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RESEARCH NOTE

FTIR Studies of the Origin of Deactivation during the Decomposition of Nitromethane on Co-ZSM5

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In situ **Fourier transform infrared spectroscopy has been used to observe the species deposited on Co-ZSM5 during the decomposition of nitromethane. At 553 K deactivation commences after 60 min. This is accompanied by the formation of bands due to NCO species between 2150 and 2300 cm^{-1} and the sudden development of a very strong band at 1662 cm^{-1}. The latter band can be assigned to the s-triazine compound, melamine, and/or derivatives of it, which cause deactivation by blocking zeolite channels. The most likely chemistry is an initial dehydration of nitromethane to isocyanic acid (HNCO) which forms melamine by reaction with ammonia derived by hydrolysis of HNCO. Cyanuric acid, the cyclic trimer of HNCO, may be an intermediate in the process.** © 1999 Academic Press

Key Words: **decomposition of nitromethane; Co-ZSM5; FTIR; deactivation; melamine.**

Selective catalytic reduction of nitrogen oxides by hydrocarbons has been widely investigated since the initial reports of Held *et al.* (1) and of Iwamoto *et al.* (2) almost a decade ago. Co-ZSM5 (and Co-ferrierite) are of particular interest because of their activity and selectivity when using methane (3–5). Many authors have suggested that this reaction proceeds through intermediate species analogous to nitromethane and/or nitrosomethane (6–9). The reaction exhibits a large deuterium kinetic isotope indicating that the limiting step is hydrogen abstraction (10). A methyl species formed in this way may then couple with NO_2 or NO. Until recently knowledge concerning the reactions of nitromethane over zeolites has been limited. Earlier studies (11) had demonstrated that it decomposed over many zeolites to give solid deposits derived from NH_3 and CO_2 but subsequent tests have also shown that conversion to N_2 is feasible over the higher hydrocarbon SCR catalysts, Ce-ZSM5 and Cu-ZSM5, when O_2 and/or NO are present (12, 13).

The inter-connection between these observations has since been established (14). Over Co-ZSM5 there is extensive decomposition of nitromethane to CO_2 and NH_3 by 523 K. However, when NO and/or O_2 are present the NH_3 is totally converted to N_2 by 633 K. Subsequent work by Lombardo *et al.* (15) has confirmed this and shown that Cu-ZSM5, Fe-ZSM5, and H-ZSM5 behave somewhat similarly.

Recent detailed investigations have shown that the reaction of nitromethane over Co-ZSM5 is quite complex (16). Initial exposure to nitromethane at 553 K gives complete conversion to CO_2 and NH_3 with smaller amounts of N_2 and HCN. However, after a few hours on-stream conversion falls to a lower level and isocyanic acid (HNCO) becomes the largest nitrogen-containing product. The most probable route to NH_3 is through dehydration of the aci (enol) form of nitromethane to HNCO followed by hydrolysis of the latter (16). FTIR/NMR measurements indicate that nitromethane decomposes in that way when adsorbed on alumina (17). In a flow system alumina gives complete conversion of nitromethane to NH_3 and CO_2 at 553 K but, unlike Co-ZSM5, there is no deactivation and HNCO is never observed (16). It was suggested that deactivation of Co-ZSM5 is attributable to the buildup of a polymer of isocyanic acid, possibly its trimer, cyanuric acid, within channels.

The aim of the present work was to observe and, if possible, to identify the deactivating species formed from nitromethane by *in-situ* FTIR measurements under reaction conditions. The measurements were carried out on pressed discs contained in a small volume, flow-through infrared cell identical to that described by Hicks *et al.* (18) and fitted with CaF_2 windows. The Co-ZSM5, H-ZSM5, and silica used were from the sources described previously (16). Co_3O_4 was formed by the calcination of $(CH_3COO)_2 \bullet 4H_2O$ (Merck, GR grade) in air at 673 K. Discs were pretreated in flowing 10% O_2/He overnight at 553 K. Spectra were obtained by accumulation of 64 scans at 2 cm^{-1} resolution using a Biorad

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FTS-7 spectrometer with a DTGS detector. The input flow to the cell (one or more of CH_3NO_2, 1100 ppm; H_2O, 2400 ppm; NO_2, 1000 ppm; O_2, 2.9% in He) was provided by a combination of electronic flow controllers and saturators as described previously (16). The output flow from the cell was sampled into a gas chromatograph (Shimadzu GC-8A) with an CTR-1 column containing molecular sieve and Porapak Q in a concentric arrangement (Alltech, Inc) and then diluted with N_2. The diluted stream was then sampled by atmospheric-type NO/NO_2 (Lear Siegler ML9842) and CO (Lear Siegler ML9830) analysers.

