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Al-TUD-1: Introducing tetrahedral aluminium

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ABSTRACT

Tetrahedral aluminium was synthesized inside the TUD-1 structure with a low Si/Al ratio. The Al ion in its tetrahedral structure was stabilized by sodium as a counter cation. However, the tetrahedral aluminium species in the TUD-1 structure reverted to a mixture of hexa-, penta- and tetrahedral coordination sites after the exchange of sodium cations with protons. The Al-TUD-1 materials were found to be catalytically active for the acetal protection of benzaldehyde.

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1. Introduction

In 1874 van't Hoff and Le Bel independently from each other described the tetrahedral structure of the carbon atom [1]. With this decisive step three dimensional structures became a mainstay in chemistry. The possibility of a tetrahedral structure of aluminium hence also was recognized. The importance of this tetrahedral structure for catalysis was thoroughly recognized with the advent of zeolites as highly versatile, crystalline and nano-porous catalysts. Tetrahedral aluminium induces Brønsted acidity, since the negatively charged aluminium needs a counter ion, such as a proton. On the other hand, calcination leads to loss of water and consequently aluminium does not fulfil the octet rule and displays Lewis acidity (Scheme 1). The crystalline character of zeolites allows for a good tunability of this acidity, however due to their small pore-size zeolites cannot be applied as catalysts for larger molecules [2].

When preparing mesoporous silicates acidity can again be induced by incorporating aluminium, thus allowing catalytic conversion of larger molecules [3–5]. Furthermore, they can function as carriers for covalent or non-covalent immobilisation of chiral catalysts again due to incorporation of metals such as aluminium [6–9]. The most prominent examples of mesoporous molecular sieves are MCM-41 (Mobil Composition of Matter) and SBA-15 (Santa Barbara Amorphous material) [3]. More recently, TUD-1 (Technische Universiteit Delft) was described, which has several advantages: tuneable pore size (5–50 nm) and surface area (500–1000 $m^2 g^{-1}$) and a three-dimensional pore structure, leading to less mass-transfer limitations than experienced in the one-dimensional pores of MCM-41 [5,10]. In addition, the material is much more stable. Its synthesis requires complexing reagents which are less expensive than the surfactants employed in the synthesis of MCM-41 or tri-block polymers for synthesis of SBA-15. Moreover, the synthesis of TUD-1 is very flexible and even allows the use of environmentally benign SiO_2 instead of commonly employed tetraethyl orthosilicate (TEOS) [11].

The pore size and surface area determining step during the synthesis of TUD-1 is the hydrothermal treatment. By varying the duration, textural properties can be varied. The introduction of metals into the amorphous siliceous TUD-1 structure is straightforward. However, due to differences in ion radius and/or valence compared to silicon, metals often display different types of coordination in the framework. A typical example is the incorporation of aluminium into the TUD-1 matrix giving rise to tetra-, penta- and hexa-coordinated aluminium sites [4,12–14].

In heterogeneous catalysis and catalysis in general it is important to have well defined catalytic sites [15]. The aim of this study was therefore to increase the amount of tetrahedrally coordinated aluminium inside the siliceous TUD-1 matrix. Tetrahedrally coordinated aluminium prepared from a highly defined and reactive precursor gives rise to Brønsted acid sites that can be employed in catalysis such as the FCC [16–18]. Additionally they can also act as anchoring sites for different ionic chiral catalysts employing non-covalent ion-exchange techniques [9,19]. In that respect two different aluminosilicates, namely H-Al-TUD-1 and Na-Al-TUD-1

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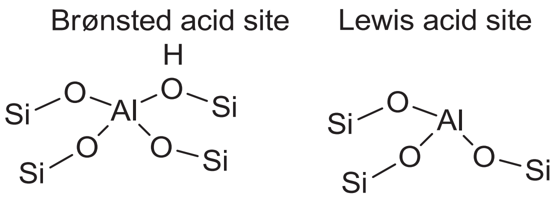


Scheme 1. Models for Brønsted and Lewis acid sites.

were synthesized and the impact of different cations on the amount of tetrahedrally coordinated aluminium as well as the textural properties was evaluated.

2. Experimental

2.1. Instruments

Powder X-ray diffraction (XRD) patterns were obtained on a Philips PW 1840 diffractometer equipped with a graphite monochromator using CuKα radiation.

The textural properties of the materials were characterized by volumetric N_2 physisorption at 77 K using Micromeritics ASAP 2010 equipment. Prior to the physisorption experiment, the samples were dried overnight at 573 K ($P \leq 10^{-2}$ Pa). From the nitrogen sorption isotherms, the specific surface area S_{BET}, the pore diameter $d_{P,BJH}$ and the pore volume $V_{p,BJH}$ were calculated. The latter two were determined from the adsorption branch of the nitrogen sorption isotherms as typically applied for TUD-1-type materials [5,10].

