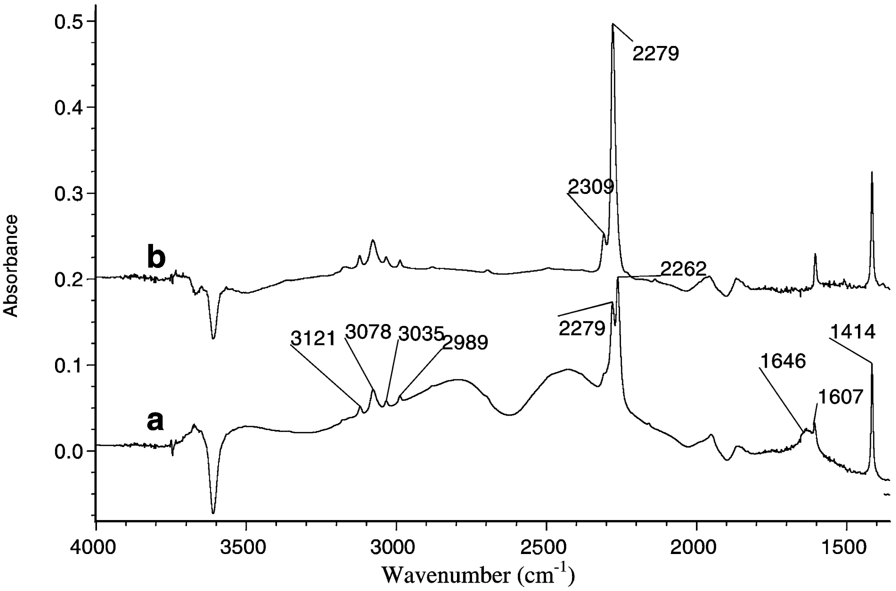


Fig. 11. IR spectra of acrylonitrile adsorbed on H–Cu–ZSM-5 at 25°C (a) and then after heating at 150°C under O_2 (b).

first corresponds to an acrylonitrile species hydrogen bonded to SiOHAl. This type of bond gives rise to the bands at 2800 and 2400 cm^{-1}. These bands could be alternatively assigned to water, but the disappearing of the band at 2262 cm^{-1} support our previous statement. The acrylonitrile species is especially characterised by the ν(C≡N) band at 2262 cm^{-1} and it is really similar to that described on H–ZSM-5 zeolite without copper. The second corresponds to an acrylonitrile species co-ordinated to Cu^+ ions and characterised by ν(C≡N) band at 2279 cm^{-1}. The ν(C–H) ethylic, ν(C=C) and δ(=CH_2) bands are identical for the two species.

Heating at 150°C shifts species bonded to hydroxyls towards Cu^+ sites. The number of acrylonitrile species remains constant, as shown by the intensity of the band at 1414 cm^{-1}. Heating allows molecule redistribution, now preferentially co-ordinated with Cu^+ ions.

Sending an acrylonitrile pulse (0.54 μmol) at 350°C on a H–Cu–ZSM-5 zeolite under stream conditions gives the spectra in Fig. 12. After 3 min (spectrum a), it appears:

- Si(OH)Al hydroxyl groups at 3595 cm^{-1};
- ν(C–H) ethylenic bands at 3089 and 3026 cm^{-1};
- multiple bands at 2260 and 2152 cm^{-1};
- bands at 1612, 1498 and 1414 cm^{-1} in the region of double bonds and bendings.

Spectrum b collected 20 min after sending a pulse shows several changes; the 2260 cm^{-1} band is broader and its maximum has shifted to 2256 cm^{-1}. The intensity of the band initially at 2152 cm^{-1} has slightly increased shifting to 2155 cm^{-1}. A new band has appeared in this region at 2047 cm^{-1}. The other bands of the spectrum remain unchanged except that at 1414 cm^{-1}, which has decreased in intensity.

Sending an oxygen pulse (spectrum c) leads to the immediate disappearing of the band at 2047 cm^{-1} and to the formation of the typical bands for ammonia co-ordinated to Cu^+ ions at 3366 and 3290 cm^{-1}.

The spectrum recorded under flow after an acrylonitrile pulse is very different from those recorded in static conditions at room temperature or after heating at 150°C.