The above arrangements have two limitations relative to the system employed for the packed bed measurements (16). First, analyses for NH_3, HCN, and HNCO were not possible. Second, the O-rings in the cell limited the maximum pretreatment temperature to 553 K rather than 723 K. However, tests with the packed-bed system showed that catalytic behaviour after the pretreatment used here was similar to that observed following the more severe treatment.

Deactivation over Co-ZSM5. Figure 1 shows the product distribution observed during decomposition of 1100 ppm nitromethane in 2.9% O_2 over a pressed disc of Co-ZSM5 at 553 K. Over the first hour there is close to complete conversion with the formation of >800 ppm CO_2 and >200 ppm N_2. This is similar to that found earlier with the packed bed system (16). On the bases of those results $\approx$400 ppm NH_3, $\approx$150 ppm of HCN, and small amounts of HNCO would also be expected, but analyses for them were not possible here, as noted above. Deactivation commences somewhat earlier in the infrared cell than in the packed bed (after $\approx$60 min rather than 120 min) probably because of differences in flow patterns and a somewhat lower mass of catalyst (65 mg versus 100 mg). Nonetheless, the fall in CO_2 production is similar, and on the basis of the packed bed results one would expect it to be accompanied by a growth in HNCO concentration to $\approx$200 ppm.

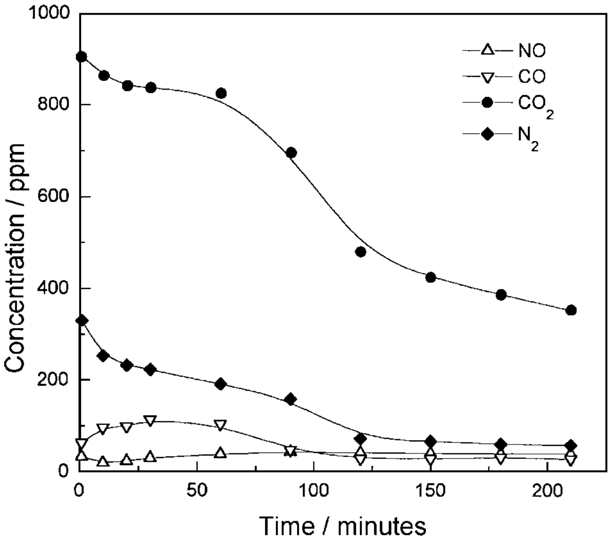


FIG. 1. Product distribution versus time during the reaction of 1100 ppm CH_3NO_2/2.9% O_2 over a 65.1-mg disc of Co-ZSM5 at 553 K.

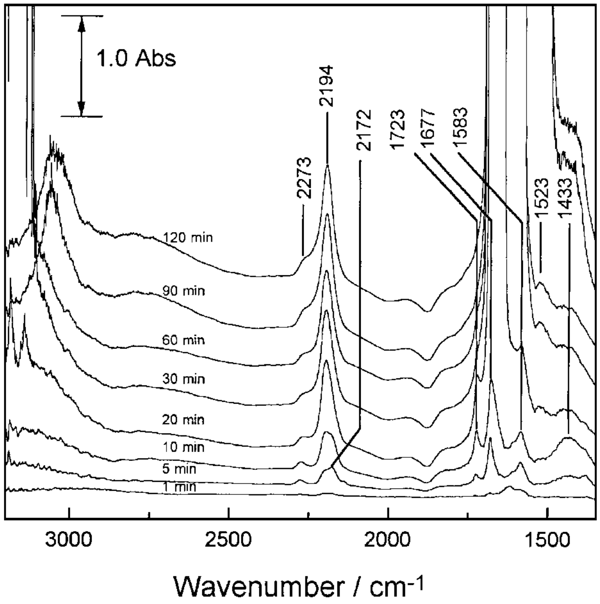


FIG. 2. Infrared spectra of Co-ZSM5 disc (65.1 mg) during reaction of CH_3NO_2/O_2 under the conditions of Fig. 1.