Chemical analysis of Si, Al and Na were performed in duplet by dissolving the samples in 1% HF and 1.25% H_2SO_4 solution and measuring them with Inductively Coupled Plasma – Optical Emission Spectroscopy (ICP-OES) on a Perkin-Elmer Optima 3000dv instrument.

Solid state ^{27}Al MAS NMR experiments were performed at 9.4 T on a Bruker Avance-400 MHz spectrometer operating at 104.2 MHz with a pulse width of 1 ms. 4-mm zirconia rotors with a spinning speed set to 11 kHz were used. The chemical shifts are reported with respect to $Al(NO_3)_3$ as an external standard at $\delta = 0$ ppm.

Transmission electron microscopy (TEM) was performed by using a Philips CM30T electron microscope with a LaB6 filament as the source of electrons operated at 300 kV.

Temperature-programmed desorption of ammonia (NH_3-TPD) measurements were carried out on a Micromeritics TPR/TPD 2900 instrument equipped with a thermal conductivity detector (TCD). About 30 mg sample was pre-treated at 550 °C in a flow of He (10 mL min^{-1}) for 1 h. Then 9.98 vol% NH_3 in He (10 mL min^{-1}) was adsorbed at 100 °C for 30 min. Subsequently, a flow of He (10 mL min^{-1}) was passed through the reactor for 30 min to remove any weakly adsorbed NH_3 from the sample. Desorption of NH_3 was monitored in the range of 100–600 °C at a heating rate of 10 °C min^{-1}.

2.2. Materials

All chemicals were obtained from commercial sources viz. Sigma–Aldrich, Acros and Alfa Aesar.

2.2.1. Synthesis of Al-TUD-1 (Si/Al = 4)[4]

Aluminium isopropoxide (6.12 g, 0.03 mol) was added to a mixture of absolute ethanol (27.65 g, 0.60 mol) and anhydrous 2-propanol (27.04 g, 0.45 mol) at 45 °C; followed by the addition of tetraethyl orthosilicate (24.99 g, 0.12 mol) and tetraethylene glycol (29.17 g, 0.15 mol). The entire mixture was stirred for an hour before dropwise addition of demineralised water (5.41 g, 0.30 mol) dissolved in absolute ethanol (27.65 g, 0.60 mol) and anhydrous 2-propanol (27.04 g, 0.45 mol).

After the addition of demineralised water the mixture was stirred for additional 0.5 h at room temperature followed by aging for 6 h. The resulting wet gel was dried at 70 °C for 21 h and 2 h at 98 °C. Hydrothermal treatment was performed in an autoclave with Teflon insert at 160 °C for 19 h. Finally the solid was calcined in air (with 1 °C min^{-1} to 550 °C, 4 h at 550 °C, with 1 °C min^{-1} to 600 °C, 10 h at 600 °C).

2.2.2. Synthesis of Na-Al-TUD-1 (Si/Al = 4)

Two Na-Al-TUD-1's were prepared with different Na/Al ratios. Samples were denoted as Na-Al-TUD-1.4 and Na-Al-TUD-0.7. The last number standing for the final Na/Al ratio determined by ICP. The synthesis of Na-Al-TUD-1.4 was as follows: To aluminium isopropoxide (4.24 g, 0.02 mol) anhydrous 2-propanol was added. The entire mixture was stirred for 2 h, then tetraethyl orthosilicate (17.30 g, 0.08 mol) was added as silica source followed by dropwise addition of a solution of triethanolamine (12.50 g, 0.08 mol) and demineralised water (5.03 g, 0.28 mol). Finally, to the clear mixture NaOH (0.97 g, 0.02 mol) dissolved in demineralised water (11.46 g, 0.64 mol) was added dropwise under vigorous stirring. The obtained molar composition was 1 SiO_2:0.125 Al_2O_3:1 TEA:0.29 NaOH:11 H_2O.

The synthesis of Na-Al-TUD-0.7 was slightly adjusted. Before the final addition of NaOH dissolved in water tetraethyl ammonium hydroxide (TEAOH, 35 wt% in H_2O, 4.37 g, 0.01 mol) was added. The molar composition was 1 SiO_2:0.125 Al_2O_3:1 TEA:0.175 NaOH:0.125 TEAOH:11 H_2O.

The obtained gels were left to stir for 0.5 h and poured into a porcelain bowl to age overnight. After drying the gels at room temperature they were dried at 98 °C for 21 h followed by hydrothermal treatment at 180 °C for 21 h in an autoclave equipped with Teflon inserts. Finally solids were calcined in air at 600 °C for 10 h with a heating rate of 1 °C min^{-1}.

2.2.3. Ion exchange

2.5 g of Na-Al-TUD-1 sample was stirred with 100 mL portions of 1 M NH_4Cl for five times, first two exchanges were performed at room temperature and last three at 80 °C. After each ion-exchange step, catalyst was washed with 50 mL portions of demi water. After ion exchange catalyst was placed in the oven to be dried at a temperature of 75 °C overnight followed by calcination in air at 550 °C for 5 h at heating rate of 1 °C min^{-1}.

