AMMOXIDATION OF PROPYLENE ON ZnNaY ZEOLITE

By

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Ammoxidation of propylene on ZnNaY zeolite has been investigated by means of adsorption, pulse, and flow reactors as well as IR spectroscopy. Instead of acrylonitrile acetonitrile has been obtained with high selectivity but low yield. Acetaldehyde and acetic acid react with ammonia to give acetonitrile but oxidation of acetaldehyde is very slow and non-selective. This indicates that acetaldehyde is the most probable intermediate which reacts with ammonia to acetonitrile. On interaction of ammonia with acetaldehyde the absorption band of acetonitrile appears in IR spectrum on both ZnNaY and NaY zeolites, although the latter is completely inactive in ammoxidation of propylene. Thus Zn-ions perform the role of active centres for initial step of the reactions. Presence of ammonia inhibits the non-selective oxidation of acetaldehyde which otherwise is totally oxidized.

Introduction

Exploratory studies of the activity of ZnNaY zeolite in ammoxidation of propylene have shown [1] that instead of acrylonitrile usually found on oxide catalysts [2, 3] acetonitrile is formed with high selectivity. It seemed thus of interest to study the mechanism of insertion of oxygen resulting in the elimination of one carbon atom, as well as the role of zinc ions as the active centers.

Experimental part

The samples of zeolite ZnNaY were prepared from sodium faujasite characterized by the formula: $0.98\ Na_2O \cdot Al_2O_3.\ 5.21\ SiO_2 \cdot xH_2O$. The exchange of sodium ions for zinc ions were carried out three times from 0.02 m $ZnCl_2$ solution at 100 °C using acetate buffer (pH = 5) for stabilization of pH. ZnNaY zeolite has been obtained with chemical analysis: 3.34% Na_2O, 8.56% ZnO, 14.46% Al_2O_3, 51.34% SiO_2, and ignition losses 20.92%; percent of exchange about 66.1%.

Adsorption isotherm of CO were determined in semiautomatic constant pressure apparatus at different temperatures [4]. Before measurement the samples of the zeolite were heated and outgassed *in vacuo* 10^{-5} torr for 15 hr at 350 °C. Carbon monoxide was obtained by dehydration of formic acid with concentrated sulphuric acid at 100 °C.
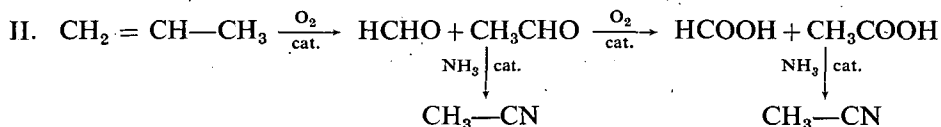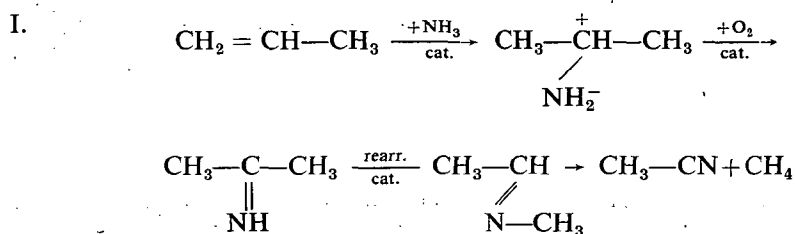
Before every catalytic test in the pulse reactor, the sample of zeolite (0.5 ml) was activated at 400 °C by flow of nitrogen for 4 hr. The chromatographic analysis has been carried out by use of chromatograph Giede 18.03. Conditions of analysis were: column with Carbowax 2 m length, column with succinate 1 m length; detector FID.

Catalytic tests by flow reactor were carried out at 350—480 °C, using feed gases of volume composition: $C_3H_6:NH_3:air=1:1:8$. Propylene used was from Fluka. Ammonia and air were technical grade, dried before using.

IR absorption spectra of adsorbed species on ZnNaY and NaY zeolites were registrated by means of spectrophotometer UR—20 (Zeiss). Samples with density about 10 mg/cm^2 were formed by pressing and placed in vacuum cell equipped with NaCl windows and connected to vacuum system. The sample could be heated in situ to 450 °C. Before each run activation has been carried out at 360 °C for 3 hr in vacuo 10^{-5} torr.