Figure 2 shows infrared spectra of the Co-ZSM5 disc recorded periodically during the experiment. During the initial 10 min one group of three bands appear at 2273, 2194, and 2172 cm^{-1}, respectively. The band at 2194 cm^{-1} grows substantially between 10 min (absorbance, $A \approx 0.4$) and 20 min ($A \approx 0.9$) and slowly thereafter to a maximum value ($A \approx 1.2$) after 120 min. A second group of bands are also evident at 1723, 1677, 1583, and 1443 cm^{-1} during the first 10 min. Between 10 and 20 min there is an astonishing growth in intensity of the second one to above the maximum measurable absorbance ($A \approx 3.2$) over the entire range 1690 cm^{-1} to 1630 cm^{-1}. The absorption here continues to grow in width, with longer periods obscuring the bands at 1723 and 1583 cm^{-1}, while reducing that at 1433 cm^{-1} to a shoulder. The spectra recorded after 20 min also show bands above 2950 cm^{-1}, but the signal to noise in this region is rather poor.

The bands between 2140 and 2300 cm^{-1} are most likely to arise from $N{=}C{=}O$ or $C{\equiv}N$ groups. In their investigation of the reduction of NO by CH_4 over Co-ZSM5, Lobree *et al.* (9) observed bands at 2260 cm^{-1} and 2156 cm^{-1} which were attributed to Al^{3+}-NCO and Co-CN species, respectively. With copper-containing catalysts, including Cu-ZSM5, the adsorption of HNCO gives isocyanate bands with frequencies which depend on the oxidation state—2230 to 2240 cm^{-1} for Cu°-NCO, 2200 to 2210 cm^{-1} for Cu^{+}-NCO, and 2180 to 2185 cm^{-1} for Cu^{2+}-NCO (19). With H-ZSM5 the adsorption of HNCO gives a band at 2260 cm^{-1} for Si^{4+}-NCO. Yamaguchi (17) examined the decomposition of nitromethane adsorbed on alumina and attributed a band at 2253–2261 cm^{-1} to a covalently bound NCO species and one at 2230–2236 cm^{-1} to anionic NCO^-. In separate experiments in this work the decomposition of nitromethane on SiO_2 at 553 K gave rise to band at 2290 cm^{-1}, but on Co_3O_4 the peak frequency was at 2188 cm^{-1}. Based on these observations, the band at 2273 cm^{-1} in Fig. 1 can be assigned to NCO bound to Al^{3+} or Si^{4+} sites and that at 2194 cm^{-1} to NCO bound to Co^{2+}. In further tests it was found that, although nitromethane was readily decomposed on H-ZSM5 as expected (16), and the bands between 1800 and 1400 cm^{-1} developed in a similar way to that with Co-ZSM5, no isocyanate species were observed. This is probably due to their ready further hydrolysis as seen with alumina and Cu-ZSM5 (16, 20). Thus, the sites responsible for the NCO band at 2273 cm^{-1} on Co-ZSM5 are likely to be weakly acidic. Finally, the weak band at 2172 cm^{-1} seen in the initial stages of nitromethane decomposition on Co-ZSM5 may be due to NCO bound to a second type of cobalt site. However, assignment to a cyanide species cannot be ruled out, especially as gaseous HCN is observable as a product in packed bed experiments (16).

Behaviour of Co-ZSM5 diluted with silica. Similar experiments to the above were carried out with Co-ZSM5 diluted with SiO_2 in order to locate the exact position of the exceptionally strong band produced between 1700 and 1600 cm^{-1} by the deposited species. Figure 3 shows the catalytic behaviour of a 26 wt% Co-ZSM5 in SiO_2 disc in comparison with that of a disc of SiO_2 alone. The mixed disc has initial yields of 800 ppm for CO_2 and 100 ppm for N_2 which must be produced primarily on the Co-ZSM5 since the corresponding yields with SiO_2 alone are 120 and <50 ppm, respectively. The diluted disc starts to deactivate from time zero since, unlike pure Co-ZSM5 in Fig. 1, it does not have sufficient reserve capacity to maintain near total conversions when blocking by deactivating species commences.