2.2.4. Synthesis of 2-phenyl-1,3-dioxolane

Freshly distilled benzaldehyde and dry ethylene glycol were used for all the reactions. The reactions were carried out under N_2 in a 10 mL Schlenk flask. Al-TUD-1 samples were calcined at 550 °C and used in the reactions. Prior to its use the ion exchanged Na-Al-TUD-1 (viz. H-Al-TUD-1, H-Al-TUD-0.7-IE and H-Al-TUD-1.4-IE) and Na-Al-TUD-1 catalysts were activated at 120 °C under high vacuum for 1 h.

Benzaldehyde (106 mg, 1 mmol), was added to ethylene glycol (5 mL) and catalyst (50 mg). Then the reaction was stirred at 78 °C for 24.5 h. Aliquots 30 μL were taken at different time intervals and the samples were centrifuged for 5 min. From this 20 μL of samples were diluted in 980 μL of mobile phase (H_2O:CH_3CN: 95:5) and analysed by HPLC.

2.2.5. Reaction of benzaldehyde with n-butanol

The reaction of benzaldehyde with *n*-butanol was carried out under N_2 in a 10 mL Schlenk flask. Benzaldehyde (106 mg, 1 mmol) was added to a mixture of *n*-butanol (296, 4 mmol) and H-Al-TUD-1 catalyst (50 mg). Then the reaction mixture was stirred at 78 °C

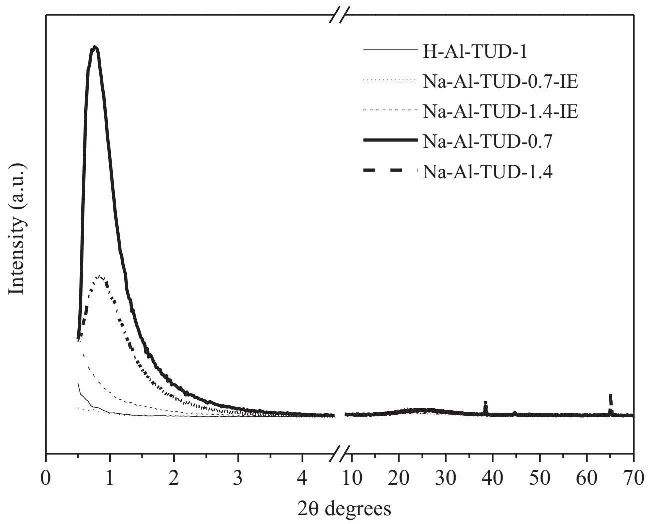


Fig. 1. XRD of H-Al-TUD-1, Na-Al-TUD-1.4, Na-Al-TUD-0.7, Na-Al-TUD-1.4-IE and Na-Al-TUD-0.7-IE, Si/Al ratio of 4.

for 24 h. After this the reaction mixture was washed with acetonitrile (1 mL). Then it was transferred to a 1.5 ml eppendorf and centrifuged for 2 min. The organic layer was separated from the catalyst and analysed by HPLC.

2.2.6. *TLC and HPLC analysis*

Thin-layer chromatography (TLC) was performed using precoated silica gel SIL G/UV 254 plates. HPLC separation was carried out using following instrument and method: Pump: waters 590, UV detector: waters 486, UV, flow: 1 mL min^{-1}. A CHROMOLITH Speed ROD, RP-18e, 50–4.6 mm, column is used for this separation with mobile phase H_2O/CH_3CN (95v:5v). The retention time of benzyl alcohol, benzaldehyde and 2-phenyl-1,3-dioxolane was found to be 3.2, 6.4 and 11.8 min. The amount of 2-phenyl-1,3-dioxolane was determined by using a calibration curve.

3. Results and discussion

3.1. *Material preparation and characterisation*

Amorphous aluminosilicate of TUD-1 structure, with a low Si/Al ratio of 4 (H-Al-TUD-1) was synthesized in order to ensure high ion-exchange capability. Tetraethylene glycol was used as a complexing reagent, since it ensures the best results in the synthesis of TUD-1 based materials with low Si/Al ratios [9,12,20]. The mesoporous character of H-Al-TUD-1 was determined by XRD as well as N_2 physisorption measurements. The sample possesses a peak at low angles, situated at 0.5 2θ degrees, characteristic for mesoporous materials (Fig. 1), however with much lower intensity than obtained in other samples. At higher degrees no crystalline alumina, δ- or θ-Al_2O_3, was detected. Minor peaks found at 38, 44 and 65 2θ degrees are due to aluminium from the sample holder. The mesoporous character was further confirmed by N_2 physisorption measurements characteristic for mesoporous materials (Fig. 2). A type IV isotherm with a type H1 hysteresis loop characteristic for mesoporous samples with a pore size distribution around 16 nm, pore volume of 1.2 cm^3 g^{-1} and surface area around 485 m^2 g^{-1} (Table 1) is clearly detectable.

