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Effect of aluminium source and content on the synthesis of zeolite ZSM-5 from kanemite *via* solid-state transformation

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The effect of the incorporation of aluminium during the synthesis of zeolite ZSM-5 from kanemite *via* solid-state transformation was studied using X-ray powder diffraction, ^{29}Si and ^{27}Al NMR spectroscopy, thermal analysis and elemental analysis. During cation exchange, which takes place in highly basic media, silicate layers of kanemite give rise to the formation of silica colloids and shorter silicate layers. For Si/Al ratios $\geqslant 19$, some aluminium is incorporated into the short silicate layers, however, most of the aluminium is incorporated into the Si–O–Si network during the condensation of the silica colloids in silica polymers when the pH is lowered to 8.5, independent of the aluminium source used ($NaAlO_2$, $Al_2(SO_4)_3$ or $Al(NO_3)_3 \cdot 9H_2O$). Mesoporous materials are synthesized from Al-containing kanemite, that is, aluminium is added during the synthesis of kanemite. The formation of silica colloids during cation exchange is the reason why, unlike the synthesis of mesoporous materials, aluminium could be added to the kanemite-template mixture during cation exchange. The highest amount of incorporated aluminium was obtained using $NaAlO_2$ because it is the aluminium source for which the pH is highest during cation exchange and consequently it is the aluminium source which yields the highest amount of silica colloid precipitates during the adjustment of the pH to 8.5.

Zeolite ZSM-5 presents a great source of interest in catalysis because of its very shape-selective properties, its high steam stability, high metal resistance (high tolerance for vanadium) and slow coke accumulation.[1] The most common method used to synthesize this material is the hydrothermal route.[2] However, it has been shown that the synthesis of silicalite 1 (Si-ZSM-5) *via* solid-state transformation from kanemite is more rapid than the hydrothermal synthesis from Cataloid SI-30 (SiO_2: 30.7%; Na_2O: 0.4%).[3–7] As a matter of fact, silicalite 1 can be synthesized after 16 h at 130 °C *via* solid-state transformation whereas it takes 3 days at the same temperature for the hydrothermal synthesis (our work). It was observed that nucleation and crystal growth were much faster for the solid-state transformation.[6] Furthermore, the major changes occurred during the beginning of crystal growth for solid-state transformation and during nucleation for hydrothermal synthesis. The results were explained by the fact that the structure of the starting materials was completely different. For solid-state transformation, the layered structure of kanemite enables nucleation to start during cation exchange and drastically shortens the synthesis time. Solid-state transformation also presents the advantage of obtaining smaller crystals which is particularly interesting for potential applications; small crystals exhibit greater catalytic activity because their relatively small size allows a faster diffusion of reactants into the catalyst.

Kanemite is a hydrated layer sodium silicate[8] that can be easily synthesized.[9] The kanemite structure has been studied by ^{1}H, ^{23}Na and ^{29}Si NMR spectroscopy[10–14] and single-crystal X-ray diffraction,[15] however the structure has not been completely elucidated yet. The physical properties of kanemite include a high capacity for ion exchange whereby sodium ions can be replaced by organic moieties such as alkylammonium cations.[9]

The synthesis of silicalite 1 from kanemite is carried out in two steps:

(1) cation exchange with the template in the liquid phase at 70 °C for 3 h, followed by adjustment of the pH to 8.5

(2) solid-state transformation of the intercalated kanemite into ZSM-5 at 130 °C

To distinguish it from the hydrothermal synthesis, we call the procedure corresponding to these two steps *solid-state transformation*.

Ferrierite[16,17] and MCM-41-like mesoporous materials[18] were synthesized by incorporating aluminium during the synthesis of kanemite (synthesis of aluminium-containing kanemite). In our case, zeolite ZSM-5 could be synthesized by incorporating aluminium during the synthesis of kanemite or during cation exchange. It was much faster to prepare kanemite from the commercially available SKS-6 precursor and to add aluminium to the kanemite–template mixture during cation exchange than to prepare aluminium-containing kanemite from water–glass and sodium hydroxide and then to mix aluminium-containing kanemite and template. This is the reason why in the following we will focus on the study of the incorporation of aluminium when added to the kanemite–template mixture during the cation exchange reaction.

