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Propane ammoxidation over gallium-modified MFI zeolites

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Abstract

This is the first report indicating that the presence of Brønsted sites, acting in synergy with redox sites in Ga-modified MFI zeolites, can catalyse the ammoxidation of propane. Two catalysts with gallium loadings of 2 and 0.3 wt.% were prepared by ion-exchange of MFI zeolites with Si/Al ratios equal to 33 and 150, respectively. The integrity of the zeolites was essentially preserved following ion-exchange, as demonstrated by surface area, porosity, and crystallinity measurements. In situ ^{13}C and ^{15}N MAS NMR studies, using propane-2-^{13}C and $^{15}NH_3$ as labelled reactants suggest that Ga-modified H-MFI catalysts promote the formation of C–N bonds when propane is reacted in the presence of ammonia and oxygen (C_3H_8:NH_3:O_2 molar ratio $=$ 1:3:2, $T = 673$ K). Conventional microcatalytic reactor results confirm the conclusions of the in situ MAS NMR investigations. Propane is converted to mainly propene and acrylonitrile, with minimal production of CO_x (CO and CO_2), in the temperature range 723–773 K. Increasing the temperature to 773 K worsens the selectivity to acrylonitrile, whereas increasing the molar ratio NH_3:C_3H_8 from 2 to 4 increases the selectivity to acrylonitrile and decreases conversion. Both the conversion and the selectivity to acrylonitrile increase when the molar ratio O_2:C_3H_8 is increased from 0.3 (sub-stoichiometric) to 2 (stoichiometric). A new reaction pathways is proposed in which a cyclic protonated pseudo-cyclopropane (PPCP) transition state is responsible for the low temperature activation of propane. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Propane; Ammoxidation; Ga-modified zeolites; Mechanism; Activation; In situ MAS NMR; Active sites

1. Introduction

Acrylonitrile is an important monomer for homo- and hetero-polymerisation, and a reagent for the synthesis of adiponitrile. The global production of acrylonitrile is over 5 million tons yearly and increases at a rate of about 3% per year. Acrylonitrile is currently commercially produced by the ammoxidation of propene in the presence of Bi–molybdate or Fe–molybdate based catalysts. Recent research trends, however, have been directed towards developing a new process starting from propane [1–3] due to its large availability and low cost relative to propene.

Many catalysts have been evaluated for the ammoxidation of propane to acrylonitrile. The most effective systems fall into two main classes: the antimonates and the molybdates. Among the antimonates, the systems which have received the greatest attention belong to the family $VSb_xM_yO_z$ with M representing most often elements such as W, Te, Nb, Sn, Bi, Al, and Ti [4–6]. Virtually all of these antimonates possess the rutile or trirutile structure. The highest propane conversion (68.8%) and largest acrylonitrile yield (39%) were observed for a catalyst whose composition is $VSb_5W_{0.5}Te_{0.5}Sn_{0.5}O_x$–$SiO_2/Al_2O_3$ [4,5,7]. The molybdate family is represented by $VMo_xM_yO_z$, where M is often Bi or Te [8,9]. Some catalysts have the scheelite structure [10], others are

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multiphase and more complex structures. Among the molybdates, the highest acylonitrile yields are claimed for a catalyst composition having the empirical formula $V_{0.3}Te_{0.23}Nb_{0.12}MoO_x$, supported on SiO_2, i.e., maximum yield of 55.1% in acrylonitrile at 86.7% propane conversion [11].

The search for new propane ammoxidation catalysts has, so far, been rather empirical. The catalysts described in the patent literature contain elements having paraffin activating properties (e.g., V) and olefin activating properties (e.g., Bi, Te), as well as O and/or NH-inserting properties (e.g., Sb, Mo). A major issue, in all cases, is to minimize the formation of CO and CO_2 (CO_x). It is thus desirable to identify new catalytic systems which are capable of activating paraffins as well as ammonia at low temperature, in order to reach higher useful product selectivities.

It has been demonstrated recently that the activation of propane on Ga-modified H-MFI zeolite catalysts occurs via a bifunctional reaction step mechanism leading to a protonated pseudo-cyclopropane transition state (PPCP) which can evolve further in four different ways leading to the formation of $C_3H_9^+$, $C_3H_7^+$, $C_2H_5^+$, and CH_3^+, as demonstrated by the scrambling of the ^{13}C label in propane, its dehydrogenation to propene, and its cracking or disproportionation to form C_1, C_2, and C_4 products [12–15]. It was further demonstrated that the carbenium ions formed on these catalysts can react with various nucleophilic molecules, e.g., CO, H_2O [16,17] and benzene [18]. The latter results support the mechanism proposed for the formation of the PPCP transition state and its subsequent evolution.