Introduction of aluminium into the TUD-1 matrix generally creates hexa-, penta- and tetrahedrally coordinated aluminium. According to ^{27}Al-MAS-NMR measurement the amount of tetrahedrally coordinated aluminium (54 ppm) in H-Al-TUD-1 is 28% (Table 1, Fig. 3). Compared to previously synthesized H-Al-TUD-1 this amount of tetrahedrally coordinated aluminium is lower (Table 1, entries 1 and 2) [12]. Tetrahedrally coordinated aluminium is responsible for Brønsted acid sites essential for catalysis or as anchoring sites for anionic chiral catalysts. H-Al-TUD-1 possesses differently coordinated aluminium sites which can induce undesired side reactions in the various applications of the material. Hexa-coordinated aluminium often recognized as extra framework species can affect adsorption and catalytic properties [21]. Earlier attempts to remove the penta- and hexa-coordinated Al from Al-TUD-1 with a Si/Al ratio of 4 by a post synthesis washing step with HCl solution was only partially successful [19]. Therefore here we aimed at a solution to increase the amount of tetrahedrally coordinated aluminium by an adjustment of previously published synthesis method [12].

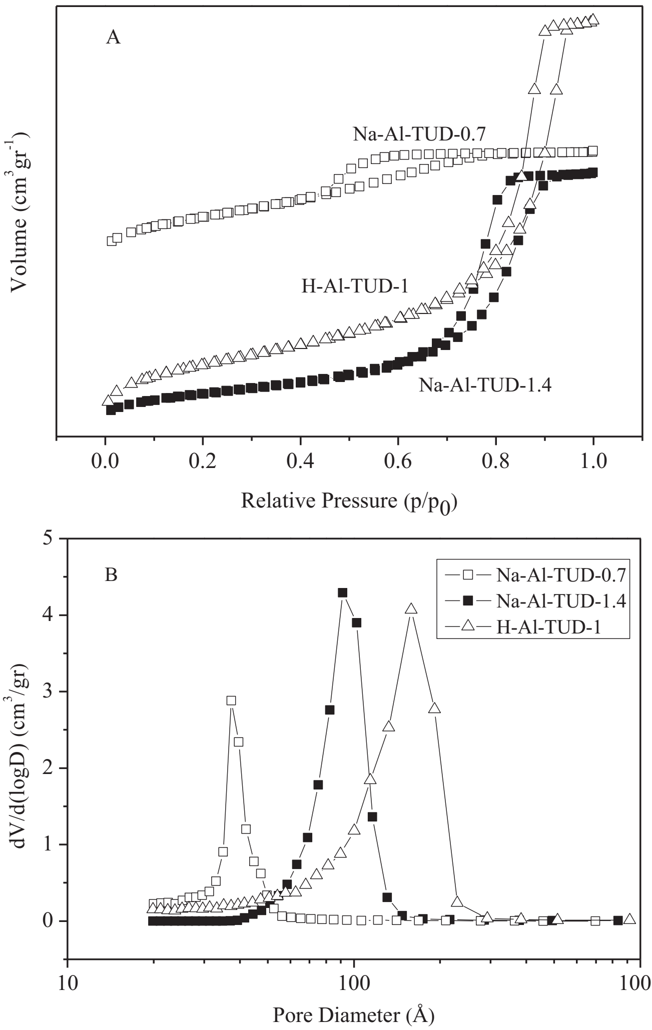


Fig. 2. N_2-physisorption isotherms (A) and pore size distribution (B) of Na-Al-TUD-1 and H-Al-TUD-1 samples.

For TUD-1 materials with a Si/Al ratio 30 it was described in the literature that complete framework incorporation as tetrahedral Al was achieved. However, this was due to crystallization and the formation of ZSM-5 in the TUD-1 structure [22]. In essence the material was ZSM-5 with a TUD-1 superstructure. Consequently a new approach had to be found. It is generally known that when aluminosilicates are synthesized in the presence of Na$^+$ aluminium becomes mainly tetrahedrally incorporated [23]. For mesoporous MCM-41 structural aluminium is thermally less stable than, for example, in zeolite Y, because the MCM-41 structure lacks strict crystallographic order at the atomic level and very small H$^+$ cations cannot satisfy the framework charge balance as efficiently as Na$^+$

Table 1
Data from ICP, N_2-physisorption and NH_3-TPD measurements of H-Al-TUD-1 and Na-Al-TUD-1 samples.

