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Influence of Decomposition Conditions of TPA–ZSM-5 on Surface and Catalytic Properties of the Resulting H · Na–ZSM-5

INTRODUCTION

The bulkier tetrapropyl ammonium (TPA) cations occluded in the structure of ZSM-5 zeolite in its TPA form are generally removed by the thermal decomposition in air at about 813 K (*1*). The decomposition in air is exothermic and hence expected to cause, under certain conditions, hot spots in the zeolite structure. This may result in excessive dehydroxylation leading to conversion of protonic acid sites, which are responsible for the catalytic activity of the zeolite (*2*), to Lewis-type ones, and may also cause dealumination. Earlier studies (*3*) on thermal analysis of TPA–ZSM-5 showed that the decomposition of TPA cations in the presence of air is a complex exothermic process occurring in two steps—the first between 663 and 773 K and the second between 773 and 973 K. On the contrary, the decomposition in inert atmosphere is endothermic and occurs in a single step and also at lower temperature (<773 K). It is, therefore, very interesting to investigate the effect of decomposition conditions on the surface and catalytic properties of ZSM-5 zeolite obtained from its TPA form.

EXPERIMENTAL

The preparation and characterization of TPA–ZSM-5 (Si/Al = 17.2) have been described elsewhere (*4*). The number of $(TPA)^+$ and Na^+ cations per unit cell of the zeolite were 3.22 and 2.22, respectively.

The TPA–ZSM-5 was decomposed at 813 K under different conditions (viz., heating rate, gas atmosphere, etc.) and the resulting zeolites designated as calcined ZSM-5 (A–F), as follows:

ZSM-5 (A). Obtained by decomposing the TPA–zeolite directly at 813 K (i.e., flash heating at 813 K) for 18 h in static air.

ZSM-5 (B). Obtained by flash heating the TPA–zeolite at 813 K for 18 h in air flowing over the zeolite (flow rate of air: 10 cm^3 min^{-1}).

ZSM-5 (C). Obtained by heating the TPA–zeolite from 303 to 813 K at a heating rate of 10 K min^{-1} in air (10 cm^3 min^{-1}) flowing over the zeolite. The heating was further continued at 813 K for 18 h.

ZSM-5 (D). Obtained by the similar procedure used for getting calcined ZSM-5 (C), except for carrying out the decomposition in static air.

ZSM-5 (E). Obtained by heating TPA–ZSM-5 in the flow of nitrogen (10 cm^3 min^{-1}) from 303 to 813 K at a heating rate of 10 K min^{-1} and heating it in the inert atmosphere for a further period of 1 h at 813 K. The nitrogen flow was then switched over to air flow and heating at 813 continued for a period of 18 h.

ZSM-5 (F). Obtained by the similar procedure used for getting ZSM-5 (E), except for carrying out the decomposition under vacuum (1–3 Torr).

Surface chemical analysis of the ZSM-5 zeolites was carried out using a VG scientific ESCA-3 MK II electron spectrometer.

The number of strong acid centers on the zeolite were measured in terms of the irreversible adsorption of pyridine at 673 K using the gas chromatographic pulse method (*5*) based on TPD under chromatographic conditions.

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The catalytic activity of the zeolites in the cracking of cumene and isomerization of *o*-xylene was determined in a pulse microreactor under the following reaction conditions: amount of catalyst, 0.05 g; reaction temperature, 623 K; carrier gas (N_2) flow rate, 810 $cm^3\ min^{-1}$; pressure, 280 kPa; and pulse size, 8.0 μl. The details of the microreactor and activity measurement were given earlier (*2*).

RESULTS AND DISCUSSION

The XPS data on the zeolites obtained under the different conditions is presented in Table 1. A comparison of the data reveals that the $I_{Al(2p)}/I_{Si(2p)}$ ratio (where $I_{Al(2p)}$ and $I_{Si(2p)}$ are the peak intensities for Al(2*p*) and Si(2*p*), respectively), which is proportional to the Al/Si ratio in the zeolite, depends on the decomposition condition; the intensity ratio is higher for the zeolites obtained by the decomposition in presence of air. This fact clearly indicates that when the decomposition is carried out in presence of air, the surface concentration of aluminum on the zeolite is increased due to dealumination. These results are consistent with those observed by Vedrine *et al.* (*6*) and Nayak and Choudhary (*4*) when H–ZSM-5 was heated at higher temperatures. The dealumination in the present case is a result of the formation of hot spots in the zeolite structure due to the exothermic decomposition of TPA–ZSM-5 in presence of air. Also the presence of water formed in the oxidation of $(TPA)^+$ cations is expected (*7*) to enhance the dealumination. In the earlier studies (*8*), dealumination of H–ZSM-5 has been observed due to hydrothermal treatments. It may be noted that the flash heating in air has caused more dealumination of the zeolite, indicating a strong influence of heating rate.

