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RESEARCH NOTE

^{29}Si MAS NMR Studies of Degalliation of Ga–MFI Zeolite during Template Removal and Deammoniation

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ZSM-5 type H gallosilicates (H−GaMFI) show high aromatization activity and selectivity in the conversion of lower alkanes to aromatics (1–7), which is a process of great commercial importance. The high aromatization activity/selectivity of this zeolite is attributed to its high activity for the dehydrogenation of alkane and naphthene intermediates (3, 6, 8). The active gallium species for the dehydrogenation are not the framework Ga (2, 6) but the extraframework gallium species (2, 3, 5, 6, 9) present in the zeolite as a result of their formation during zeolite synthesis or pretreatment (3, 6, 9). However, the extraframework Ga species are active in cooperation with the framework Ga (i.e., protonic acid site), involving a bifunctional mechanism (5, 6).

In GaMFI zeolite there is an isomorphous substitution of gallium for Si. Since the Ga^{3+} cation (0.62 Å) is larger than the Si^{4+} cation (0.42 Å), the stability of framework Ga in the zeolite is expected to be low. Because of the low stability of framework Ga, the zeolite is degallinated during its pretreatments, drastically affecting its acidity and catalytic activity/selectivity (10–13). It is very difficult to reproduce the preparation of H−GaMFI, probably because of the different extents of degalliation during removal of TPA from TPA−GaMFI and/or during deammoniation of NH_4−GaMFI, depending on the conditions employed for TPA removal and deammoniation. The degalliation of H−GaMFI in its thermal and hydrothermal treatments was thoroughly investigated earlier (12, 13).

To reproduce the zeolite, it is necessary to study its degalliation during TPA removal and also during deammoniation under different conditions, viz., nature of zeolite bed zeolite particles in shallow bed or deep bed, under static air or air flowing over the zeolite, dry or moist air flowing over the catalyst, slow or fast heating for attaining the maximum temperature of the calcination. The present investigation was undertaken for this purpose. Degalliation of the zeolite during TPA removal and deammoniation was followed by measuring the framework Si/Ga ratio by ^{29}Si MAS NMR and the zeolite acidity (which is attributed to the framework Ga) by pyridine chemisorption at 400°C.

The synthesis/preparation and characterization of GaMFI zeolite (with bulk Si/Ga = 33 and crystal size = 5–6 μm) in its TPA (i.e., as synthesized) and NH_4 forms were given earlier (7). Removal of occluded organic template from TPA−GaMFI and deammoniation of NH_4−GaMFI were carried out under various experimental conditions [viz., deep bed or shallow bed calcination under static air at slow or very fast (flash) heating rates, under flowing dry or moist air, etc.], given in Tables 1 and 2. The shallow zeolite bed was made by spreading the zeolite powder as a thin layer (about 1 mm thick). In the deep bed calcination, the zeolite bed was 2 cm long. The calcination under airflow (6000 $cm^3\ g^{-1}\ h^{-1}$) was carried out by passing dry or moist (4.2 mol% water in air) air over the zeolite particles (50–72 mesh size) packed in a quartz reactor. In all the cases, the period of calcination, after attaining the maximum temperature, was 4 h.

^{29}Si MAS NMR spectra of the zeolite samples were recorded at 59.5 MHz using a Bruker MSL 300-MHz spectrometer. The pulse width and a flip angle were 2 μs and 45°, respectively. The samples were spun at 3–3.5 KHz. The zeolite samples were also characterized for their acidity by measuring the chemisorption of pyridine at 400°C using the GC pulse technique, as described earlier (7).

The ^{29}Si MAS NMR spectra of the TPA–gallosilicate and NH_4–GaMFI zeolites calcined or pretreated under different conditions showed two distinct NMR peaks, one at −105 ppm and a second at −112 ppm, corresponding to Si (1Ga) and Si (0Ga) chemical shifts, respectively. A representative ^{29}Si MAS NMR spectrum of the zeolite is given in Fig. 1. The ^{29}Si MAS NMR spectra were deconvoluted using the SIMFIT program for Gaussian peaks at −102, −105, and −112 ppm, thus avoiding the NMR peak (at −102 ppm)

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TABLE 1

Conditions for the Removal of TPA from TPA–GaMFI and Their Influence on the Framework and Nonframework Ga in the Zeolite (Calcination Period = 4.0 h)

Nature of zeolite bed	TPA removal conditions: Heating rate ($^\circ$C min^{-1})	Maximum temperature ($^\circ$C)	Static or flowing air	FW Si/FW Ga ratio	Non-FW Ga/FW Ga ratio
Shallow	20	600	Static air	36.0	0.09
Deep	20	600	Static air	43.0	0.29
Shallow	Flash heating	600	Static air	80.0	1.38
Deep	Flash heating	600	Static air	82.0	1.44
Packed	20	600	Flowing dry air	66.0	0.97

due to the defect sites [Si(OH)]. Since the zeolite samples show only the Si(0Ga) and Si(1Ga) peaks, the following simplified equation is used to estimate the framework Si/Ga ratio (14):

$$(\mathrm{Si/Ga})_{\mathrm{NMR}} = [I_{\mathrm{Si(0Ga)}} + I_{\mathrm{Si(1Ga)}}]/0.25 I_{\mathrm{Si(1Ga)}}. \quad [1]$$

Here, I_{Si} is peak intensity.