M-TUD-1	$n_{Si/Al}$ [b]	$n_{Na/Al}$ [b]	Tetrahedral aluminium (%)	S_{BET} ($m^2\,g^{-1}$)	$d_{P,BJH}$ (nm)	$V_{P,BJH}$ ($cm^3\,g^{-1}$)	NH_3-*TPD* ($mmol\,g^{-1}$)
H-Al-TUD-1	5.4	–	28	485	16	1.2	1.03
H-Al-TUD-1[a]	4	–	43	600	15	1.1	–
Na-Al-TUD-1.4	4.2	1.4	>95	255	9.1	0.8	0.85
Na-Al-TUD-0.7	3.6	0.7	>95	384	2.9	0.3	0.91
Na-Al-TUD-1.4-IE	3.3	0.06	33	165	16	0.71	0.37
Na-Al-TUD-0.7-IE	6.1	0.07	36	301	3.7	0.32	1.07

[a] Ref. [12].
[b] After calcination.

cations [24]. In the synthesis of Al-MCM-41 sodium aluminate was employed as source of Al. This ensured a high degree of structural order and all of the aluminium was in tetrahedral position [25–27]. However, our attempts to use either triethanolamine or tetraethylene glycol as a template with sodium aluminate in the TUD-1 synthesis, led to the synthesis of greyish material with a low surface area. We therefore turned our attention to NaOH to introduce Na^+ instead of protons as charge balance for the tetrahedral coordination of trivalent aluminium. In the synthesis of MCM-41, application of NaOH allowed the synthesis of MCM-41 with Si/Al ratio close to the Loewenstein limit (Si/Al ratio of 1) with all aluminium in tetrahedral coordination [28–30].

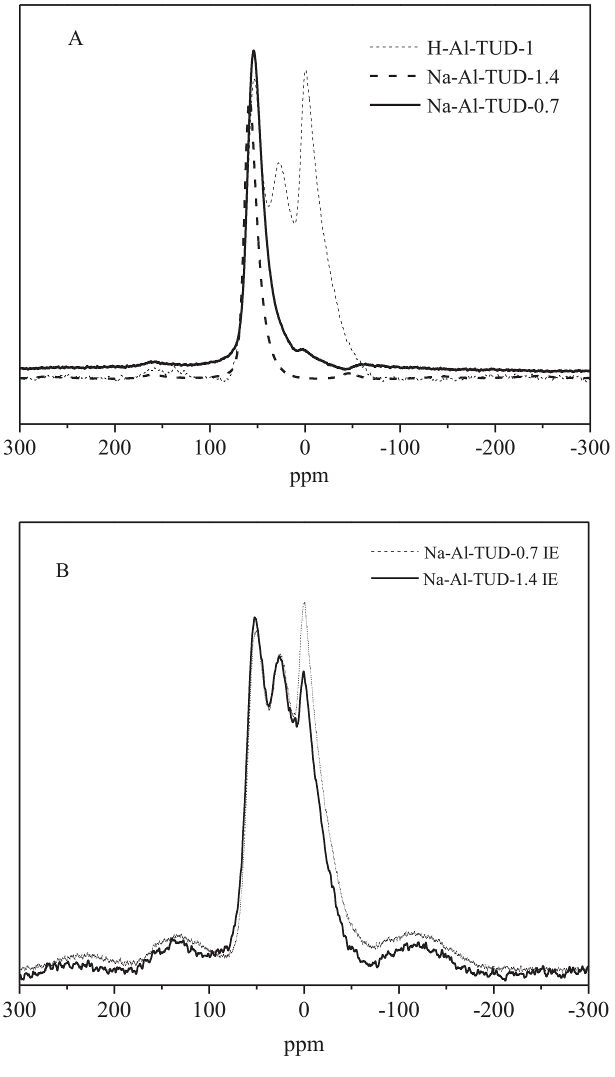


Fig. 3. ^{27}Al-MAS-NMR spectrum of H-Al-TUD-1 and Na-Al-TUD-1 samples (A) and ion-exchanged Na-Al-TUD-1 samples (B).

Applying NaOH during the synthesis two different samples Na-Al-TUD-1 were successfully synthesized. Triethanolamine rather than tetraethylene glycol (which is commonly used for synthesis of H-Al-TUD-1 materials with low Si/Al as it is easier to remove by calcination than triethanolamine) was employed as complexing reagent and aluminium isopropoxide as source of aluminium. The mesoporous character was demonstrated by XRD and N_2-physisorption measurements. XRD measurements revealed that both samples synthesized display a strong peak at low angles characteristic for mesoporous samples (0.8 2θ degrees, Fig. 1).

The type IV isotherm obtained from N_2-physisorption measurements further confirmed the mesoporous characteristics of these materials (Fig. 2). Their hysteresis loops are different from those found in the H-Al-TUD-1. For the sample having a higher amount of Na (Na-Al-TUD-1.4) the adsorption and desorption branches are almost vertical and nearly parallel belonging to H1 hysteresis loop characteristic for uniform, near cylindrical pores. In contrast Na-Al-TUD-0.7 displays a H4 hysteresis loop where the desorption branch is much steeper than the adsorption branch due to non-uniform pores.