The reaction of CO and H_2O with olefins (Koch reaction) is known to proceed easily at ambient temperature over acidic zeolites [17]. The first step of this reaction is the protonation of the olefin on a Brønsted site leading to a carbenium ion. The latter reacts with CO and H_2O to yield the corresponding carboxylic acid. When the reaction is carried at low partial pressure of propane, isobutyric acid was formed through propenium or propylene intermediate species [16,17].

The formation of transient carbenium species at low propane partial pressure was also confirmed previously when reacting propane with benzene on these catalysts [17,18]. The observation of cumene and *n*-propylbenzene as primary reaction products evidenced the role of propenium ions. The formation of butanes was inhibited in the presence of benzene, due to the trapping of the highly reactive propene carbenium ions by benzene and the subsequent formation of alkylbenzenes.

The initial purpose of the present work was to demonstrate that a nucleophilic molecule such as NH_3 could also react with transient carbenium ions species formed from propane via the PPCP transition state, to form a C–N bond. Although amines could not be produced (in the absence of oxygen), it was later found that C–N bonds can indeed be formed when oxygen was added. We show in this contribution that Ga-modified H-MFI catalysts are new systems for the ammoxidation of propane and propose a novel route and mechanism explaining the formation of C–N bonds, e.g., acrylonitrile, and the low observed yield in CO_x.

2. Experimental

2.1. Preparation of H-MFI and Ga-modified H-MFI catalysts

MFI zeolites with $Si/Al = 150$ and $Si/Al = 27$ were obtained from Zeolyst and The PQ Corporation, respectively. The zeolites were calcined in N_2 up to 673 K and then in air at 773 K for 2 h to remove any organic residues (from the templates used for their synthesis) possibly present. The (Na,H)-MFI form were thus obtained. Fully protonated H-MFI catalysts were obtained by NH_4^+ ion-exchange and calcination [13]. Ion-exchange was carried out by suspending and stirring the (Na,H)-MFI zeolites in a buffer solution of NH_4Cl–NH_3 at pH 9.2 at 298 K for 2 h. The solids were then filtered and the process was repeated for a further two times. Finally, the solids were washed with copious amount of water and dried overnight in an air oven at 393 K. The resulting products, NH_4^+-MFI, were then calcined in nitrogen up to 423 K, maintained for 2 h at 423 K, and then heated further to 723 K. They were then switched to air and heated further to 773 K for an additional 3 h to obtain the H-MFI zeolites.

Ga-modified H-MFI zeolites were obtained as follows. A known quantity of gallium nitrate (Aldrich Chemical; 99.99% purity) solution (0.05 M) was stirred with a known quantity of zeolite and maintained at pH 2. The mixture was refluxed for 4 h at 373 K and filtered. The solid was washed and dried overnight in an oven at 393 K. The materials were then calcined at 423 K for 2 h, heated further to 723 K under flowing N_2, at which point the atmosphere was changed to air and heating continued up to 823 K, finally yielding the Ga/H-MFI catalyst.

2.2. Catalysts characterisations

Transmission (VG STEM) and scanning (SEM, Phillip CEM200) electron microscopies showed the presence of some gallium as Ga_2O_3 on the surface of the zeolite crystals. Energy dispersive X-ray analysis (EDX, Phillip) was used to determine their Ga content and Si/Al ratio. Nitrogen adsorption isotherms to evaluate their surface area and porosity were determined by the volumetric method using a Micromeritics model ASAP 2000 adsorption apparatus, using about 100 mg of catalyst. The crystallinity of the initial H-MFI zeolites and of their Ga-modified products were carried out using a powder X-ray diffractometer (Siemens D5005).

The catalysts used in the present work are designated Ga2Z33 and Ga0.3Z150, where the number following Ga is the Ga loading (wt.%) and the figure following Z is the Si/Al ratio of the zeolite after Ga-exchange.

2.3. In situ ^{13}C and ^{15}N MAS NMR

Propane-2-^{13}C (99%, ^{13}C), ammonia-^{15}N (98%, ^{15}N) and oxygen (99.6%) were obtained from Cambridge Isotope Laboratories, Aldrich and BOC, respectively. Powdered catalyst samples (ca. 50 mg) were packed into home-made NMR cells fitting exactly into the double-bearing Bruker 7 mm zirconia rotors. The catalysts were evacuated at a pressure of 10^{-6} Torr overnight at ambient temperature, heated to 673 K at a rate of $2\,K\,min^{-1}$, then calcined for 2 h, and finally cooled to 298 K before adsorption of the reactants which were dosed volumetrically. After introduction of the reactants, the NMR cells were immersed in liquid N_2 to ensure their quantitative adsorption. The NMR cells were then carefully sealed. Typical loadings were two molecules of propane-2-^{13}C, six of $^{15}NH_3$, and four of oxygen per unit cell of MFI zeolite.