Results and discussion

Two different mechanisms may be proposed a priori for the heterogeneous catalytic ammoxidation of propylene resulting in the formation of acetonitrile. They may be represented by following schemes:

I.

$$CH_2 = CH-CH_3 \xrightarrow[\text{cat.}]{+NH_3} CH_3-\overset{+}{\underset{\diagup}{CH}}-CH_3 \xrightarrow[\text{cat.}]{+O_2}$$
$$NH_2^-$$

$$CH_3-\underset{\underset{NH}{\parallel}}{C}-CH_3 \xrightarrow[\text{cat.}]{rearr.} CH_3-\underset{\underset{N-CH_3}{\diagup\diagup}}{CH} \rightarrow CH_3-CN+CH_4$$

II. $CH_2 = CH-CH_3 \xrightarrow[\text{cat.}]{O_2} HCHO + CH_3CHO \xrightarrow[\text{cat.}]{O_2} HCOOH + CH_3COOH$

$$\quad\quad\quad\quad\quad\quad\quad NH_3 \Big| \text{cat.} \quad\quad\quad\quad\quad\quad NH_3 \Big| \text{cat.}$$

$$\quad\quad\quad\quad\quad\quad\quad CH_3-CN \quad\quad\quad\quad\quad\quad CH_3-CN$$

Pulse experiments revealed that isopropylamine is not oxidized to acetonitrile on ZnNaY zeolite. The presence of isopropylamine at the surface of that zeolite after contacting it with the mixture of propylene and ammonia also could not be detected, in the IR spectra. Mechanism I could be thus discarded and experiments were carried out to show that Mechanism II is operating and to demonstrate the role of Zn-ions.

Measurements of the adsorption of CO on samples of different degree of exchange showed that the amount of CO adsorbed specifically increases with increasing degree of Zn-exchange. (Fig. 1).

However, the isosteric heat of adsorption ($Q_{isost.}$) as calculated from the Clausius—Clapeyron equation remains practically constant indicating that one type of active centres are involved in specific adsorption of CO independently of the degree of exchange of Zn-ions (Table I).

Table I

Results of CO adsorption on ZnNaY zeolite (at 0 °C)

Ion exchange %	$Q_{isost.}$ kcal/mol	N_{Zn}	N_{CO}
44	16.2	11.7	2.0
65	17.7	17.3	3.0
81	18.4	21.6	3.6

N_{Zn} — number Zn^{+2} ions in an elementary cell
N_{CO} — number CO molecules adsorbed in an elementary cell

It should be mentioned that the exchange could not be extended beyond about 80% even by using dehydration, which indicates that the exchange equilibrium was already reached. It may be thus concluded that zinc ions locate themselves firstly in about half of the S_I positions (every second hexagonal prism) and then occupy statistically all other positions.
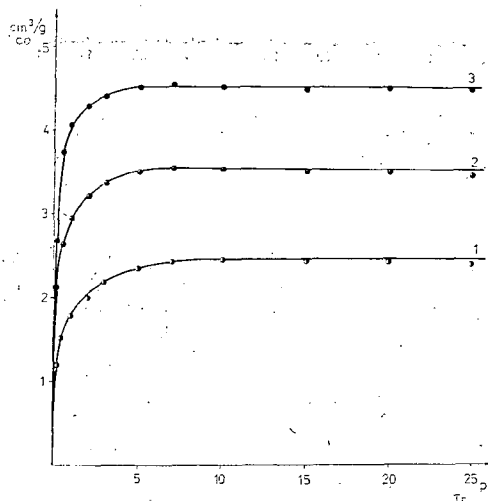

Fig. 1. Specific adsorption of CO on ZnNaY zeolite at 0 °C for ion exchange: 1—44%, 2—65%, 3—81%

Pulse tests, carried out to prove the primary intermediates of propylene oxidation on ZnNaY zeolite at 400 °C, led to following conclusions:
— reactions of acetaldehyde as well as acetic acid with ammonia to acetonitrile proceed with high yield and high selectivity,
— oxidation of acetaldehyde to acetic acid on ZnNaY zeolite proceeds with difficulty and a variety of different products is obtained.
It may be thus concluded that acetaldehyde is the main intermediate in the ammoxidation of propylene, its reaction with ammonia to form acetonitrile being much faster than its oxidation to acetic acid or other products.