Experimental

Synthesis

The starting materials for the solid-state transformation from layered silicate were kanemite, prepared from an SKS-6 precursor (Clarian Tokoyama Company, Japan), an aqueous solution of tetrapropylammonium hydroxide (TPAOH) 22.5 wt% and the aluminium sources tested were sodium aluminate ($NaAlO_2$), aluminium sulfate ($Al_2(SO_4)_3$), alumi-

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Table 1 Effect of Si/Al ratio on the incorporation of aluminium, the aluminium source is $NaAlO_2$

Starting Si/Al ratio	65 (Al = 3%)	19 (Al = 5%)	10 (Al = 10%)		5.5 (Al = 15%)	
Starting amount of TPAOH/ml g^{-1} of kanemite	2	2	2	4	2	4
XRD after CER	Disintegrated kanemite	Partially disintegrated kanemite	Partially disintegrated kanemite	Amorphous	Partially disintegrated kanemite	SASH low crystallinity
XRD after SST	MFI	MFI	MFI low crystallinity + SASH	MFI (major) + SASH (minor)	MFI (minor) + SASH (major)	MFI (major) + SASH (minor)
δ ^{27}Al NMR after SST/ppm	51.6 + spinning side bands	52.3 + spinning side bands	56.0 + spinning side bands	57.1 + spinning side bands	56.7 + spinning side bands	57.2 + spinning side bands
Amount of TPA after SST/wt%	9.7	8.9	9.7	7.4	1.9	5.2
Measured Si/Al ratio after SST (ICP)	58.4	29.2	14.3	23.2	12.5	12.3

CER = cation exchange reaction; SST = solid-state transformation; SASH = sodium aluminium silicate hydrate.

nium nitrate ($Al(NO_3)_3 \cdot 9H_2O$) and aluminium hydroxide ($Al(OH)_3$).

Zeolite ZSM-5 was prepared by dispersing 1 g of kanemite and the aluminium source in 10 ml of an aqueous solution of template (x ml of 22.5 wt% TPAOH and $10 - x$ ml of deionized water). The mixture was heated at 70 °C for 3 h with stirring. After cooling to room temperature, the pH of the suspension was lowered to 8.5. The resulting product was filtered off and washed with deionized water and dried overnight at room temperature to yield kanemite–TPA powder. Zeolite ZSM-5 was synthesized in a *ca.* 5 cm^3 closed glass ampoule in an oven at 130 °C for 72 h.

Analysis

X-Ray powder diffraction patterns of the samples were recorded using a MXP 18 diffractometer (Mac Science Co. Ltd.) with monochromatic CuKα radiation.

^{29}Si and ^{27}Al MAS NMR spectroscopic characteristics of the samples were determined using a BRUKER AMX500 spectrometer operating at 99.36 MHz, with the samples placed in a 4 mm ZrO_2 rotor spinning at 4 kHz. Because the structure of ZSM-5 precursors (intercalated kanemite and derivatives) is broken during calcination, the samples were studied as synthesized, that is in presence of template. It is known that the presence of TPA cations causes an increase in the relaxation time T_1 for Q_4 ^{29}Si nuclei in ZSM-5 zeolites. For a Si/Al ratio equal to 16, T_1 was found to be 119.9 s in the presence of template.[19] For our work, a total of 20 scans were recorded for each sample. A delay five times larger than the value of T_1 for the Q_4 sites was used in order to obtain quantitative results.

Elemental analysis was carried out by inductively coupled plasma spectroscopy (Thermo Jarrel Ash IRIS/AP). The samples ($\approx$0.012 g) were dissolved in concentrated hydrofluoric acid ($\approx$2 ml) and made up to 100 ml with deionized water in a volumetric flask.

TG-DTA measurements were carried out with a Mac-Science TG-DTA 2000 analyzer. The amount of template was evaluated by heating the samples to 1000 °C in a dry air flow (100 ml min^{-1}) at a heating rate of 5 °C min^{-1}.