In situ ^{13}C and ^{15}N MAS NMR spectra were recorded on a Bruker Avance DSX400 spectrometer at 100.6 and 40.6 MHz, respectively, at a spinning rate of ca. 2 kHz, with 90° pulses of 4 μs and 4 s recycle delays for ^{13}C and 60° pulses (4 μs) and 4–60 s recycle delays for ^{15}N. Quantitative conditions were achieved by using high-power gated proton decoupling with suppressed NOE effect. Some non-^{1}H-decoupled spectra were recorded to identify reaction products and intermediates. ^{13}C chemical shifts are given in ppm as referred to external tetramethylsilane (TMS). ^{15}N chemical shifts are given in ppm as referred to a saturated $^{15}NH_4NO_3$ aqueous solution by using glycine-^{15}N at 11.5 ppm as a secondary standard.

In a typical NMR experiment, the sealed NMR cell was rapidly heated to a selected temperature at which it was maintained for a given time. The NMR spectrum was recorded at 293 K after rapid quenching of the sample cell in liquid nitrogen. After collection of the NMR spectra, the cell was returned to pre-determined reaction conditions and heated for progressively longer periods of time.

2.4. Catalytic microreactor (MCR) studies

The catalytic microcatalytic reactor studies were conducted in a conventional plug-downflow fixed bed reactor (10 cm^3, 0.8 cm i.d., mass of catalysts = ca. 1 g) under steady-state operating conditions. The reaction products were analysed using on-line gas chromatographic (GC) analysis, the transfer line between the reactor and the gas chromatograph being maintained at 473 K to prevent condensation of the products. The gas chromatograph was equipped with three different columns: a CP-Wax 52B to separate functionalised hydrocarbons (oxygenates, nitrogen-containing compounds, aromatics) detected using a flame ionization detector; a Porapak-D column to separate non-polar hydrocarbons, NH_3, H_2O and CO_2, and a molecular sieve column to separate the permanent gases and CO. In the latter two cases, the products were detected using a thermal conductivity detector. HCN formation was evidenced by its adsorption in a solution of NaOH solution and subsequent titration [19].

Molar feed compositions, i.e., C_3H_8:NH_3:O_2 were in the range 1:2:0.3 to 1:4:2 with a total flow rate of $0.96\,l\,h^{-1}$, estimated at STP conditions. Conversion

Table 1
Characterization of the Ga2Z33 and Ga0.3Z150 Ga/H-MFI catalysts and their parent zeolites

Catalyst	Ga_2O_3 (wt.%)	Si/Al ratio	BET surface area ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	V_{meso} ($cm^3\,g^{-1}$)	Crystallinity (XRD)
Z27	–	27.0	396.1	119.0	128.8	(1 0 0)
Z150	–	150.0	416.3	125.2	135.7	(1 0 0)
Ga2Z33[a]	2.12	32.6	383.3	115.7	131.3	ca. 90
Ga0.3Z150	0.28	150	385.3	100.6	102.9	ca. 85

[a] Some framework aluminium is extracted during the gallium ion-exchange at acidic pH.

(%), selectivities (%C), and yields in products were determined on the basis of moles of propane converted. Different reaction conditions were used to evaluate the effect of temperature, feed composition, and zeolite acidity on the performance of the catalysts.

3. Results and discussion

3.1. Catalyst characterization

Both the Ga2Z33 and Ga0.3Z150 catalysts, as well as their parent zeolites, were characterized. The results are reported in Table 1.

The introduction of gallium at pH 2, necessary to avoid the precipitation of Ga hydroxide, was found to alter slightly the integrity and crystallinity of the zeolite as demonstrated by some reduction in surface area, meso- and microporosiy, and crystallinity. The decrease in crystallinity is estimated to be about 10–15%. This is not surprising as it is known that Al from the zeolite framework can be extracted in acidic conditions [12] which is confirmed by the analysis of the chemical analysis of the higher Al content MFI zeolite material before ($Si/Al = 27$) and after ($Si/Al = 32.6$) Ga ion-exchange.

TEM and SEM microscopies showed the presence of some Ga_2O_3 at the surface of the zeolite crystals. EDX confirmed the Ga content of the catalysts. Less gallium is present in the catalyst based on H-MFI with a Si/Al ratio equal to 150, as expected from the ion-exchange method which was used to introduce gallium.

3.2. In situ MAS NMR investigations

The reaction of ^{13}C-labelled propane (labelled in the 1 or 2 position) over Ga/H-ZSM-5 was studied previously by in situ MAS NMR. It was found propane activation occurs via the PPCP transition state, resulting in the scrambling of the ^{13}C label and a 1:2 ratio of C_3H_8-2-^{13}C:C_3H_8-1-^{13}C in the products. Other alkanes (C_1–C_4) also result from the evolution and reaction of the PPCP transition state [12,13], because of cracking and disproportionation.

At 673 K and low NH_3/C_3H_8 and O_2/C_3H_8 ratios, we observed mainly cracking products, i.e., a product distribution analogous to that occurring when propane is the only reactant [12,13]. This is not surprising.

