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THERMAL DECOMPOSITION OF TPA-ZSM-5 ZEOLITES: EFFECT OF GAS ATMOSPHERE AND Si/Al RATIO

V.R. CHOUDHARY and S.G. PATASKAR

Chemical Engineering Division, National Chemical Laboratory, Pune 411 008 (India)

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ABSTRACT

The thermal analysis of TPA-ZSM-5 (Si/Al = 13.6–39.7) and TPA-silicalite in the presence of inert and oxidizing gas atmospheres has been carried out in the temperature range 303–1273 K. The decomposition of TPA cations in the presence of air is a complex exothermic process. It occurs in two steps, one between 663 and 773 K and the other between 773 and 973 K. However, the decomposition in inert (nitrogen) atmosphere is endothermic and occurs in a single step and also at lower temperatures (< 773 K). The decomposition is strongly influenced by the Si/Al ratio.

The TPA cations associated with the acid sites are more stable than those associated with the non-acid sites of the zeolite. The activation energy of the decomposition increases with the increase in the Al content of the zeolite.

INTRODUCTION

ZSM-5 zeolites are generally synthesized first in their TPA (tetrapropyl amine) form which are then transformed to the desired cation-exchanged form(s) after removing the organic part (TPA cations) from the precursor crystals of the zeolites by thermal decomposition at ~ 813 K [1]. Thus, the thermal decomposition of TPA-ZSM-5 and TPA-silicalite to remove the bulkier TPA cations occluded in the zeolite structure is an important step in the preparation of ZSM-5-type zeolites which can be used as adsorbents or, when converted to the desired cation-exchanged forms, as catalysts. It is, therefore, very interesting to investigate the removal of the organic part of TPA-ZSM-5 zeolites under different conditions. Recently, Parker et al. [2] studied the gaseous product(s) formed during decomposition of ZSM-5 and silicalite precursors in an inert atmosphere using thermogravimetric analysis combined with mass spectroscopy.

The present work was undertaken with the objectives of studying the thermal decomposition of TPA-ZSM-5 with different Si/Al ratios and TPA-silicalite under inert and oxidizing atmospheres.

TABLE 1

Composition of TPA-ZSM-5 zeolites

Si/Al ratio	Mole ratio			
	Al_2O_3	SiO_2	Na_2O	$(TPA)^+$
13.6	1.00	27.2	0.63	1.00
17.2	1.00	34.4	0.42	1.22
22.0	1.00	44.0	0.52	1.65
31.1	1.00	62.2	0.56	2.35
39.7	1.00	79.4	0.65	2.84

EXPERIMENTAL

TPA-ZSM-5 and TPA-silicalite zeolites

The TPA-ZSM-5 (Si/Al = 13.6–39.7) zeolites were synthesized by a method described elsewhere [1].

The chemical composition of these zeolites is given in Table 1.

TPA-silicalite was synthesized by a method similar to that used for the preparation of TPA-ZSM-5, except that the crystallization was carried out in the absence of aluminium and sodium. The chemical analysis of TPA-silicalite showed that it contained SiO_2 (87.2 wt%), TPA-OH (12.5 wt%) and traces of Na.

The TPA-zeolites were characterized [3,4] for their crystalline nature by X-ray diffraction and for the morphology and crystal size by scanning electron microscopy.

Thermal analysis

The TPA-zeolites dried at 373 K in an air oven for 12 h were used for the thermogravimetric analysis. The thermogravimetric (TG), differential thermogravimetric (DTG) and differential thermal analysis (DTA) data on the zeolites were obtained under inert (N_2) and oxidizing (air) atmospheres using an automatic thermal analyser (Netzsch Model STA 409). The experimental conditions were as follows: sample size, 25 mg; reference compound, α-alumina; sample holder, platinum crucible; temperature range, 303–1273 K; heating rate, 10 K min^{-1}; atmospheres: static air, flowing air (80 cm^3 min^{-1}), and nitrogen (80 cm^3 min^{-1}).

The cylinder gases (nitrogen and air) were of high purity ($>$ 99.99%) and passed over activated 4A molecular sieves to remove traces of moisture.