Results

Influence of the Si/Al ratio

$NaAlO_2$ was arbitrarily chosen to study the effect of the Si/Al ratio on aluminium incorporation during cation exchange. $NaAlO_2$ is also the aluminium source which was used to prepare aluminium-containing kanemite for the synthesis of ferrierite[16,17] and mesoporous materials.[18] Decreasing starting Si/Al ratios of respectively 65 (Al = 3%); 19 (Al = 5%); 10 (Al = 10%) and 5.5 (Al = 15%) were chosen (Table 1). The pH of the kanemite–TPAOH–$NaAlO_2$ mixture was in the range 12.5–13.0 independent of the starting Si/Al ratio. Powder with a disintegrated kanemite structure was obtained after cation exchange when the amount of TPAOH (aqueous solution of 22.5% of template by weight) was 2 ml g^{-1} of kanemite independent of the Si/Al ratio (Table 1). For Si/Al ratio = 10

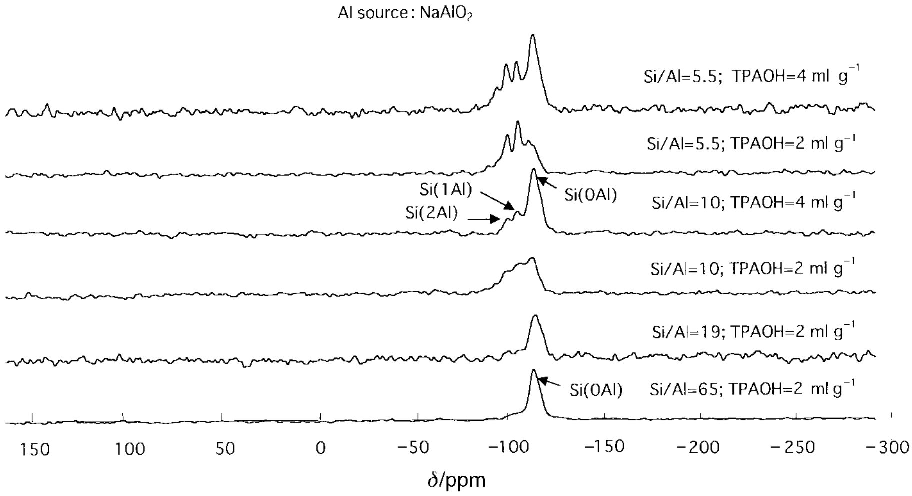

Fig. 1 ^{29}Si NMR spectra of the samples after solid-state transformation. Effect of the starting Si/Al ratio on the incorporation of aluminium. The aluminium source is $NaAlO_2$.

Table 2 Effect of the aluminium source on the incorporation of aluminium for a starting Si/Al ratio equal to 10

Al source	$NaAlO_2$	$Al_2(SO_4)_3$	$Al(NO_3)_3 \cdot 9H_2O$
Starting amount of TPAOH/ml g^{-1} kanemite	4	4	4
pH after CER	13.2	12.3	11.0
Amount of TPA after SST/wt%	7.4	5.7	3.7
Measured Si/Al ratio after SST (ICP)	23.2	23.3	20.9

CER = cation exchange reaction; SST = solid-state transformation.

and 5.5 an amorphous phase and sodium aluminium silicate hydrate (a compound having the structure of a high-silica variety of zeolite Na-P) with low crystallinity are obtained, respectively.

Pure zeolite ZSM-5 can be synthesized *via* solid-state transformation for Si/Al ratio $\geqslant 19$ (Table 1). However, for Si/Al ratio $\leqslant 10$, MFI structure compounds and sodium aluminium silicate hydrate are formed even if the amount of template used is increased.

^{29}Si NMR spectra of the samples after solid-state transformation (Fig. 1) show that with decreasing Si/Al ratios, the signal changes from a single sharp one in the range -113 to -112 ppm for Si/Al ratio $\geqslant 19$ to a broad signal in the same chemical shift range for Si/Al ratio = 10 when TPAOH = 2 ml g^{-1} of kanemite. Three distinct signals are observed if the amount of template is doubled for Si/Al ratio = 10 or if Si/Al is decreased. ^{27}Al NMR of the samples after solid-state transformation was performed so as to ascertain the nature and environment of the incorporated aluminium. A single signal in the range 51–57 ppm (Table 1) assigned to Al in a tetrahedral environment was observed in the ^{27}Al-NMR spectra indicating that aluminium is incorporated into the framework.[18,20] As for the synthesis of ZSM-5 by hydrothermal synthesis, spinning side bands were also observed.[2]

ICP results for the samples after solid-state transformation show that for a starting Si/Al ratio $\leqslant 19$, the measured Si/Al ratio after cation exchange was higher than the starting Si/Al ratio.