When the NH_3/C_3H_8 ratio was high (e.g., 5), also at 673 K, no noticeable reaction was observed. We attribute this to the neutralisation of the zeolite Brønsted sites by NH_3. It is indeed known that desorption of NH_3 from H-MFI is only completed at about 723 K under flow conditions. Partial or complete neutralisation of the zeolite Brønsted acidity by NH_3 should thus be expected in sealed NMR cells when the temperature is below 723 K and when the amount of NH_3 exceeds the number of Brønsted sites. In the same respect, one should also be aware that reactions are conducted in batch conditions, with long contact times, in the in situ NMR cell, thus in a situation differing greatly from that used for the microreactor tests.

An intermediate reactant ratio of C_3H_8-2-^{13}C: $^{15}NH_3$: $O_2 = 2:6:4$ per unit cell of H-MFI (catalyst Ga2Z33) was therefore used in the subsequent mechanistic NMR investigations. Figs. 1 and 2 show the spectra observed at $T = 673$ K, for increasing reaction times, in the 118–129 and 177–188 ppm regions (^{13}C, Fig. 1) and the 260–310 ppm region (^{15}C, Fig. 2).

Changes occur in the 10–20 ppm region of the ^{13}C NMR spectra which are characteristic of the scrambling of the ^{13}C label in propane. They also indicate that the adsorption of propane on the zeolite may be in competition with the adsorption of products.

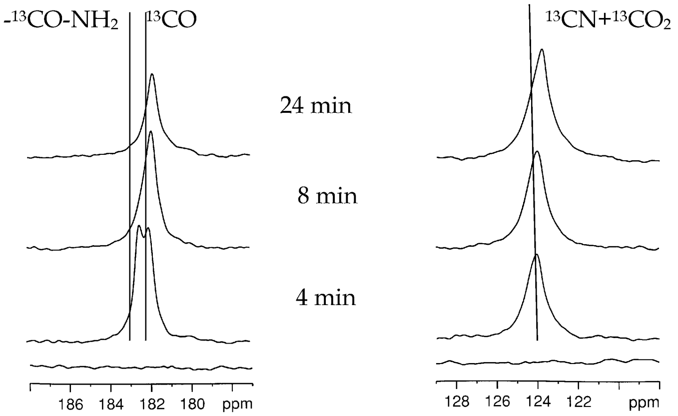


Fig. 1. In situ ^{13}C MAS NMR spectra observed when reacting a C_3H_8:NH_3:O_2 mixture with molar ratio 1:3:2 over Ga2Z33 at 673 K. Propane-2-^{13}C and $^{15}NH_3$ were used as reactants.

This observation is currently receiving additional attention. However, no cracking of propane, i.e., the formation of ethane or methane, and its disproportionation indicated by the formation of butanes, are observed.

The ^{13}C MAS NMR spectra observed after 4 min show one peak at ca. 124 ppm and two peaks at ca. 182 and 183 ppm (Fig. 1). After further heating at 673 K for a total 8 and 24 min, the resonance originally at 124 ppm shifts to 123 ppm, whereas only one peak remains at ca. 182 ppm. The ^{13}C peak at ca. 124 ppm may be assigned to –C═C–, –CN groups and/or CO_2 species, and the peaks at ca. 182 ppm to CO and/or –C═O groups in compounds such as CH_3CONH_2 (178 ppm), CH_2═$CHCONH_2$ (177 ppm) [20]. Chemical shifts are altered upon adsorption of a compound on catalyst surface. As the carbon nuclei of CO, CO_2 and the compounds with chemical shift at ca. 124 and 182 ppm do not have a directly bonded proton, no discrimination is possible in the absence of ^{1}H decoupling.

As CO and CO_2 are likely to be the dominant products at long reaction times, it is believed that the peaks observed at 123 and 182 ppm, after 24 min, may possibly correspond to CO_2 and CO, respectively. The presence of a second peak at 183 ppm may thus indicate that another species was formed besides CO when the catalyst was heated for 4 min at 673 K, i.e., one involving an amino group, –$CONH_2$. The peaks in the 124 ppm region are unlikely to correspond to –C=C– groups as their resonances are usually broad when unsaturated compounds are adsorbed and thus difficult to detect. We thus propose that the peak at ca. 124 ppm corresponds to –CN groups. The decrease of the peak at 183 ppm in Fig. 1 could then indicate that the R–$CONH_2$ compounds formed after heating at 673 K for 4 min are converted to R–CN products with loss of CO which can be oxidized to CO_2. If R is a CH_2=CH– group which is not detected due to line broadening, these observations suggest that acrylonitrile may be formed from CH_2═CH–$CONH_2$ as intermediate. This proposal is consistent with the mechanism proposed by Centi and Perathoner over V–Sb oxide catalysts [21].