Bands at 2260 and 1414 cm^{-1} are the fingerprint of an acrylonitrile species present on the surface and linked by hydrogen bond to Si(OH)Al sites. The absence of acrylonitrile species co-ordinated to Cu^+ sites can be likely due to an excessively high reactivity of these molecules on Cu^+. The shape of the bands at

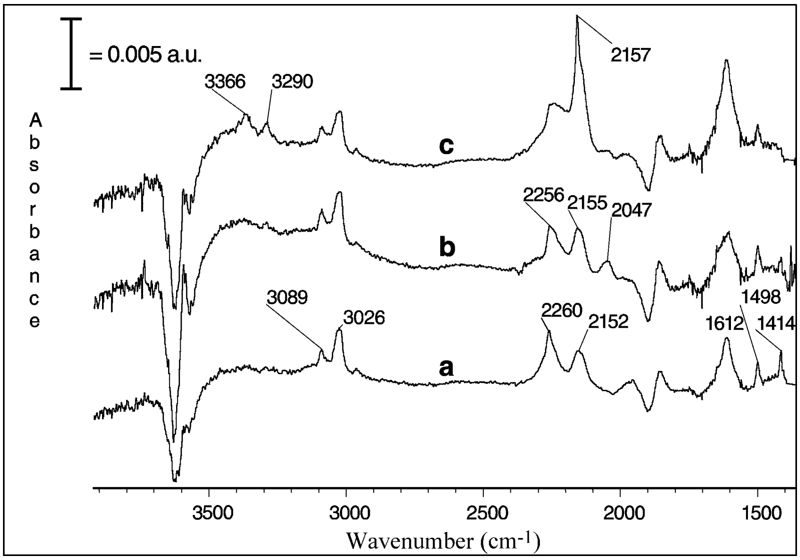


Fig. 12. IR spectra of adsorbed species after introduction of acrylonitrile pulse (0.54 μmol) over H–Cu–ZSM-5 at 350°C under helium flow: (a) 3 min; (b) 19 min and then reaction with 200 μl O_2; (c) 3 min.

2260 and 2152 cm^{-1} point out the presence of other hidden species.

The ethylenic species having ν(C–H) stretches at 3089 and 3026 cm^{-1} (different from the corresponding acetonitrile species) are characteristics of an ethylene species co-ordinated onto a Cu^+ ion. According to Davidov [50], the C_2H_4–Cu^+ complex formed on Cu_2O/Al_2O_3 gives rise to bands at 3090, 3030, 2990 cm^{-1} ν(=CH_2), 1545 cm^{-1} ν(C=C) and 1430 cm^{-1} δ(CH_2). Ethylenic compounds indeed give very strong co-ordination complexes with Cu^+, as shown by the downward shift of more than 100 cm^{-1} of the ν(C=C) vibration. In the present case, complexation is even stronger, adsorbed ethylene ν(C=C) vibration being associated to the band at 1498 cm^{-1}. These ethylene molecules can only come from acrylonitrile dissociation.

The molecule will be cut to form ethylene and $Cu^+C{\equiv}N$ cyanide species. According to Nakamoto [51] in fact ionic alcalin cyanides have a vibration at 2080 cm^{-1}, while covalent cyanides of IB group of copper present the stretch at 2150 cm^{-1} ($[Au(CN)_2]^-$–ν(CN) at 2164 and 2141 cm^{-1}). Being Cu^+ ions able to co-ordinate up to 4 CO and/or CH_3CN ligands [52], we can assume that Cu^+ is initially in this case in co-ordination with (CN) and (CH_2=CH_2) ligands at the same time. The possibility to have several species co-ordinated on the same copper ion explains the undefined shape of those bands.

The apparently slow formation of isocyanide $Cu^+N{\equiv}C$ species at 2047 cm^{-1} (spectrum b) characterised in our previous work [18] should be due to Cu^+CN isomerisation or to another kind of evolution (inversion during dissociation) of adsorbed acrylonitrile. Sending an oxygen pulse, we exactly reproduce what previously observed with isocyanide species [18], i.e. $Cu^+(NH_3)_n$ formation via an isocyanate species.