The Na-Al-TUD-1 samples have a Si/Al ratio of around 4 (Table 1). For the sample with higher amount of sodium, Na-Al-TUD-1.4, the surface area is lower (255 $m^2\,g^{-1}$) compared with Na-Al-TUD-0.7 (384 $m^2\,g^{-1}$) due to presence of micropores. In contrast, the pore volume as well as pore size are larger for the sample Na-Al-TUD-1.4. Most importantly ^{27}Al-MAS-NMR proves beyond doubt that virtually all Al in the Na-Al-TUD-1 samples is tetrahedrally coordinated (Fig. 3, Table 1).

The synthesis of amorphous aluminosilicate of TUD-1 structure with well-defined tetrahedrally coordinated aluminium was achieved by in situ introduction of Na^+ as NaOH. This leads to decrease of surface area, pore volume as well as the pore size due to larger radius of the sodium cations in Na-Al-TUD-1 than is the case with protons in H-Al-TUD-1. Depending on the amount of sodium introduced uniform, near-cylindrical pores can be created yielding a more ordered TUD-1 based catalysts. Even with a Na/Al ratio lower than 1 almost all Al is tetrahedrally coordinated and a Na-Al-TUD-1 amorphous and mesoporous in nature as H-Al-TUD-1 is obtained. Clearly the presence of Na^+ during the synthesis of amorphous mesoporous TUD-1 materials leads to more defined heterogeneous catalysts. This approach leads to accessible tetrahedral aluminium sites inside the mesoprous Al-TUD-1 in contrast to micro/mesoporous TUD-1 composites containing tetrahedral aluminium sites in zeolitic channels that were described earlier [22]. Synthesis of amorphous three-dimensional Al-TUD-1 with nearly all of aluminium in tetrahedral coordination was achieved. Clearly all three types of Al-TUD-1 have a mesoporous structure and a typical rather amorphous organisation (Fig. 4).

For the catalytic activity the acidity of the materials is essential. While for immobilisation via ion exchange it is equally possible to utilize Na^+ or H^+ as a counter ion of the tetrahedral Al, in catalysis this is expected to play an important role. Acidity of these samples was therefore determined by NH_3-TPD (Fig. 5) [31]. The H-Al-TUD-1, as expected, displays higher total acidity than the Na-Al-TUD-1's.

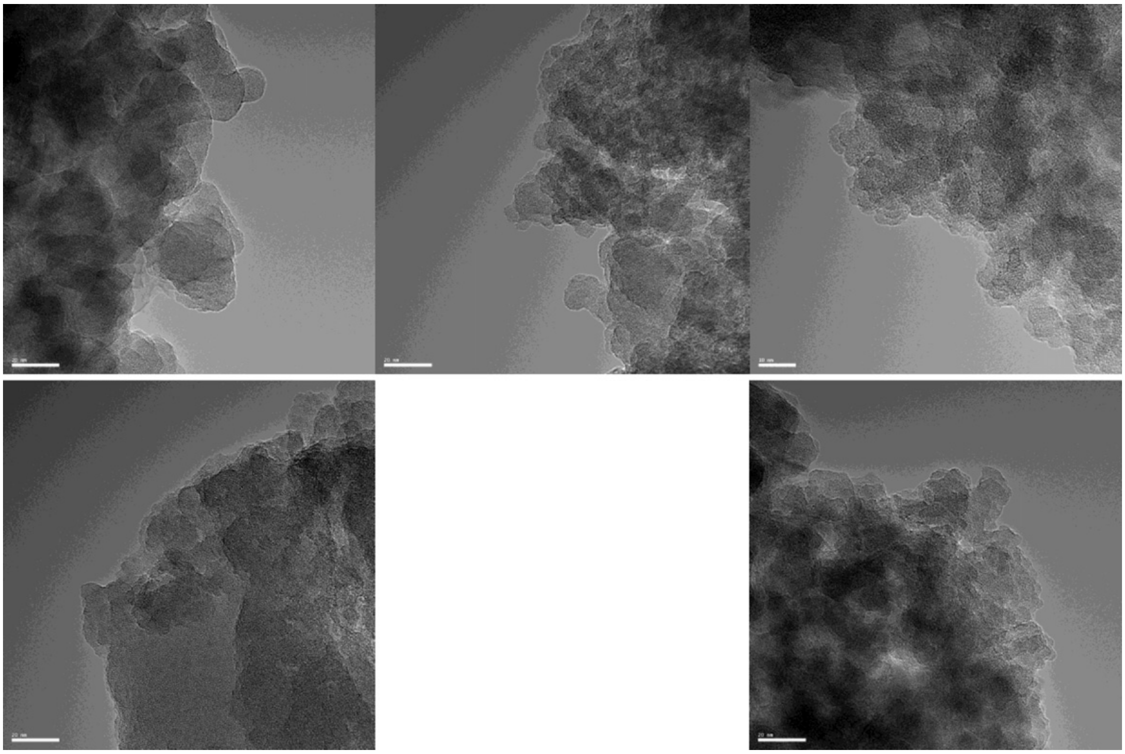


Fig. 4. TEM images of Na-Al-TUD-1.4 (upper left), Na-Al-TUD-0.7 (upper middle), H-Al-TUD-1 (upper right), Na-Al-TUD-0.7-IE (lower left) and Na-Al-TUD-1.4-IE (lower right). The bars represent 20 nm.