The irreversible adsorption of pyridine at 673 K was measured for obtaining the number of strong protonic acid sites in the zeolites. Earlier study (*2*) has shown that the irreversible adsorption of pyridine selectivity measures the protonic acid sites on H–ZSM-5 zeolites, as Lewis acid sites formed by the dehydroxylation are not easily accessible to it.

A comparison of the acidity data on the ZSM-5 zeolites (Table 2) reveals that the decomposition conditions strongly influence the number of strong protonic acid centers on H · Na–ZSM-5 zeolite formed in the decomposition of TPA–ZSM-5. The calcined ZSM-5 zeolites with the highest acidity could be obtained by the decomposition of the zeolite in inert atmosphere, while removing the traces of carbonaceous material in the zeolite by oxidizing it in air. The lower acidity of the calcined zeolite obtained by the decomposition of the TPA–

TABLE 1

XPS Data for Calcined ZSM-5 Zeolite Obtained from Decomposition of the TPA–ZSM-5 at Different Conditions

ZSM-5 zeolite	O (1*s*)		Si (2*s*)		Si (2*p*)		Al (2*p*)		$I_{Al(2p)}/I_{Si(2p)}$
	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$	E_b	$\Delta E_{1/2}$	
A	532.4	2.5	154.4	3.0	103.5	2.6	74.4	2.2	0.080
B	532.5	2.6	154.5	3.1	103.3	2.5	74.5	2.3	0.072
C	533.5	2.7	155.3	3.0	103.9	2.6	75.5	2.0	0.065
D	533.8	2.8	155.3	2.9	104.1	2.6	76.3	2.4	0.070
E	532.2	2.6	154.5	2.8	103.5	2.2	75.5	2.8	0.057
F	532.3	2.5	154.3	2.9	103.6	2.5	75.1	2.5	0.060

Note. E_b = electron binding energy (eV) and $\Delta E_{1/2}$ = peak width at half height (eV).

TABLE 2

Acidity and Catalytic Activity of ZSM-5 (A–F) Zeolites Obtained by Decomposition of TPA–ZSM-5 at Different Conditions

ZSM-5 zeolite	No. of strong acid sites per unit cell	Conversion of cumene (%)	Conversion of *o*-xylene (%)
A	0.87	26.5	1.6
B	0.87	26.9	1.7
C	0.99	30.4	2.1
D	0.96	30.1	2.0
E	1.10	37.2	2.4
F	1.06	33.6	2.3

ZSM-5 in the presence of oxidizing atmosphere is expected, apart from the dealumination, as indicated by the XPS results (Table 1) also due to the dehydroxylation of the zeolite during the oxidative decomposition. The dehydroxylation is expected to occur at the hot spots in the zeolite channels.

The data on the catalytic activity of the zeolites in the cumene cracking and *o*-xylene isomerization reactions (which are the model reactions used in the studies of protonic acid sites) at 623 K are included in Table 2. The change in the catalytic activity in both the reactions due to the changes under the decomposition conditions is quite consistent with the corresponding change in the acidity (i.e., strong acid sites measured in terms of irreversible adsorption of pyridine at 673 K) of the zeolite.

The conventional procedures for removing $(TPA)^+$ cations is to heat TPA–ZSM-5 zeolite in presence of air at 813 K (*1*). However, the present work has clearly shown that it is beneficial to carry out the decomposition first in an inert atmosphere and then in air to remove the traces of carbonaceous material deposited in the channels and the external surface of the zeolite crystals. Among the decomposition variables [viz., heating rate, static air or air flowing over the zeolite, and atmosphere (inert oxidizing or vacuum)], the atmosphere and heating rate affected the surface and catalytic properties of the zeolite very significantly. However, these variables showed little effect in the case of H–ZSM-5 formed in the decomposition of NH_4–ZSM-5 (*2*). In the present case, the observed effects are mostly due to the fact that the decomposition in presence of air is an exothermic process, whereas in presence of an inert atmosphere (or under vacuum) it is an endothermic one. The exothermic decomposition leads to the formation of hot spots in the zeolite channels, which cause dealumination and also dehydroxylation of the zeolite, resulting in the decrease in its protonic acid sites and catalytic activity. The results show that the choice of decomposition conditions should be in the following order: initial decomposition in N_2 or under vacuum (N_2 preferred) followed by the air treatment; decomposition in air at lower heating rate (flowing air preferred over static one); decomposition in air under flash heating.

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