An introductory IR investigation of simultaneous chemisorption of $C_3H_6 +$ $+ O_2 + NH_3$ mixture on ZnNaY zeolite at 350 °C confirmed the results of catalytic tests showing the appearance of a well developed absorption stretch band of CN group in nitrile (2240—2268 cm^{-1}); however the spectrum is difficult to interpret in the range 1300—1800 cm^{-1} (Fig. 2).

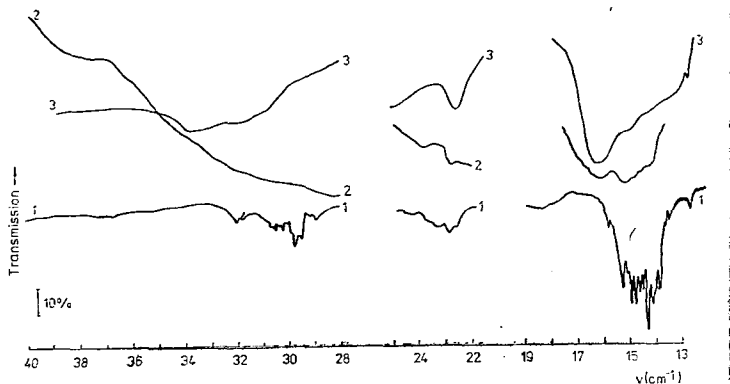Fig. 2. IR spectra of ammoxidation of propylene: 1 — gaseous CH$_3$CN
2 — CH$_3$CN chemisorbed on ZnNaY zeolite at 320 °C,
3 — C$_3$H$_6$ + O$_2$ + NH$_3$ chemisorbed on ZnNaY zeolite at 350 °C

For comparison the spectra of acetonitrile chemisorbed on ZnNaY zeolite at 320 °C, as well as that of gaseous acetonitrile are also shown in this figure.

The mechanism of propylene ammoxidation on ZnNaY and NaY zeolites were then followed in more detail by IR spectroscopy. In the first experiment the mixture of $C_3H_6 + O_2$ (1:1, 26 torr, at 400 °C, contact time 120 s) was chemisorbed on ZnNaY zeolite, then the sample was cooled to 45 °C and outgassed to $3 \cdot 10^{-1}$ torr (Fig. 3). Only H_2O (the stretch band of OH group) and a trace of COO$^-$ were detectable as oxidation products. Then ammonia was introduced into IR cell (3 torr at 45 °C) which was then outgassed to $3 \cdot 10^{-1}$ torr and the sample was heated to 400 °C. From 350 °C the stretch band of nitrile group (about 2280 cm^{-1}) appeared in IR spectrum. The fact that no primary oxidation products could be seen may be connected with very small yield of propylene oxidation which is limiting step in propylene ammoxidation. In spite of a lack of clear appearance of primary propylene oxidation products, their concentration is sufficient for nitrile formation.

In the next experiments the reaction of acetaldehyde with ammonia was investigated. Acetaldehyde was introduced into IR cell and chemisorbed on ZnNaY zeolite and then ammonia to obtain a mixture at room temperature (14 torr, CH$_3$CHO: :NH$_3$=2:5) (Fig. 4). Then the zeolite sample was heated to 300 and 400 °C. At 300 °C the nitrile group's stretch band appeared, which persisted after outgassing to 10^{-1} torr the ZnNaY zeolite. The same experiment was carried out using NaY zeolite. The nitrile group's stretch band was also observed but its intensity was much smaller than in the case of ZnNaY zeolite.