Again Na-Al-TUD-0.7 in which not all tetrahedral Al is balanced by a sodium ion is more acidic than Na-Al-TUD-1.4.

To impart Brønsted acidity to the Na-Al-TUD-1 materials an ion exchange was performed. With ammonium chloride an almost complete exchange of Na^+ against H^+ was achieved (Table 1). For Na-Al-TUD-0.7-IE acidity similar to H-Al-TUD-1 was achieved in terms on number of acid sites. In terms of acid strength Na-Al-TUD-0.7-IE possesses slightly higher amount of medium to strong acid sites (NH_3 desorption above 300 °C) and lower amount of weak acid sites compared to H-Al-TUD-1 (Fig. 5). For Na-Al-TUD-1.4-IE, however, a loss of structural integrity, surface area and pore size was observed, combined with a loss of acidity (Table 1, Fig. 5). Having comparable number of tetrahedrally coordinated aluminium as Na-Al-TUD-0.7-IE, and lower Si/Al ratio, not all of acid sites in Na-Al-TUD-1.4-IE seem to be accessible (compare NH_3 TPD results, Table 1, entries 5 and 6). Na ^{27}Al-MAS-NMR reveal that both ion-exchanged samples contained tetra-, penta- and hexa-coordinated Al (Fig. 3B). Clearly, they had undergone a structural rearrangement during ion-exchange. This is also visible in the TEM images (Fig. 4).

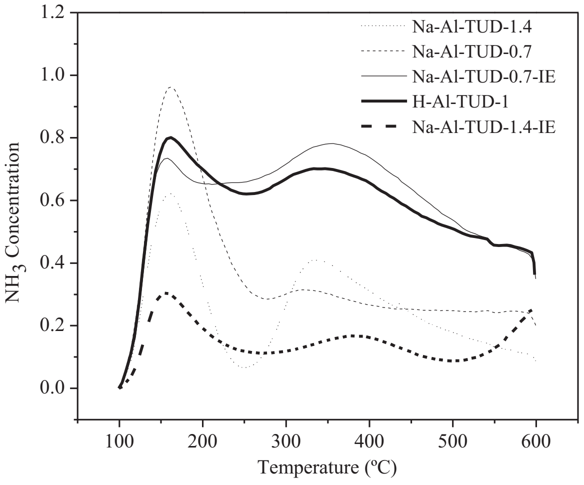
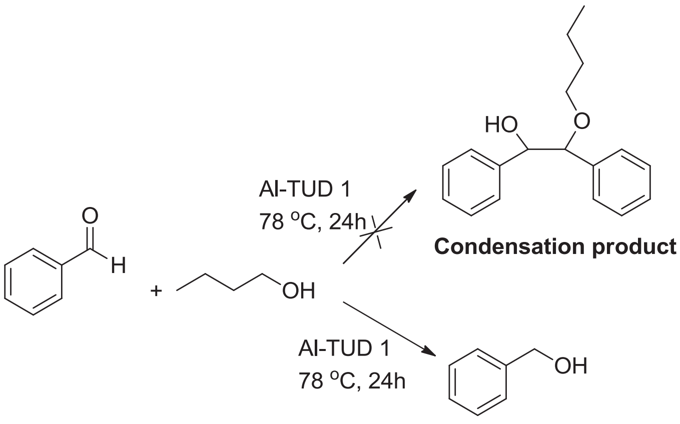


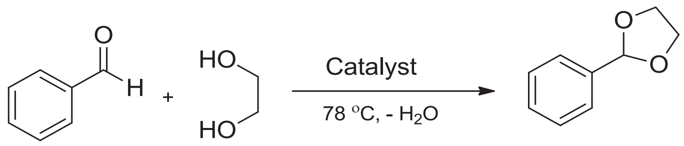
Fig. 5. TPD-NH_3 data of Na-Al-TUD-1.4, Na-Al-TUD-0.7, H-Al-TUD-1, Na-Al-TUD-0.7-IE and Na-Al-TUD-1.4-IE.

3.2. Catalysis

All Al-TUD-1 materials were studied for their catalytic activities. Two reactions viz. (i) reaction of benzaldehyde with *n*-butanol and (ii) the acid catalysed acetal formation by the reaction of benzaldehyde with ethylene glycol were studied, in order to ensure comparability with earlier studies. Earlier, Zhou et al. carried out the reaction of benzaldehyde with *n*-butanol using ZSM-5, TUD-1 and Al-TUD-1 [22]. The authors reported that an aldol reaction lead to the formation of an unusual condensation product (Scheme 2). Nevertheless, the structure of the condensation product reported



Scheme 2. Reaction of benzaldehyde with *n*-butanol.