Fig. 2 shows the ^{15}N MAS NMR spectra obtained for the same system and conditions. Initially ($t = 0$ min), a NH_3 peak is observed at ca. -8 ppm (not shown). A new peak appears at ca. 284 ppm after heating of the catalyst at 673 K. Its intensity increases with longer reaction times. Although the chemical shift of the peak at 284 ppm is close to that of N_2, it can also correspond to compounds with –CN functionalities, in particular if these compounds interact strongly with the catalyst, in which case chemical shifts may be strongly altered. In addition, it should be also recognized that nitrogen does not interact strongly with the zeolite. Thus, a 20 ppm shift of its resonance is unlikely. We thus propose that the resonance at 284 ppm is characteristic of –CN groups.

As a final remark, it should be considered that the reaction in the NMR cells is conducted at long contact times and that deep oxidation of propane and NH_3 to

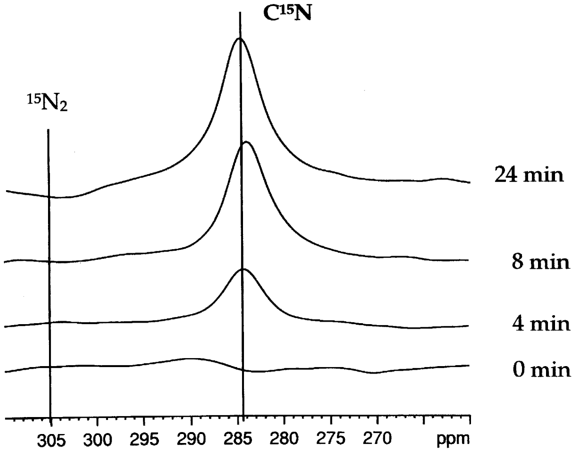


Fig. 2. In situ ^{15}N MAS NMR spectra observed when reacting a C_3H_8:NH_3:O_2 mixture with molar ratio 1:3:2 over Ga2Z33 at 673 K. Propane-2-^{13}C and $^{15}NH_3$ were used as reactants.

yield CO, CO_2 and N_2 may thus occur. However, the amount of O_2 available is not high enough to attribute the peaks at 182 and 124 ppm in the ^{13}C NMR spectra and 284 ppm in the ^{15}N NMR spectra to only CO, CO_2 and N_2, respectively. Other products must be formed.

The in situ ^{13}C and ^{15}N MAS NMR results strongly suggest, therefore, that the cracking of propane and the formation of higher hydrocarbons over Ga/H-MFI catalysts is inhibited in the presence of ammonia and that the formation of –CN bonds, such as those of acrylamide and acrylonitrile, may be formed when oxygen is also present. The microreactor tests described in the next section support this conclusion and demonstrate that molecular level mechanistic studies may indeed provide new leads for the discovery of novel catalytic transformations.

3.3. Microcatalytic reactor results

Propane ammoxidation using Ga/H-MFI catalysts was investigated in various conditions using a plug-downflow fixed bed reactor, the product composition being determined by on-line GC analysis. In all cases the formation of acrylonitrile was observed.

Fig. 3 shows the effect of temperature for the Ga2Z33 catalyst (WHSV of 0.3 h^{-1} and C_3H_8:NH_3:O_2 molar ratio = 1:4:0.3). Increasing the temperature from 723 to 773 K increases conversion from 18 to 27%. This observation is not surprising as higher temperature facilitates the activation of C–H bonds (e.g., dehydrogenation). However, the selectivity to acrylonitrile (S(ACN)) decreases from 37 to 15%C and the selectivities to propene and CO_x increases marginally. Increasing temperature thus promotes not

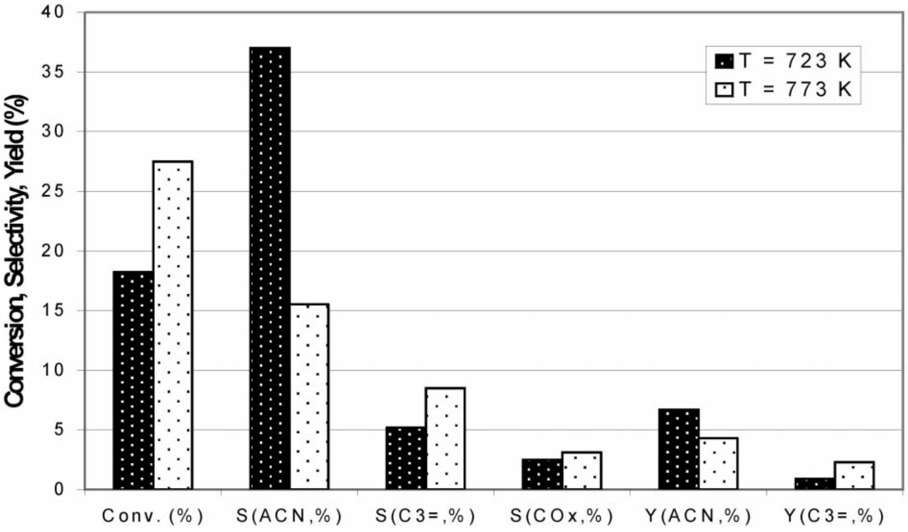


Fig. 3. Effect of temperature on conversion and selectivities to acrylonitrile and other products. Catalyst: Ga2Z33, WHSV = 0.33 h^{-1}, C_3H_8: NH_3: O_2 = 1:4:0.3.