From TG-DTA analysis of the samples after solid-state transformation, it was observed that for a very high amount of aluminium (Si/Al ratio = 5.5) a much smaller amount of template is present in the framework.

Influence of the aluminium source

In order to better understand the effect of using aluminium in excess, we have studied the influence of the aluminium source for a starting Si/Al ratio equal to 10.

The pH of each aluminium source in water (equivalent to a 10% aluminium mixture relative to silicon but containing no kanemite and no template) was measured. $Al_2(SO_4)_3$ and $Al(NO_3)_3 \cdot 9H_2O$ gave an acid solution, the pH values were 3.8 and 2.5, respectively. The pH of the $Al(OH)_3$ solution was equal to 6.1 and that of the $NaAlO_2$ solution was equal to 11.4. Thus, the nature of the aluminium source has an influence on the pH of the kanemite–TPAOH mixture (Table 2). It was observed that a powder of quasi-amorphous structure was obtained after cation exchange using $NaAlO_2$ and $Al_2(SO_4)_3$ sources and a powder with a partially disintegrated kanemite structure was obtained when using a $Al(NO_3)_3 \cdot 9H_2O$ source (Fig. 2). Besides the quasi-amorphous phase, peaks of $Al(OH)_3$ were observed by X-ray diffraction for the $Al(OH)_3$ source.

An MFI structured compound and sodium aluminium silicate hydrate were formed after solid-state transformation for $NaAlO_2$, $Al_2(SO_4)_3$ and $Al(NO_3)_3 \cdot 9H_2O$ sources when using a TPAOH amount of 4 ml g^{-1} of kanemite (Fig. 3). In addition to the MFI structured compound, the peaks for $Al(OH)_3$ were still observed after solid-state transformation when an $Al(OH)_3$ source was used and for a TPAOH amount equal to 2 ml g^{-1} of kanemite. An amorphous phase and the peaks of $Al(OH)_3$ were observed when the amount of TPAOH was doubled.

^{29}Si NMR spectra of the samples after solid-state transformation were completely different from that of pure sodium aluminium silicalite hydrate (Fig. 4). For all aluminium sources a sharp signal in the range -113 to -110 ppm corresponding to Q_4 Si(OAl) and generally accompanied by one or several small signals at lower field were observed. ^{27}Al NMR spectra of the samples after solid-state transformation show that except for the $Al(OH)_3$ source, a sharp signal was observed in the range 53–57 ppm independent of the aluminium source indicating that aluminium is in a tetrahedral environment (Fig. 5). For the $Al(OH)_3$ source, a main peak in the range 5–6 ppm (the signal for Al in $Al(OH)_3$ is at 8.1 ppm) and a small sharp signal in the range 50–52 ppm indicate that the major fraction of aluminium is in an octahedral environment.[20]

From ICP analysis of the samples after solid-state transformation, it was observed that the Si/Al ratio measured after cation exchange was higher than the initial Si/Al ratio independent of the aluminium source (Table 2).

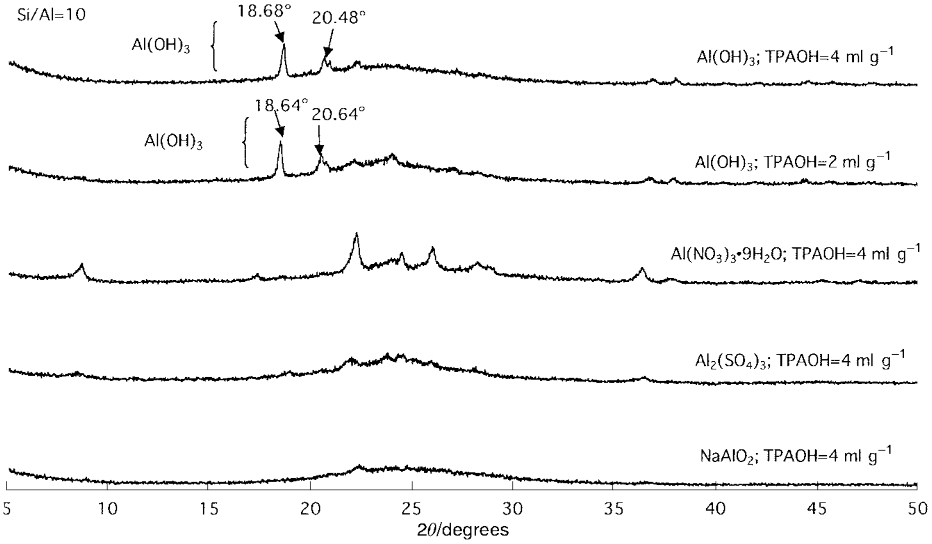

Fig. 2 X-Ray diffraction patterns of the samples after cation exchange. Effect of the aluminium source, the starting Si/Al ratio is equal to 10.