RESULTS AND DISCUSSION

Thermal analysis of TPA-zeolites in inert atmosphere

The thermal curves (TG, DTG and DTA) for TPA-ZSM-5 (Si/Al = 13.6–39.7) and TPA-silicalite in the temperature range 303–1273 K in an inert atmosphere (maintained by passing nitrogen (oxygen free) over the zeolite sample at a flow rate of 80 cm^3 min^{-1}) are presented in Fig. 1.

The removal of TPA cations in the inert atmosphere is due to the thermal cracking of the cations, which is an endothermic process, as shown by the minimum at ~ 735 K in the DTA curves (Fig. 1). The following reactions are expected to occur [2].

Thermal cracking involving Hofmann or sequential Hofmann reactions

$$(C_3H_7)_4N^+(OZ)^- \rightarrow 4C_3H_6 + HOZ + NH_3 \tag{1}$$

and

$$(C_3H_7)_4N^+OH^- \rightarrow 4C_3H_6 + NH_3 + H_2O \tag{2}$$

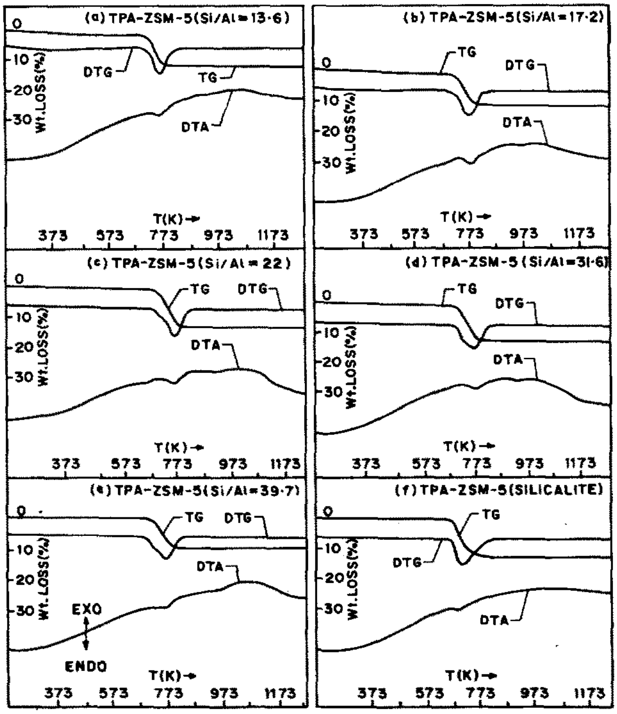

Fig. 1. TG/DTG/DTA curves for the decomposition of TPA-ZSM-5 zeolites (with different Si/Al ratios) in a flow of nitrogen.

Secondary reactions (catalytic conversions)

$$C_3H_6 \xrightarrow{HNa\cdot ZSM\text{-}5} \text{hydrocarbons} \qquad (3)$$

The results on the thermal analysis of the TPA-zeolites are presented in Table 2. The DTA curve for all the TPA-zeolites (except for TPA-silicalite) shows two endothermic peaks (Fig. 1), the first at about 735 K due to thermal cracking of TPA^+/TPA–OH and the second at 950 K due to the dehydroxylation of the zeolites. However, the weight loss due to dehydroxylation is negligibly small. The expected maximum weight loss due to dehydroxylation of HNa-ZSM-5 formed after the removal of TPA cations is about 0.33, 0.40, 0.27, 0.18 and 0.11% for the ZSM-5 zeolite with Si/Al ratios of 13.6, 17.2, 22.0, 31.1 and 39.7, respectively.

It can be noted from the results (Table 2) that the decomposition of TPA-silicalite occurs at a temperature much lower than that required for the decomposition of the TPA-ZSM-5 zeolites. This fact reveals that the presence of structural Al causes an increase in thermal stability of TPA cations in the ZSM-5 zeolite. This increase in thermal stability due to the presence of Al is a result of the strong interaction of TPA cations with negative structural Al atoms. Since the number of TPA cations per unit cell of TPA-ZSM-5 zeolites is much higher than the number of Al atoms available (Al–Na) for such interactions, the TPA cations are expected to be present in two different forms, the first comprising those associated with Al^- (i.e., an acid site) and the second comprising those not associated with Al^-. In

TABLE 2

Data on the thermal analysis of TPA-ZSM-5 zeolites and TPA-silicalite in a flow of nitrogen