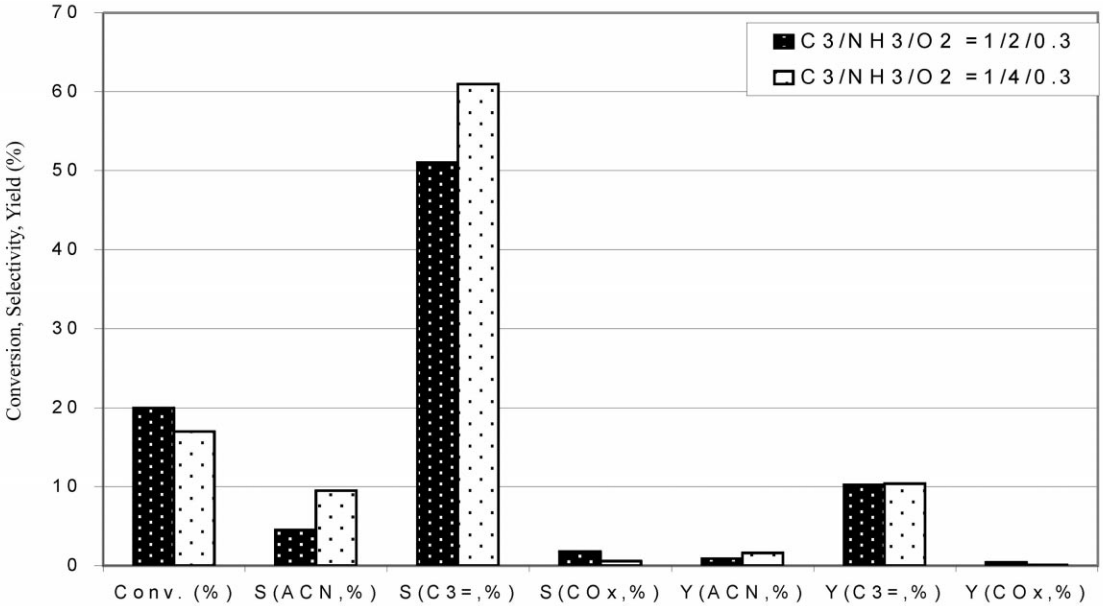


Fig. 4. Effect of ammonia concentration on conversion and selectivities to acrylonitrile and other products. Catalyst: Ga0.3Z150, WHSV $= 0.33\,\mathrm{h}^{-1}$, $T = 773\,\mathrm{K}$.

only the activation and dehydrogenation of propane, but also the formation of CO_x and that of heavier hydrocarbons and other products. The formation of the heavier hydrocarbons (acid-catalysed reactions) and other products is responsible for the decreased selectivity to acrylonitrile.

It was reported previously [22] that feed composition plays a significant role in directing the activity and products selectivities in the ammoxidation of propane. The effect of NH_3 and O_2 were thus also evaluated.

Fig. 4 shows the effect of NH_3 on the performance of the Ga0.3Z150 catalyst (WHSV $= 0.33\,\mathrm{h}^{-1}$, $T = 773\,\mathrm{K}$). Feed molar compositions are C_3H_8: NH_3: O_2 = 1:2:0.3 and 1:4:0.3, i.e., in the presence of sub-stoichiometric amounts of oxygen. Conversion decreases slightly when the ammonia concentration is increased. It can be explained by the inhibition effect of NH_3 towards C_3H_8 activation, as both NH_3 and C_3H_8 compete for the same active sites (Lewis sites associated to Ga species and Brønsted sites from the zeolite) for their initial activation. The selectivity to acrylonitrile is doubled. The latter observation is not surprising as a higher concentration of NH_3 will certainly favour the formation of –CN bonds by either the classical mechanism or via nucleophilic attack of NH_3 on the PPCP transition state or one of its evolutionary products. A marginal increase is observed in the selectivity to propene which can be as high as 50–60%. It may indicate that the critical step in its transformation to an allyl-type intermediate and the evolution of the latter by N– or O– insertion to form an alcoholate or an imine intermediate is limited by the restricted availability of oxygen.