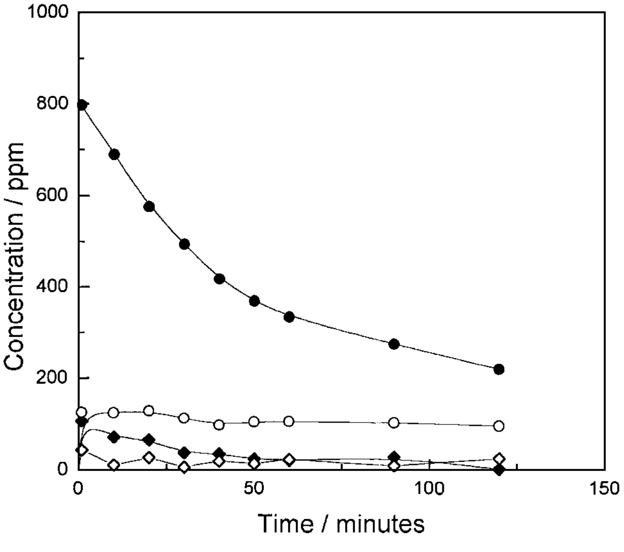


FIG. 3. Product distributions versus time during the reaction of 1100 ppm CH_3NO_2/2.9% O_2 over a 26 wt% Co-ZSM5/SiO_2 disc (72.3 mg, closed symbols) and over a SiO_2 disc (35.8 mg, open symbols) at 553 K: ●, CO_2 concentration (Co-ZSM5/SiO_2); ◆, N_2 concentration (Co-ZSM5/SiO_2); ○, CO_2 concentration (SiO_2); ◇, N_2 concentration (SiO_2).

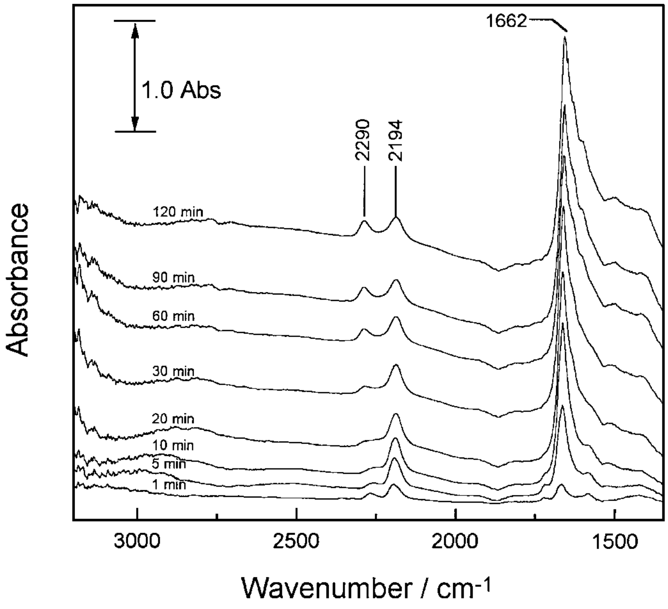


FIG. 4. Infrared spectra of a 26 wt% Co-ZSM5/SiO_2 disc (72.3 mg) during reaction of CH_3NO_2/O_2 under conditions of Fig. 3.

FTIR spectra of the diluted disc during the course of deactivation are shown in Fig. 4. The same bands are developed as with pure Co-ZSM5 in Fig. 2 but the very strong one below 1700 cm^{-1} never overflows. Its peak frequency is 1662 cm^{-1} with overlapping shoulders on the low wavenumber side. The bands at 2273, 2194, 2172, 1723, and 1583 cm^{-1} are also much reduced in intensity, compared to Fig. 2, as expected if the species responsible for them are confined to Co-ZSM5. On the other hand, the band at 2290 cm^{-1}, which grows steadily, is due to NCO on the SiO_2 diluent since it was also observed when nitromethane was reacted over the SiO_2 disc under the same conditions.