Si/Al ratio in TPA-zeolite	Peak temperature (K)		Temp. range of decomposition (K)	Total weight loss (%)	No. of TPA cations per unit cell
	DTA	DTG			
13.6	735 (endo) 950 (endo)	740	683–783	10.0	3.28
17.2	735 (endo) 950 (endo)	740	663–773	10.1	3.25
22.0	730 (endo) 950 (endo)	735	663–773	11.60	3.70
31.1	730 (endo) 950 (endo)	735	663–763	11.20	3.60
39.7	730 (endo) 950 (endo)	735	653–763	9.80	3.20
Silicalite	667 (endo)	687	643–758	12.3	3.95

silicalite, the TPA cations are associated with non-acid sites. On the other hand, in ZSM-5 zeolites the TPA cations are associated with both the acid and non-acid sites. The cations associated with acid sites are more stable and decompose at a higher temperature. This is consistent with earlier observations [2].

The strong influence of the presence of Al on the thermal stability of TPA cations was further confirmed by determining the activation energy for the decomposition of these cations from the thermogravimetric data as follows.

For evaluating the activation energy of first-order solid-decomposition reaction under non-isothermal conditions, Coats and Redfern [5] derived the following expression

$$\log[-\ln(1-\alpha)/T^2] = \log(AR/aE)[1-(2RT/E)] - E/2.3RT \tag{4}$$

where α is the fractional decomposition; T the temperature; A the frequency factor; E the activation energy; R the gas constant; and a the heating rate. The activation energy can be obtained from the slope of a linear plot of $\log[-\ln(1-\alpha)/T^2]$ vs. $1/T$.

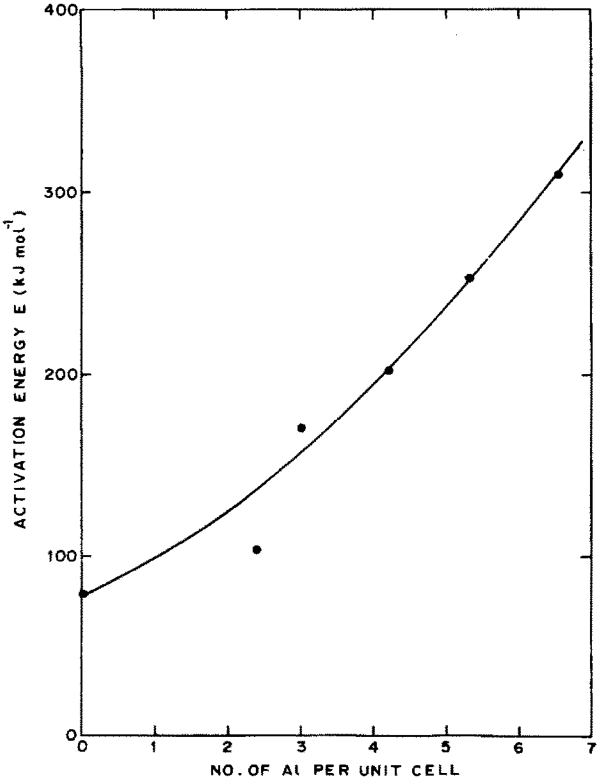

Fig. 2. Variation of the activation energy of decomposition of TPA-ZSM-5 with its Al content.

Figure 2 shows that the activation energy of the decomposition of TPA-ZSM-5 is strongly dependent on the Al content of the zeolite. The number of TPA cations associated with acid sites is increased with the increase in the Al content. Hence, the increase in the activation energy with the increase in the Al content of the zeolite is expected to be mostly due to the strong interaction of TPA cations with the structural Al^- (i.e., acid sites).