To rationalise further on the effect of oxygen, further tests were conducted at 773 K with C_3H_8:NH_3:O_2 molar ratios equal to 1:4:0.3 and 1:4:2 using both Ga2Z33 and Ga0.3Z150 catalysts. The results are shown in Fig. 5. Higher concentration in oxygen increases conversion and selectivity to acrylonitrile, while decreasing substantially the selectivity to propene and to a smaller extent that to CO_x. The effect of oxygen appears to be more important for the catalyst containing a smaller amount of acidic sites. A smaller CO_x selectivity is not unexpected if less propene is formed as CO_x formation is known to result, in part from the oxidation of propene [23]. The higher selectivity to acrylonitrile proves further the importance of oxygen which can react with intermediates formed by direct

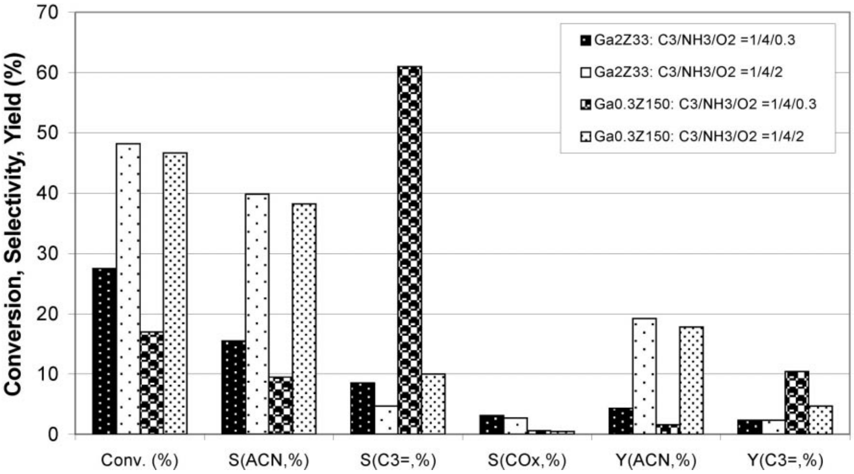


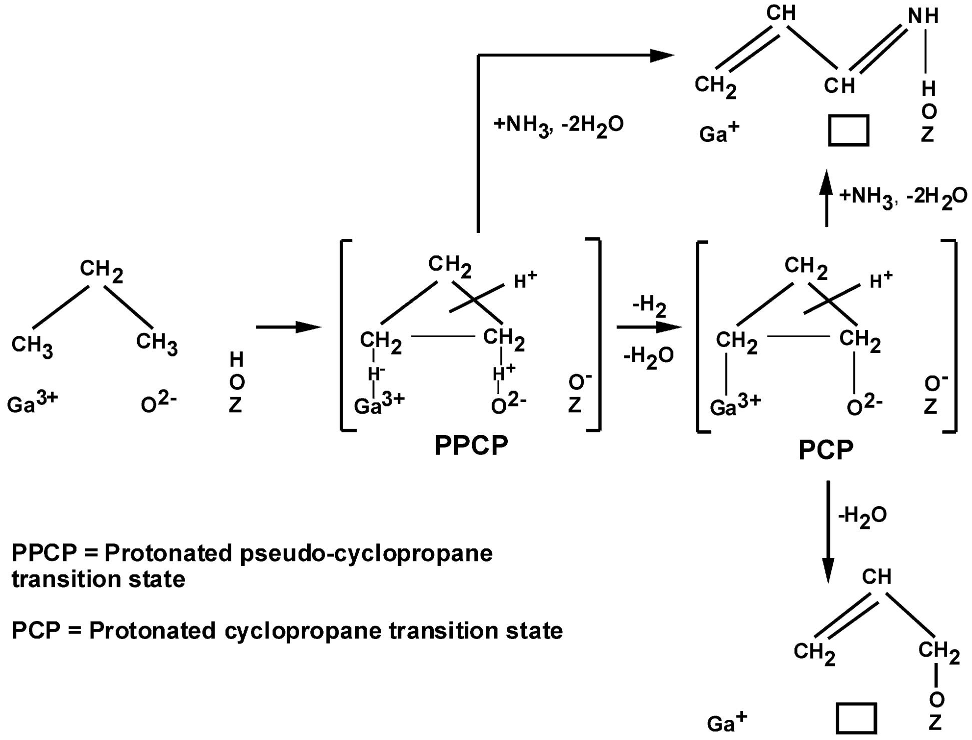
Fig. 5. Effect of oxygen concentration and Si/Al ratio on conversion and selectivities to acrylonitrile and other products. WHSV $= 0.33\,h^{-1}$, $T = 773\,K$.

addition of NH_3 to the PPCP transition state or species evolving from it, and/or its role in the formation and reaction of surface allyl or alcoholate species as postulated in the classical mechanism [2,24]. Conversion does not decrease proportionally to the Al content of the zeolite-based catalyst. It indicates that propane activation by this type of catalysts is not the rate determining step. O and N insertions are thus the crucial steps for the formation of acrylonitrile from propane on the type of catalysts used in this study. The effect of O_2 and NH_3 concentrations were discussed above. The need for an optimal concentration in Brønsted acid sites was demonstrated by the MAS NMR experiments, as discussed before. Lower selectivities to propene with the more acidic Ga2Z33 catalyst may also result from a higher contribution of acid-catalysed secondary reaction, such as oligomerisation, aromatisation, and ammoxidation of these higher olefins and aromatic products. This possibility is currently being investigated although it does not affect our above proposals and conclusions.