Summarising our results, acrylonitrile transformation on H–Cu–ZSM-5 zeolite can be schematised as follow [17]:

$$\begin{aligned}CH_2 = CH\text{–}CN &\rightarrow Cu^+ \xrightarrow{-C_2H_4} Cu^+(CN)\\ &\rightleftarrows Cu^+(NC) \xrightarrow{O_2} Cu^+NCO \qquad (2)\end{aligned}$$

$$Cu^+NCO \xrightarrow{H_2O} Cu^+(NH_3)_n \xrightarrow{NO} N_2 + H_2O + Cu^+ \qquad (3)$$

These Cu^+(NC) isocyanide species are detectable only in the presence of very small quantities of oxygen. Their accumulation on Cu^+ sites is due to the rate-limiting step, which constitutes the last step: isocyanide oxidation. When oxygen was totally absent, we could thus form isocyanide species on at least one-fifth of Cu^+ ions present in the zeolite [18]. In the presence of 5% O_2, the slow rate does not exist and the above reaction takes place too rapidly to allow species detection. Finally, $NO + Cu^+(NH_3)_n$ or NH_4^+ reaction to give N_2 is very fast [18].

4. Conclusion

The possible intermediates between propane and acrylonitrile (reaction 1), between acrylonitrile and monocarbonated species (reaction 2) are connected to the catalytic role of H^+ and Cu^+ cations, respectively. Three species or intermediate molecules have been characterised in this sequence: NO^+ nitrosonium ion, acrylonitrile and $Cu^+(NC)$ copper isocyanide. This study gave evidence of working synergy between H^+ and Cu^+ ions present in cationic position, for deNO_x catalytic properties of H–Cu–ZSM-5 zeolite.

The study of the zeolite without copper, which is a catalyst moderately active in the NO_x SCR, allowed establishing propane–acrylonitrile sequence via NO^+. In the absence of copper, this sequence is blocked at the acrylonitrile step, but we think that NH_3 or NH_4^+ remains the key intermediate. So in this case acrylonitrile hydrolysis must be invoked or alternatively allyl oxime should directly transpose into acrylamide; in the presence of water coming from propane combustion, hydrolysis into $CH_2{=}CHCOO^-$ and NH_4^+ can be taken into account, NH_4^+ ion being immediately recovered by the most acid site on zeolite. NH_4^+ ammonium ion in cationic position is a powerful reductor of NO even at mild temperatures [53]. We can imagine an identical process for acetamide (detected at the same time as acrylonitrile). A tentative correlation between acetonitrile produced as an intermediate and the corresponding NO conversion did not give concluding results, but it is difficult to take into account acetonitrile and the other compounds produced at the same time.

In presence of copper, the reaction becomes too fast to allow intermediate detection. This detection becomes possible when decreasing oxygen amount in the reacting flow, so that a slow step is introduced in the reaction pathway. The intermediates characterised in these conditions are representative of the reaction because conversion is near 50% and a weak increase in the oxygen ratio leads to species disappearing and to the maximum of conversion.

Copper plays multiple roles in this reaction. First of all copper in the zeolite keeps the initial Cu^+ form, all the complex with C_2H_4 [50], NCO [54] and NH_3 [55] being typical for this oxidation state. The main property of Cu^+ is to co-ordinate several species at the same time, hence concentrating reacting species on the same site. On the contrary, Cu^{2+} can co-ordinate only one species [52]. Its second characteristic is to dissociate acrylonitrile molecule into ethylene and CN or NC. This dissociation into two entities doubles the deNO_x properties of these molecules. In fact, the so-formed ethylene is an effective NO_x reducing agent in these conditions [56]. Fig. 10 shows clearly that for about 5% oxygen in the flow, the combustion of one molecule of propene gives rise to the reduction of two NO molecules.

In conclusion, the results of this study about NO_x SCR by propane in excess of O_2 allow proposing an original and detailed reaction pathway. Even if, in practical applications, this model catalyst is not technically performing for diesel or lean-burn engines waste treatment, the results presented give valuable information on the nature of the active sites, reacting agents activation and intermediate molecule evolution, which can be used to study other complex reactions.

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