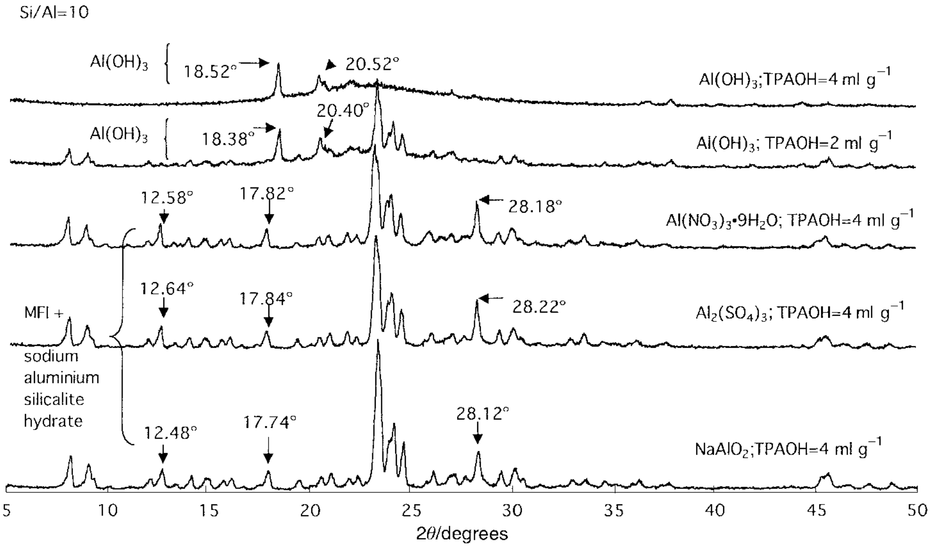

Fig. 3 X-Ray diffraction patterns of the samples after solid-state transformation. Effect of the aluminium source, the starting Si/Al ratio is equal to 10.

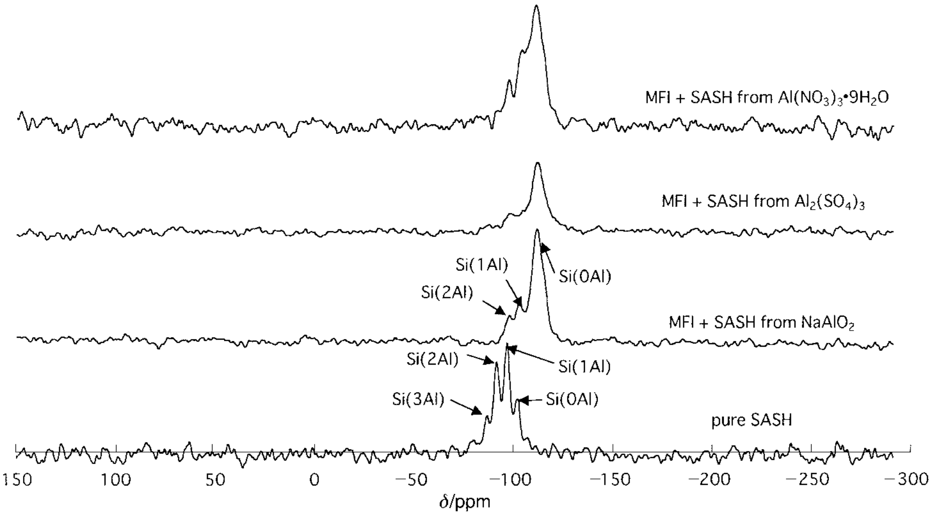

Fig. 4 ^{29}Si NMR spectra of the samples after solid-state transformation. Effect of the aluminium source, the starting Si/Al ratio is equal to 10. The starting TPAOH amount is 4 ml g^{-1} of kanemite. The spectrum of pure SASH (sodium aluminium silicate hydrate) is also represented for comparison.