It may be noted that the activation energies obtained from the thermogravimetric data are quite apparent as there is a strong possibility of the decomposition being controlled at least partially by the diffusion of gaseous products. It has been found earlier [6,7] that diffusion in ZSM-5 zeolites is strongly influenced by Na content because of the reduction in the effective channel diameter [8]. Further, the undecomposed TPA cations blocking the zeolite channels are expected to increase the diffusional resistance. The decomposition of TPA cations associated with non-acid sites occurs at lower temperatures. However, because of the diffusional resistance caused by the blockage of the zeolite channels by the undecomposed cations associated mostly with acid sites, the gaseous products have to follow a longer path to diffuse out of the zeolite crystal. The TPA cation in TPA-silicalite was shown [9] to be situated with its nitrogen atom at the centre of a channel intersec-

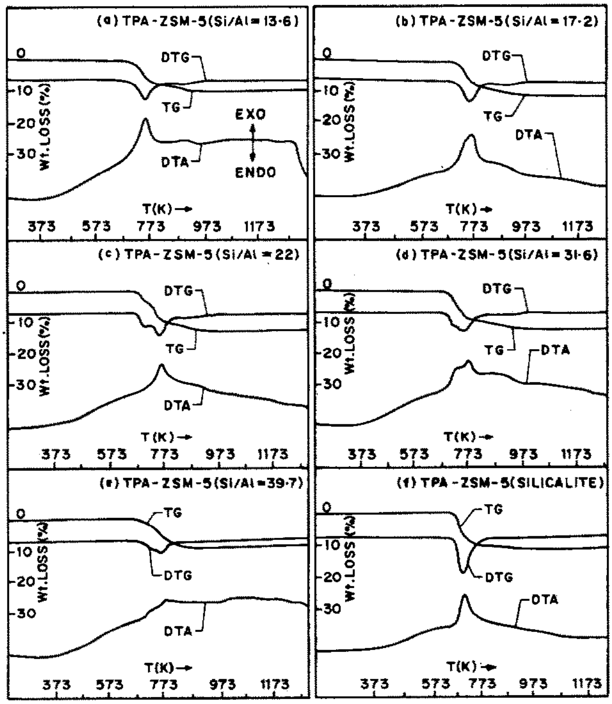

Fig. 3. TG/DTG/DTA curves for the decomposition of TPA-ZSM-5 zeolites (with different Si/Al ratios) in a flow of air.

tion with the propyl groups extending down the four channels. In case of TPA-silicalite (with four TPA cations per unit cell), the total channel length required for accommodation of the TPA cations is estimated to be about 10.8 nm (length of propyl group = 0.675 nm), which is higher than the total length of the channels (8.8 nm [10]) per unit cell. This fact indicates that the TPA cations are very closely packed in the zeolite structure. This also leads to the conclusion that the channels of TPA-ZSM-5 (with 3.6 ± 0.4 TPA cations per unit cell (Table 2)) are almost completely occupied by TPA cations and/or TPA-OH.

Thermal analysis of TPA-zeolites in oxidizing atmosphere

Thermal curves for decomposition of TPA-zeolites in the presence of air flowing over the zeolite sample (air flow rate, 80 $\mathrm{cm^3\ min^{-1}}$) are presented in Fig. 3. There was no significant change in the trends of the thermal curves when the decomposition of the zeolites was carried out in static air. The results of the thermal analysis in the presence of air flowing over the zeolite sample and in the presence of static air are given in Tables 3 and 4, respectively.

The results show that the decomposition of TPA cations in the presence of air is an exothermic process (as indicated by maxima in the DTA curve) and occurs in two steps, the first step from 663 to 773 K and the second step from 773 to 973 K. The endothermic peak in the DTA curve at 950 K is

TABLE 3

Data on the thermal analysis of TPA-ZSM-5 zeolites and TPA-silicalite in a flow of air

Si/Al ratio in TPA-zeolite	Peak temperature (K)		Weight loss (%)			No. of TPA cations removed per unit cell		
	DTA	DTG	Stage I	Stage II	Total	Stage I	Stage II	Total
13.6	750 (exo) 953 (endo)	745	6.1	4.2	10.3	2.0	1.38	3.38
17.2	740 (exo) 750 (exo) 950 (endo)	745	7.5	3.1	10.6	2.41	1.00	3.41
22.0	763 (exo) 950 (endo)	700 760	8.8	2.9	11.7	2.80	0.92	3.72
31.1	740 (exo) 778 (exo) 953 (endo)	735 773	9.3	2.3	11.0	2.98	0.74	3.70
39.7	773 (exo) 950 (endo)	763	7.8	2.1	9.9	2.49	0.71	3.20
Silicalite	695 (exo)	693	12.0	0.4	12.4	3.89	0.11	4.00

TABLE 4

Data on the thermal analysis of TPA-ZSM-5 zeolites and TPA-silicalite in static air