Reactivity of deactivating species. Figure 5 shows FTIR spectra of the species formed on a Co-ZSM5/SiO_2 disc after exposure to CH_3NO_2/O_2 for 120 min at 553 K, followed by exposure to He, H_2O, D_2O, H_2O again and, finally, NO_2. Purging with He causes some reduction in the intensity of the Si-NCO band at 2290 cm^{-1}, but that of the deposited species at 1662 cm^{-1} is only slightly affected. Treatment in 2400 ppm of H_2O for 30 min reduces the intensity of the latter by about one-third and both isocyanate bands are smaller again. The isocyanate bands are almost eliminated after 60 min in 8000 ppm of D_2O. This also shifts the major band of the deposited species from 1662 to 1602 cm^{-1} and

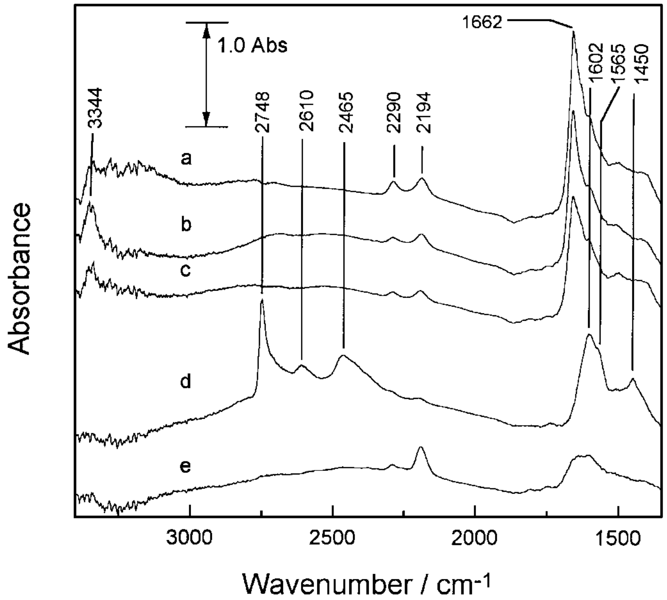
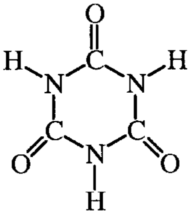


FIG. 5. Infrared spectra of a 26 wt% Co-ZSM5/SiO_2 disc at 553 K after successive exposures to flowing (a) 1100 ppm CH_3NO_2/2.9% O_2 for 120 min; (b) He alone for 30 min; (c) 2400 ppm H_2O for 30 min; (d) 8000 ppm D_2O for 60 min; (e) 8000 ppm H_2O for 30 min and then 1000 ppm NO_2 for 10 min.

a band at 1450 cm^{-1} appears more clearly. Separate experiments with discs of SiO_2 and Co-ZSM5 exposed to D_2O indicate that the band at 2748 cm^{-1}, and its low wavenumber tail, are attributable to OD groups on these materials. The other bands at 2610 cm^{-1} and 2465 cm^{-1} are likely to be due to OD or ND groups produced by deuteration of adsorbed species. The corresponding hydrogen-containing species prior to exchange would be expected at $\approx$3550 cm^{-1} and $\approx$3350 cm^{-1}, respectively. The signal to noise of the spectrometer was too poor for measurements above 3500 cm^{-1} but spectrum 5(b) in particular does show a distinct band at $\approx$3350 cm^{-1} as expected.

While the species responsible for the 1662 cm^{-1} band could not be removed by exposure to D_2O, or by further treatment with 8000 ppm H_2O at 553 K, they were readily removed by exposure to 1000 ppm NO_2 with an extensive fall in band intensity over just 10 min (Fig. 5e). There was some regrowth in the intensity of the two isocyanate bands at 2192 and 2290 cm^{-1} during the removal process.

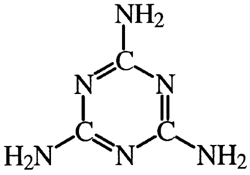
In the packed bed experiments (16) nitromethane reacted over Co-ZSM5 at a much lower temperature in NO_2/O_2 than in O_2 or NO/O_2, and it also exhibited less deactivation. With the different configuration in the FTIR cell some deactivation and deposit formation was evident when using $CH_3NO_2/NO_2/O_2$ over Co-ZSM5 diluted with SiO_2, but the rate of deactivation was slower than in the absence of NO_2.