It may be noted that since the T sites in the MFI structure are not crystallographically identical, determination of the framework (FW) Si/Ga ratio by ^{29}Si MAS NMR is not very accurate (15). Nevertheless, the changes in FW Si/Ga ratios are large enough to draw conclusions about the degalliation. The FW Si/Ga ratios obtained by ^{29}Si MAS NMR are listed in Tables 1 and 2.

Degalliation of the zeolite during TPA removal in a deep bed at a slow heating rate (20°C min^{-1}) under static air is higher than that of the zeolite calcined in a shallow bed under similar conditions. In the deep bed calcination, the water formed from the combustion of the template is retained in the zeolite bed for a longer period. This results in a higher degalliation because of the more severe hydrothermal treatment received by the zeolite as compared with zeolite in the shallow bed.

The heating rate (used to achieve the maximum temperature) also shows a strong effect on the degalliation of the zeolite. When flash heating is used, the zeolite calcined in both the deep and shallow beds undergoes a degalliation larger than that observed when the heating is slow (20°C min^{-1}). This is expected because of the sudden increase in zeolite temperature resulting in the formation of water vapor at higher concentration and also because of the increase in zeolite temperature due to exothermic combustion of the organic template in the zeolite channel. Thus, because of the increase in both the temperature and concentration of water vapor, the zeolite is subjected to severe thermal and hydrothermal treatments, leading to a greater extent of degalliation. This is consistent with earlier observations (12, 13).

The degalliation of zeolite in flowing air is also higher than that in static air. In flowing air, much more oxygen is available for combustion of the occluded organic template than is available in static air. Hence, template combustion occurs at a faster rate in flowing air, causing an increase in

TABLE 2

Deammoniation Conditions for NH_4–GaMFI and Their Influence on the Framework and Nonframework Composition and Strong Acidity of the Zeolite

Nature of zeolite bed	NH_4 removal conditions: Heating rate ($^\circ$C min^{-1})	Maximum temperature ($^\circ$C)	Static or flowing air	FW Si/FW Ga ratio	Non-FW Ga/FW Ga ratio	Acidity (mmol g^{-1})
Shallow	20	600	Static air	45.2	0.36	0.24
Deep	20	600	Static air	48.1	0.44	0.23
Shallow	Flash heating	600	Static air	48.8	0.46	0.22
Deep	Flash heating	600	Static air	62.8	0.87	0.13
Packed	20	400	Flowing dry air	43.1	0.30	0.25
Packed	20	800	Flowing dry air	65.0	0.94	0.12
Packed	20	400	Flowing moist air	60.9	0.82	0.14
Packed	20	600	Flowing moist air	78.8	1.35	0.10
Packed	20	800	Flowing moist air	Very high		0.05

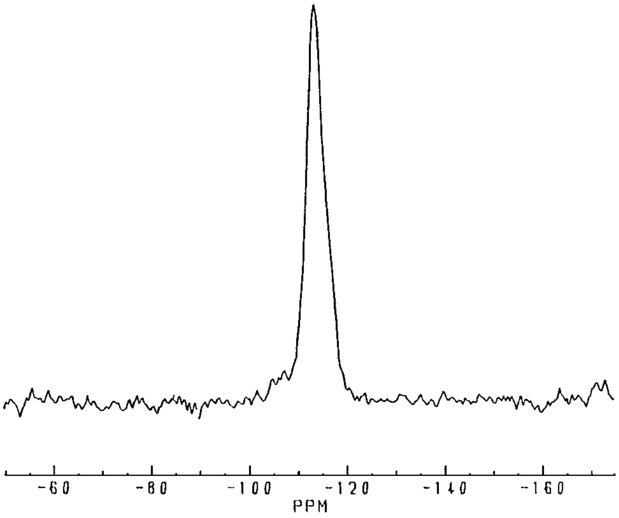

FIG. 1. ^{29}Si MAS NMR spectrum of Ga–MFI zeolite obtained by deammoniating NH_4–GaMFI in a shallow bed at 600°C at a heating rate of 20°C min^{-1} in static air.

zeolite temperature and, consequently, an increase in degalliation. Our earlier study (12) showed a strong influence of temperature on degalliation.

Similarly, the degalliation of NH_4–GaMFI zeolite during its deammoniation is influenced by the shallow or deep bed and slow or flash heating in static air at 600°C (Table 2). In this case, the degalliation results from a hydrothermal treatment due to the formation of water by zeolite dehydroxylation at 600°C. The concentration of water vapor in the zeolite is higher under deep bed or flash heating conditions, resulting in greater degalliation. A the higher temperature, the zeolite is subjected to more severe hydrothermal treatment (i.e., high temperature combined with higher concentration of water vapor formed due to dehydroxylation of the zeolite at the higher temperature). Hence it is degallinated to a greater extent. In the presence of moisture in the air, the extent of degalliation is greater and the influence of temperature is much stronger (Table 2).

A comparison of the FW Si/Ga ratio or non-FW Ga/FW Ga ratio with acidity (Table 2) shows that the acidity of the zeolite is consistent with the extent of degalliation. Acidity decreases with increasing non-FW Ga/FW Ga ratio or (FW Si/Ga ratio).

In conclusion, TPA removal and deammoniation conditions have a strong influence on the extent of degalliation of Ga–MFI zeolite. The degalliation results from the hydrothermal treatment of the zeolite due to formation of water in the combustion of organic template (TPA) or because of the dehydroxylation of the zeolite.

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