An investigation using IR method was also carried out for the sequence: chemisorption of CH_3COOH, addition of NH_3 and heating to 400 °C zeolites ZnNaY and NaY. In both cases the absorption bands characteristic for ammonium acetate appeared, and then from 150 °C those of acetamide after dehydration of acetate. In both cases the stretch band of nitrile group appeared from about 200 °C.
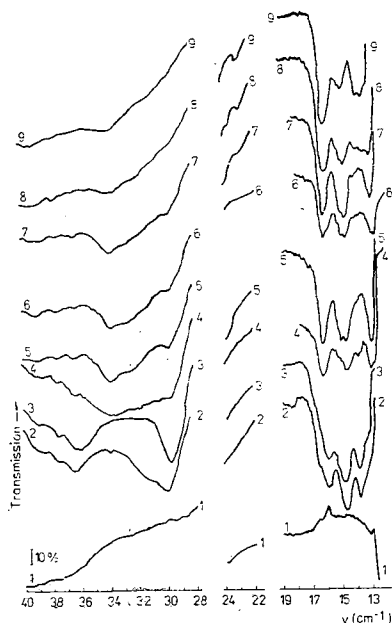
Fig. 3. IR spectra chemisorbed species on ZnNaY zeolite for the sequence: $C_3H_6+O_2 \rightarrow NH_3 \rightarrow$ heating. 1 — the background of ZnNaY zeolite, 2 — after chemisorption of $C_3H_6+O_2$ (1:1, at 400 °C, 26 torr, contact time 120 s), 3 — after outgassing to $3 \cdot 10^{-1}$ torr, 4 — after NH_3 dosage and outgassing to $3 \cdot 10^{-1}$ torr at 45 °C, 5 — heating at 250 °C, 6 — 300 °C, 7 — at 350 °C, 8 — at 425 °C, 9 — at 425 °C after outgassing to $1 \cdot 10^{-5}$ torr
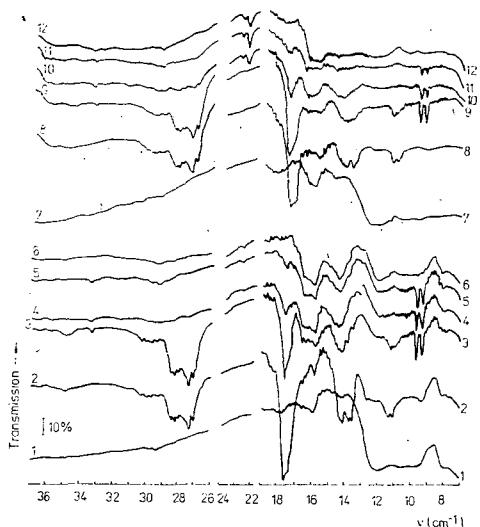
Fig. 4. IR spectra for the sequence: $CH_3CHO \rightarrow$ $\rightarrow NH_3 \rightarrow$ heating on NaY and ZnNaY zeolites: a) 1 — the background of NaY zeolite, 2 — after chemisorption of CH_3CHO (10 torr, 45 °C), 3 — after NH_3 dosage a mixture: $CH_3CHO:NH_3=$ $=2.5:5$, 15 torr, 45 °C), 4 — heating to 300 °C, 5 — heating to 400 °C, 6 — spectrum after outgassing NaY zeolite sample to $3 \cdot 10^{-1}$ torr; b) 7 — the background of ZnNaY zeolite, 8 — after chemisorption of CH_3CHO (10 torr, 45 °C), 9 — after NH_3 dosage (a mixture: $CH_3CHO:NH_3=2:5$, 14 torr, 45 °C), 10 — heating to 300 °C, 11 — heating to 400 °C, 12 — spectrum after outgassing ZnNaY zeolite sample to $3 \cdot 10^{-1}$ torr

Following conclusions may be formulated on the basis of results obtained:
— the oxidative ammonolysis of propylene on ZnNaY zeolite is very selective, but the conversion is low (2.18% at 450 °C); pure NaY is completely inactive which indicates that Zn-ions perform the role of active centers,
— acetaldehyde and acetic acid easily react with ammonia to give acetonitrile, but oxidation of acetaldehyde to acid on ZnNaY is very slow and non-selective; no isopropylamine could be detected in IR spectra; this indicates that acetaldehyde is the most probable intermedate,

— on interaction of ammonia with adsorbed acetaldehyde IR absorption band of acetonitrile appear on both ZnNaY and NaY zeolites, which indicates that Zn-ions play the role in the initial step of the reaction,

— it may be concluded that the ammoxidation of propylene on ZnNaY zeolite, proceeds through a consecutive series of steps, the first being the oxidation of propylene to acetaldehyde with the participation of Zn-ions. Acetaldehyde reacts then with ammonia to form acetonitrile. It is noteworthy that the presence of ammonia inhibits the non-selective oxidation of acetaldehyde which otherwise is totally oxidized.

References

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