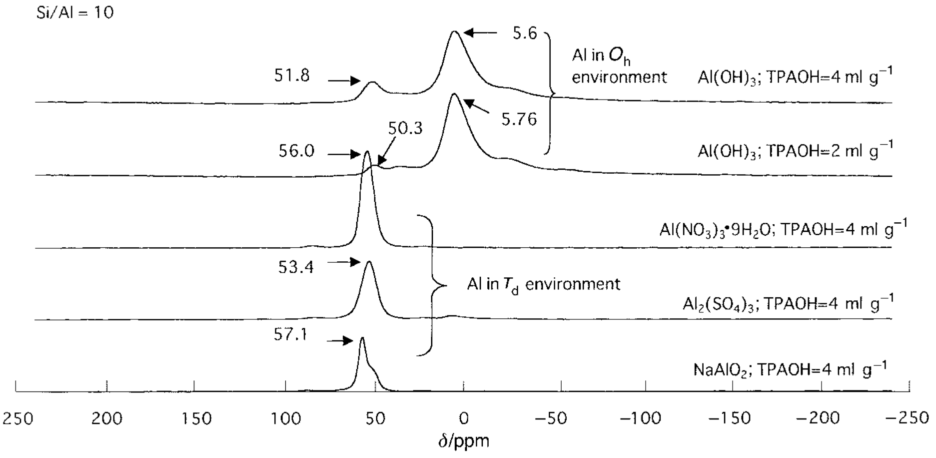

Fig. 5 ^{27}Al NMR spectra of the samples after solid-state transformation. Effect of the aluminium source, the starting Si/Al ratio is equal to 10.

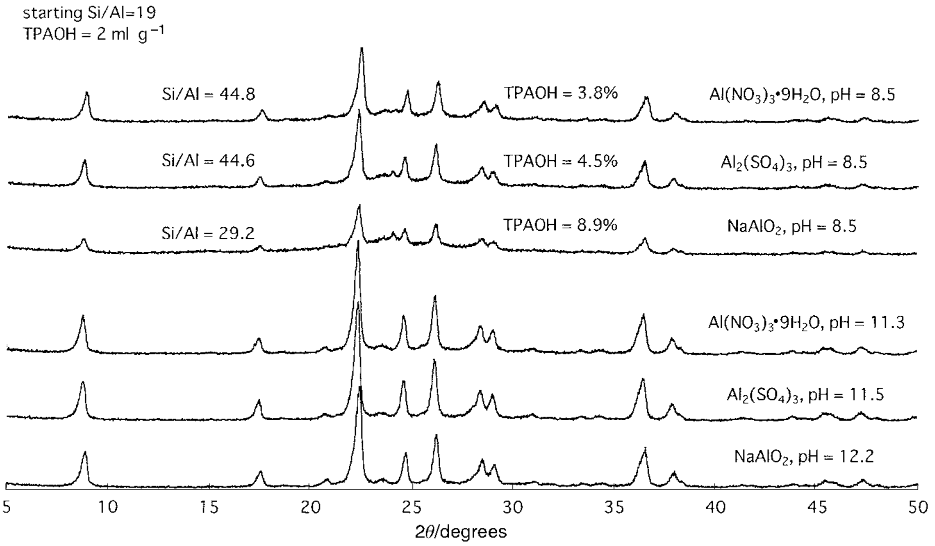

Fig. 6 X-Ray diffraction patterns of the samples after cation exchange. Effect of the adjustment of the pH after cation exchange. The starting Si/Al ratio is equal to 19 and the starting TPAOH amount is equal to 2 ml g^{-1} of kanemite.

TG-DTA analysis of the samples after solid-state transformation showed that Al(NO$_3$)$_3$·9H$_2$O is the Al source for which the lowest amount of template is present (Table 2).