Scheme 3. Reaction of benzaldehyde with ethylene glycol.

by Zhou et al. is not similar to the aldol product (β-hydroxy ketone) [32–34]. Therefore, we have tested the H-Al-TUD-1 catalyst for the reaction of benzaldehyde with *n*-butanol at 78 °C for 24 h. In our case, no condensation product was observed and the HPLC analysis revealed formation of benzyl alcohol (4%) (Scheme 2). The formation of benzyl alcohol can easily be explained with a Meerwein–Ponndorf–Verley reduction, a reaction that Al-TUD-1 was earlier shown to catalyse [35,36].

Furthermore, the catalysts were tested for the reaction between benzaldehyde and ethylene glycol (Scheme 3). All reactions were carried out at 78 °C for 24.5 h. It was found that, during the reaction of benzaldehyde with ethylene glycol the two Na-Al-TUD catalysts were virtually not active. Only Na-Al-TUD-0.7 having less sodium than the Na-Al-TUD-1.4 showed some activity, a yield of 5.6% of 2-phenyl-1,3-dioxolane was obtained after 24.5 h. Acidic H-Al-TUD-1 as a catalyst yielded 40% of 2-phenyl-1,3-dioxolane after 0.5 h which remained constant up to 24.5 h (Fig. 6). Furthermore, ion-exchanged H-Al-TUD-1.4-IE and H-Al-TUD-0.7-IE were used for the reaction of benzaldehyde with ethylene glycol under similar reaction. The H-Al-TUD-1.4-IE and H-Al-TUD-0.7-IE catalysed reactions gave a maximum yield of 51% and 53% after 4 h and 2 h respectively (Fig. 6).

The ion-exchanged materials are acidic and thus display catalytic activity. Maximum yield of 2-phenyl-1,3-dioxolane is achieved after 2 h; the reaction proceeds a little slower, possibly due to the reduced surface area. Also the presence of residual sodium inside the Al-TUD-1 materials and other structural changes could have induced this.

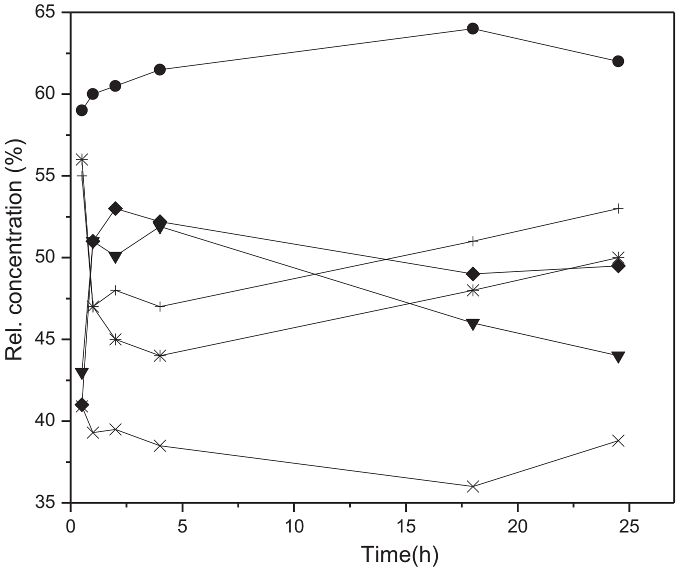


Fig. 6. (i) Composition of reaction mixture containing 2-phenyl-1,3-dioxolane (•) and benzaldehyde (×) as function of time during H-Al-TUD-1 catalysed condensation reaction, (ii) composition of reaction mixture containing 2-phenyl-1,3-dioxolane (▼) and benzaldehyde (+) during H-Al-TUD-1.4-IE catalysed condensation reaction and (iii) composition of reaction mixture containing 2-phenyl-1,3-dioxolane (♦) and benzaldehyde (*) during H-Al-TUD-0.7-IE catalysed condensation reaction.

Even though the adjusted synthesis procedure of H-Al-TUD-1 (introducing additional steps compared to earlier published synthesis method [12]) does not lead to increased catalytic performance in selected reactions, the presence of sodium instead of protons as counter ions certainly provides interesting application possibilities as a carrier instead of being a catalyst itself.

4. Conclusions

We have successfully synthesized all tetrahedral aluminium inside an amorphous mesoporous material of TUD-1 structure with a low Si/Al ratio. Tetrahedral aluminium is effectively stabilized only when sodium is employed as counter balancing cation. Upon ion-exchange, replacing sodium cations by protons, aluminium ions inside TUD-1 structure reverts back to combination of hexa-, penta- and tetrahedral coordination sites as seen by synthesis of H-Al-TUD-1 without the presence of a sodium salt. With sodium as counter ion the materials displayed low acidity and thus low catalytic activity. The synthesized Al-TUD-1 materials with protons as counter ions were catalytically active in the synthesis of 2-phenyl-1,3-dioxolane.

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