SCHEME 1

Identification of deactivating species. It seems highly likely that the species giving rise to the 1662 cm^{-1} band is responsible for the deactivation of Co-ZSM5 for nitromethane decomposition since it grows in concert with decreases in the yield of CO_2. In our previous packed-bed experiments (16) gaseous HNCO became the major nitrogen-containing product during the later stages of deactivation and it was suggested that deposition of HNCO as its cyclic trimer, cyanuric acid (Scheme 1) might be responsible for deactivation. That seemed reasonable since deactivation was confined to temperatures below 573 K, above which thermodynamic data (21) is consistent with both vapourisation of solid cyanuric acid and its depolymerisation back to HNCO. However, this now seems untenable as a total explanation since the strongest bands of cyanuric acid, measured here as a KBr disc, were at 1715, 1463, and 1391 cm^{-1}, in agreement with the literature (22). The band seen at 1723 cm^{-1} in Fig. 2 during the initial stages of reaction may be due to cyanuric acid but its intensity declines as the main 1662 cm^{-1} band grows. The same is true for reaction on Co-ZSM5 diluted with SiO_2 in Fig. 4. This suggests that cyanuric acid reacts further and/or its production ceases as another process takes over. In the previous packed bed experiments NH_3 was seen in concentrations up to 400 ppm while CO_2 production was stable but only after a breakthrough time of some tens of minutes (16). This was attributed to ammonia adsorption but equally well it could be due to consumption of NH_3 by reaction with cyanuric acid. The most likely final products from such a reaction are melamine (Scheme 2) and derivatives of it.

The spectrum of melamine has three strong bands of similar intensity at 1648, 1545, and 1427 cm^{-1} (23, 24). Recent force constant calculations (24) indicate that the band near 1650 cm^{-1} is due to ring distortion modes and that near 1550 cm^{-1} is due to NH_2 deformation ones, rather than the reverse, as originally proposed (23). With deuterated melamine the 1650 cm^{-1} shifts to a somewhat lower wavenumber resulting in a series of strong



SCHEME 2

overlapping bands between 1585 and 1531 cm^{-1} with the next strongest one at 1448 cm^{-1} (23). These correspond reasonably well to those observed following exposure of the material deposited from nitromethane to D_2O in Fig. 5. The ND_2 stretching bands of melamine also occur in the range 2600 cm^{-1} to 2450 cm^{-1} (23), where the deposited material absorbs.

Even so, the spectral match to that of melamine alone is not perfect and there are several reasons why this might be so. Melamine is close in size to 1,3,5 trimethylbenzene which is the largest diameter single ring aromatic synthesised by the methanol-to-gasoline process over H-ZSM5 (25) and exhibits very restricted diffusion in the catalyst (26). Thus if melamine was synthesised from HNCO, perhaps via cyanuric acid, within channels, then it will be severely constrained in ways which are likely to affect NH modes in particular. Also, the reference spectra are all for solid material with considerable intermolecular interactions in a three-dimensional structure. Within channels the molecules will be isolated, or with at most one-dimensional interactions between them, and this difference is also likely to affect spectral details. Finally, at high temperature melamine may polymerise further to melam (a linear dimer) and melem (a fused ring trimer) and other less defined structures (27), most of which are likely to be too large to be accommodated within channels. Thus a variety of structures with similar ring arrangements, and hence, ring distortion modes, may be combining to produce the tailing 1662 cm^{-1} band which is so prominent during the decomposition of nitromethane.

Melamine is made commercially from HNCO by a reaction carried out in the presence of ammonia (28) and cyanuric acid can also be converted to it by reaction with ammonia (29). Melamine and its polymers are extremely stable substances, even more so than cyanuric acid, with decomposition points well above 600 K. The temperatures required for decomposition/hydrolysis of the bulk compounds on alumina are $\approx$573 K for cyanuric acid, $\approx$683 K for melamine, and $\approx$698 K for melem (30). The material deposited from nitromethane shows some slow hydrolysis at 553 K (Fig. 5) which is not surprising if the species are present as isolated molecules within channels. Removal of deposited melamine by reaction with NO_2 (Fig. 5e) should not be surprising, either, given that NO_2 will oxidise soot at that temperature (31).

In summary, *in situ* Fourier transform infrared spectroscopy shows that the deactivation of Co-ZSM5 for the decomposition of nitromethane is accompanied by the formation of bands due to NCO species between 2150 and 2300 cm^{-1} and the sudden development of a very strong band at 1662 cm^{-1}. The latter band can be assigned to the s-triazine compound, melamine and/or derivatives of it, which causes deactivation by filling the zeolite channels or blocking entrances. The most likely chemistry is an initial dehydration of nitromethane to isocyanic acid (HNCO) which forms melamine by reaction with ammonia derived by hydrolysis of HNCO. Cyanuric acid, the cyclic trimer of HNCO, may be an intermediate in the process.

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