Influence of the pH after stirring the kanemite–TPAOH–Al mixture at 70 °C for 3 h

The aluminium sources which were used were NaAlO$_2$, Al$_2$(SO$_4$)$_3$ and Al(NO$_3$)$_3$·9H$_2$O. For both starting Si/Al ratios 10 and 19, samples for which the pH was not adjusted after cation exchange were compared to samples for which the pH was adjusted to 8.5. Remember that the phase which is recovered after filtration when the pH is not adjusted after cation exchange corresponds to the fraction which did not dissolve. And the phase which is recovered when the pH is adjusted to 8.5 corresponds to the fraction which did not dissolve plus the fraction which precipitated during the formation of the three dimensional gel network.

Starting Si/Al ratio = 10, TPAOH = 4 ml g^{-1} of kanemite. When the pH was not adjusted after cation exchange, sodium aluminium silicate hydrate started forming when NaAlO$_2$ was used (XRD spectra with low crystallinity, not shown). Partially disintegrated kanemite was obtained for Al$_2$(SO$_4$)$_3$ and Al(NO$_3$)$_3$·9H$_2$O (not shown). The XRD spectra of the samples for which the pH was adjusted after cation exchange are shown in Fig. 2.

Starting Si/Al ratio = 19, TPAOH = 2 ml g^{-1} of kanemite. The pH of the suspension was lower than when the starting Si/Al ratio was equal to 10 mainly because the amount of template used was smaller (Fig. 6). As for Si/Al ratio = 10, NaAlO$_2$ gives the most basic conditions for cation exchange. The fraction which did not dissolve still has the structure of kanemite for the three aluminium sources. However, when the pH was adjusted to 8.5, disintegrated kanemite and an amorphous phase were formed, the amorphous phase being the most important for the NaAlO$_2$ source. NaAlO$_2$ is also the aluminium source for which the amount of incorporated aluminium (ICP analysis) and the amount of incorporated template (TG-DTA analysis) are the highest (Fig. 6). It was also observed by ICP analysis that for both aluminium ratios, some aluminium was present in the phase which did not dissolve during cation exchange.

Discussion

The peaks for Al(OH)$_3$ observed by XRD and the signal for aluminium in an octahedral environment observed by ^{27}Al NMR after solid-state transformation showed that Al(OH)$_3$ could not be dissolved during the stirring of the kanemite–TPAOH mixture at 70 °C for 3 h. The fact that Al(OH)$_3$ can be used for the synthesis of ZSM-5 *via* hydrothermal synthesis at 170 °C[21] indicates that the cation exchange conditions are too mild to enable the dissolution of Al(OH)$_3$.

Starting Si/Al ratio = 10

It is known that in the absence of aluminium, silicate layers of kanemite give rise to the formation of silica colloids (soluble fraction) and shorter silicate layers (insoluble fraction) during the stirring of the suspension at 70 °C for 3 h in basic media.[7] With a NaAlO$_2$ source, sodium aluminium silicate hydrate (a compound having the structure of a high-silica variety of zeolite Na-P) starts forming during cation exchange before the pH is adjusted to 8.5 (XRD of the samples for which the pH was not adjusted after cation exchange). Thus, it seems that, like in the absence of aluminium, silica colloids and short silicate layers are formed, however, because of the highly basic conditions and the important amount of aluminium and sodium (coming from kanemite and from the aluminium source), the short silicate layers segregate into smaller segments and all the species rearrange to form sodium aluminium silicate hydrate which is a stable compound in highly basic media. However, this compound is destroyed when the pH is adjusted to 8.5 (giving an amorphous powder). Concerning Al$_2$(SO$_4$)$_3$ and Al(NO$_3$)$_3$·9H$_2$O sources, the less basic conditions (pH = 12.3 and 11.0 respectively, the pH was 13.2 for NaAlO$_2$) and the smaller amount of sodium (coming only from kanemite) lead to the formation of silica colloids, but in lower amounts, and shorter silicate layers during cation exchange. For these two aluminium sources, it is probable that aluminium is incorporated into the Si–O–Si network mainly during the adjustment of the pH to 8.5 when a three dimensional gel network is formed. Thus when the starting Si/Al ratio is equal to 10, the measured Si/Al ratio is about the same for the three aluminium sources, NaAlO$_2$, Al$_2$(SO$_4$)$_3$ and Al(NO$_3$)$_3$·9H$_2$O after cation exchange ($20.9 \leqslant$ Si/Al ratio $\leqslant 23.3$) however, the way aluminium is incorporated into the Si–O–Si network is different.