Si/Al ratio in TPA-zeolite	Peak temperature (K)		Weight loss (%)		
	DTA	DTG	Stage I	Stage II	Total
13.6	763 (exo) 947 (endo)	760	7.0	3.2	10.2
17.2	727 (exo) 768 (exo) 874 (exo) 960 (endo)	730	7.7	3.0	10.7
22.0	779 (exo) 960 (endo)	768	8.2	3.4	11.6
31.1	742 (exo) 779 (exo) 957 (endo)	763	9.0	2.1	11.1
39.7	760 (exo)	735	6.5	3.3	9.8
Silicalite	683 (exo) 703 (exo)	678	11.0	1.3	12.3

mostly due to the dehydroxylation of HNa-ZSM-5 zeolites formed after the decomposition of TPA cations.

In the case of TPA-silicalite most of the decomposition ($\geqslant$ 95%) occurs at 773 K. However, for the TPA-ZSM-5 zeolites only 60–80% decomposition of TPA cations occurs in the first step (i.e., up to 773 K) and the decomposition is completed in the second step. The evolution of heat during decomposition (as indicated by the exothermic DTA peaks) shows that the decomposition is oxidative and involves, though not complete, at least partial oxidation of the TPA cations and/or products of thermal decomposition.

A comparison of the results of TPA-ZSM-5 zeolites with those of TPA-silicalite leads to the conclusion that the occurrence of decomposition in two steps is due to the presence of TPA cations in two different forms. The TPA cations associated with non-acid sites are decomposed in the first step while the TPA cations associated with acid sites are decomposed in the second step.

The oxidative decomposition of TPA-ZSM-5 zeolite is expected to occur in the following manner. At the start of decomposition, since all the zeolite channels are blocked with occluded TPA cations, oxygen (kinetic diameter of O_2 = 0.35 nm) from the bulk gas phase cannot enter the channels. Therefore, initially, the decomposition of the TPA cations associated with non-acid sites occurs due to thermal cracking; the gaseous products diffuse from the zeolite crystals and are oxidized, at least partially, in the intercrystalline space. After some of the zeolite channels are cleared of TPA cations, oxygen diffuses into the zeolite structure and there is the possibility of oxidation of TPA cations and/or products of their thermal decomposition within the zeolite channels. Because of diffusional limitations, oxidative decomposition within the zeolite channels is expected to occur mostly in the oxygen-deficient condition leading to the formation of heavy, complex oxygenates which are difficult to remove from the structure because of their very low diffusivity. These oxygenates could be removed by further oxidizing them and/or by converting them to simpler products which can easily diffuse from the zeolite structure. This is probably the reason for the requirement of higher temperatures (as high as 973 K) for the complete removal of TPA cations from the ZSM-5 and silicalite zeolites in the presence of air (Fig. 3). It may be noted that complete removal of TPA cations from the zeolites in inert atmosphere occurs at about 773 K (Fig. 1 and Table 2).

The oxidative decomposition of TPA cations in the zeolites is a very complex process as indicated by the complex TG, DTG and DTA curves (Fig. 3).

CONCLUSIONS

The thermal analysis of TPA-ZSM-5 and TPA-silicalite in presence of nitrogen and air leads to the following conclusions.

The presence of inert or oxidizing atmosphere has no significant effect on the total weight loss of the decomposition. However, decomposition in the presence of air occurs at higher temperatures; complete removal of the cations from the zeolites occurs at about 973 K. While the removal of TPA cations from the zeolites in the presence of inert atmosphere is easier, the complete removal of the cations only occurs at about 773 K. The removal of TPA cations in the presence of air occurs in two steps, one between 663 and 773 K and the other between 773 and 973 K, whereas decomposition of the cations in inert atmosphere occurs in a single step. The decomposition of TPA cations in air is a very complex process.

The decomposition of TPA cations is strongly dependent on the Al content of the zeolite. The activation energy of decomposition increases with increasing Al content.

TPA cations are located at two different sites, viz. acid sites and non-acid sites, in the ZSM-5 zeolite; the maximum number of cations occluded in the TPA form of the ZSM-5 zeolite is four. The TPA cations associated with the acid sites are more stable than those associated with the non-acid sites of the zeolite.

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