All the above results prove that Brønsted acid sites play a role in synergy with Ga species, in the transformation of propane in the presence of ammonia and oxygen, and that the formation of acrylonitrile may also take place via a reaction pathway involving Brønsted acid sites, which is at variance with classical observations.

We therefore propose an alternate route, as depicted in Figs. 6 and 7. Fig. 6 shows the bifunctional (redox and Brønsted sites) activation of propane leading to the PPCP transition state which can either react with NH_3 to form an imine species (with loss of water) or convert to a protonated cyclopropane transition state (PCP, with loss of H_2 or H_2O). The latter can be converted to an alcoholate species by insertion of oxygen and loss of water, or to an imine species by reaction NH_3 and loss of water. Our data may rather be explained by concerted mechanism of oxygen insertion possibly with the formation of intermediate alcoholate species. Usually such mechanism responsible for Cox formation. However, this kind of mechanism has been observed for ethane ammoxidation into acetonitrile [3].

Fig. 7 shows the overall reaction scheme which includes the conventional route and the novel route we propose. The PPCP and PCP transition states can evolve directly to the C_3-imine and acrylonitrile by addition of ammonia and oxygen. CO_x production is reduced because less propene is present as an intermediate. The dispersion of redox sites (Ga in the present case) in a zeolite framework may be responsible for the higher yields in selectively oxidized products due to the reduced electron delocalization in the small and isolated redox sites, as proposed for other alkane oxidation processes [25]. This scheme also shows that



PPCP = Protonated pseudo-cyclopropane transition state

PCP = Protonated cyclopropane transition state

Fig. 6. Proposed scheme for the initial activation of propane in the presence of ammonia and oxygen on Ga-modified H-MFI catalysts.

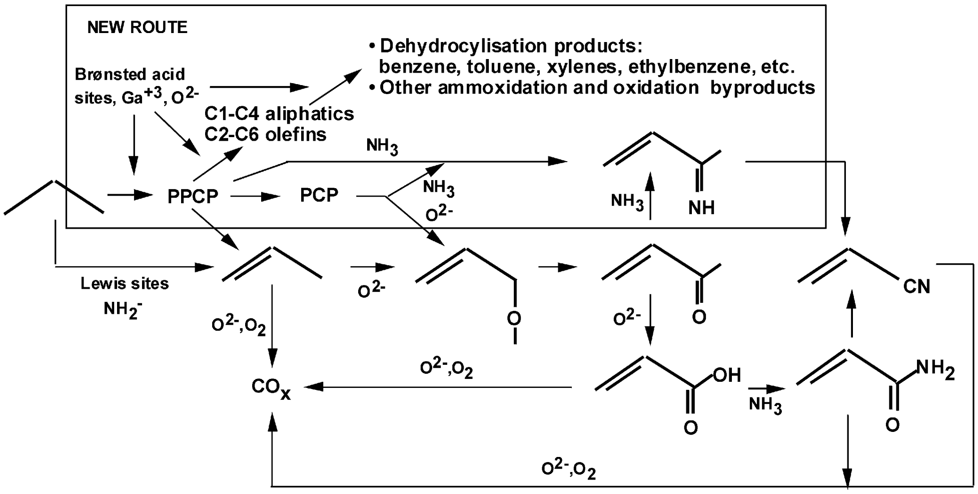


Fig. 7. Overall mechanistic scheme for the ammoxidation of propane over Ga-modified H-MFI catalysts.

increased zeolite acidity may lead to the formation of higher hydrocarbon products and their derivatives, in particular when the C_3H_8/NH_3 and/or C_3H_8/O_2 ratios are high.

4. Conclusions

This is the first report showing that Brønsted sites acting in synergy with redox sites can catalyse the ammoxidation of propane. Ga/H-MFI catalysts are effective for the ammoxidation of propane. Conversions of about 50% have been observed with a selectivity to acrylonitrile of about 45% and a yield in CO_x smaller than 1%. Such a performance compares well with that of conventional multicomponents mixed oxides catalysts.

A new pathway and a possible mechanism leading to the formation of acrylonitrile are proposed. The proposed transition states resulting from the activation of propane via a bifunctional reaction step are a protonated pseudo-cyclopropane (PPCP) and a protonated cyclopropane (PCP) species.

Our results further confirm that the activation of propane and other light alkanes via a PPCP-like transition state is a new route for their upgrading and functionalisation to higher value products when reactions occur below 723 K.

Part of our future work with this type of catalyst system comprises the optimisation of the catalyst and operating conditions for the ammoxidation of propane as well as the exploration of their application to the synthesis of acrylic acid.

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