For the three aluminium sources two compounds are formed after solid-state transformation: an MFI structured compound and a sodium aluminium silicate hydrate, indicating that there is sufficient sodium derived from kanemite to form sodium aluminium silicate hydrate. XRD spectra showed that the MFI structured compound is the major product. This was confirmed by ^{29}Si NMR spectra which were completely different from the ^{29}Si NMR spectrum of sodium aluminium silicate hydrate. Now the question is whether aluminium is in the MFI structured compound or not. ^{29}Si NMR spectra of the compounds after solid-state transformation are similar to the spectrum of ZSM-5 prepared *via* hydrothermal synthesis[22] indicating that aluminium is present in the MFI structured compound, *i.e.* that ZSM-5 is formed after solid-state transformation. The slight difference in the ^{29}Si NMR spectra indicates that the distribution of aluminium is slightly different according to the aluminium source.

Starting Si/Al ratio = 19

It has been observed by ICP analysis of the samples for which the pH was not adjusted after cation exchange that some aluminium is incorporated into the short silicate layers during cation exchange. Then when the pH of the suspension is lowered to 8.5 after stirring, the soluble fraction precipitates. Because $NaAlO_2$ was the aluminium source for which the pH of the suspension was the highest during cation exchange, it was also the aluminium source for which the dissolution of kanemite was the highest, that is the amount of silica species formed was the highest and consequently it was the aluminium source for which the most amorphous phase and intercalated template were obtained after adjustment of the pH to 8.5.[7] Furthermore, it is also the aluminium source for which the incorporation of aluminium is the most important after adjustment of the pH to 8.5 indicating that the amount of incorporated aluminium is proportional to the amount of the soluble fraction which precipitates and that aluminium incorporates into the Si–O–Si network when silica colloids condense in silica polymers (formation of the three dimensional gel network).

Aluminium-containing mesoporous materials were synthesized from aluminium-containing kanemite, aluminium being incorporated into the Si–O–Si network during the synthesis of kanemite.[18] It is known that the way kanemite transforms into zeolite in the presence of short-chain alkylammonium ions and the way it transforms into mesoporous material in the presence of long-chain alkylammonium ions are different.[7] We can compare our work with the work of Thiesen *et al.*[23] who have carried out their experiments under similar conditions to ours (the pH was adjusted to 12.5 and the dispersion was held at 70 °C for 3 h. After cooling to room temperature, the pH was adjusted to 8.5). If the aluminium is incorporated during the synthesis of mesoporous materials, it cannot be easily fixed into the Si–O–Si network because small silicate species such as silica colloids (monomers, dimers,…hexamers) cannot be formed. The dissolution process, which is due to the partial destruction of the silicate structure by long-chain alkylammonium ions, leads to the formation of fragments of silicate layers. However, these fragments do not have time to segregate into smaller silicate species, that is into silica colloids, because they are immediately carried away by the long-chain alkylammonium ions to be aggregated into cylindrical forms.

Conclusion

Four aluminium sources were tested for the incorporation of aluminium into the Si–O–Si network when synthesizing zeolite ZSM-5 from kanemite *via* solid-state transformation: $NaAlO_2$, $Al_2(SO_4)_3$, $Al(NO_3)_3 \cdot 9H_2O$ and $Al(OH)_3$. $Al(OH)_3$ could not be dissolved during cation exchange and was immediately excluded.

Concerning the three other aluminium sources, when aluminium is in excess (starting Si/Al ratio = 10), the way it is incorporated during cation exchange depends on the aluminium source and the formation of sodium aluminium silicate hydrate in addition to ZSM-5 after solid-state transformation cannot be avoided.

When aluminium is not in excess (starting Si/Al ratio = 19), shorter silicate layers and silica colloids form during cation exchange independent of the aluminium source. The highest amount of intercalated template and the highest amount of incorporated aluminium were observed for the $NaAlO_2$ source. The reason for this has been explained by the fact that $NaAlO_2$ is the aluminium source for which the pH of the suspension is the highest and consequently the aluminium source for which the formation of silica colloids is the most important during cation exchange.

Unlike the synthesis of mesoporous materials, aluminium could be added after the preparation of kanemite for the synthesis of zeolite ZSM-5 because small silicate species, such as silica colloids, could be formed during cation exchange making the incorporation of aluminium easy when condensing to silica polymers when the pH was lowered to 8.5.

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