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# Al-RUB-41: a shape-selective zeolite catalyst from a layered silicate†

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**A new zeolite catalyst, Al-RUB-41, was synthesized for the first time. It was tested as a catalyst in methanol amination, and showed a shape-selective performance that results in a highly favorable product distribution. The shape-selective nature was also evidenced by using Pt-Al-RUB-41 as a bifunctional catalyst for decane hydroconversion. With its unique pore architecture and remarkable shape-selective character, Al-RUB-41 presents a significant commercial potential in industrial catalysis.**

Zeolites represent an important class of heterogeneous catalysts as they not only offer superior activity with high surface areas, but also provide shape/size selectivity. As a well-established family of nanoporous crystalline materials, zeolites are of paramount importance for the chemical industry, since shape/size selectivity is a vital consideration for many industrial catalytic processes.[1] Zeolites with small- and medium-pore systems (*i.e.*, 8MR and 10MR pore openings) are of great interest for the chemical industry due to the commercial potential they present in many processes dealing with molecules in this size regime. However, in the last couple of decades there was only limited success in the quest for new framework topologies with small- and medium-pores. Topotactic transformation of layered silicates into zeolitic frameworks offers promise as a prolific strategy for obtaining new framework topologies.[1] One of the recent zeolite structures discovered *via* this approach is RUB-41.[2] It is an all-silica zeolite obtained through the conversion of novel layered silicate RUB-39 into a three-dimensional zeolitic framework, which was assigned the structure code RRO.[3] Each new zeolite framework has the potential to offer unique features that can be beneficial for industrial applications; however, for applications in catalysis incorporation of functional T-atoms such as Al is essential. In this communication we describe the synthesis of Al-RUB-41 for the first time, where Al is introduced into the RRO framework following various methodologies and using a variety of starting materials. We also demonstrate the use of this new zeolite as a catalyst in methanol amination, which is an important test reaction since methylamines are critical intermediates in chemical industry and are extensively used for the synthesis of fine and specialty chemicals.[4]

In a recent liquid phase separations investigation, all-silica RUB-41 was shown to possess an intriguing pore architecture, which results in a unique shape-selective character.[5] The two-dimensional pore system is situated in the interlayer space formed *via* topotactic condensation of the RUB-39 layers. The dimensions of these intersecting 8- and distorted 10-membered ring channels were determined by structural analysis as 5.8 Å × 4.1 Å and 5.9 Å × 4.1 Å, respectively.[2,3]

In the literature the standard recipe for synthesis of all-silica RUB-39 takes 21 days at 150 °C using dimethyldipropylammonium hydroxide as the structure directing agent (SDA).[3] Controlled calcination of the resulting product results in the RUB-41 zeolite. In order to incorporate Al into the framework, we first developed a direct-synthesis recipe, where Al was introduced into the starting synthesis mixture as an additional ingredient. After 21 days of crystallization at 150 °C and subsequent calcination, a zeolite product with RRO topology could be obtained; however, characterization of the product revealed that the Al incorporation into the structure was limited. In order to increase Al incorporation and decrease crystallization duration —and thus increase productivity— a new synthesis procedure was developed where RUB-39 seed crystals were utilized. This seeding approach was first carried out using synthesis mixtures with $SiO_2/Al_2O_3$ = 200 and $SiO_2$/SDA = 2. After 15 days of crystallization at 140 °C and subsequent calcination, Al-RUB-41 was obtained. Powder X-ray diffraction (XRD) patterns of Al-RUB-39 and Al-RUB-41 are presented in Fig. 1. Elemental analysis showed that for this Al-RUB-41 product Si/Al is 120. Nitrogen adsorption/desorption experiments on Al-RUB-41 showed a high surface area (477 $m^2 g^{-1}$) and pore volume (0.36 $cm^3 g^{-1}$), indicating the presence of an open micropore system (Fig. S1, ESI†).

By slightly modifying the synthesis mixture composition ($SiO_2/Al_2O_3$ = 30) with same synthesis procedure, Al-RUB-41 product with a higher Al content (Si/Al ≈ 8) could also be obtained (Fig. S2, ESI†). Characterization of the products resulting from this seeded-synthesis approach using $^{27}Al$ NMR showed that Al was successfully incorporated into the framework and is exclusively present as tetrahedrally coordinated species (Fig. S3, ESI†). However, the crystallization duration was still considerably long, and therefore productivity was quite low for this synthesis recipe, especially considering potential scale-up of production for utilization in commercial applications. In order to overcome these obstacles

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† Electronic supplementary information (ESI) available: Detailed synthesis, characterization and catalytic testing procedures, XRD patterns, $N_2$-isotherms, $^{27}Al$ NMR results. See DOI: 10.1039/c0cc03895d

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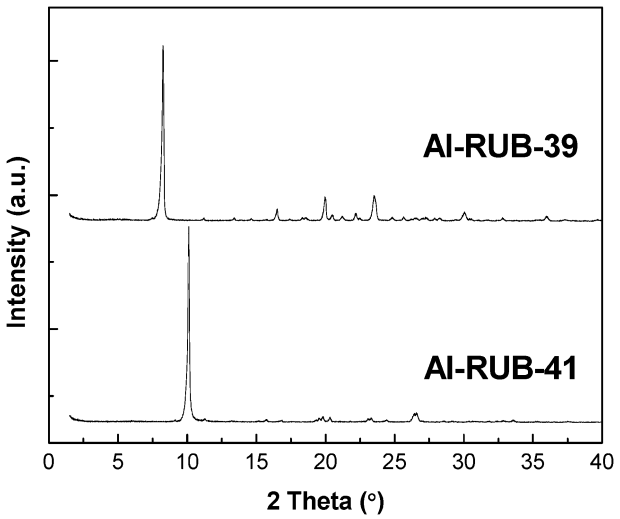


**Fig. 1** Powder XRD patterns of Al-RUB-39 and Al-RUB-41 prepared *via* the direct crystallization route (synthesis mixtures with $SiO_2/Al_2O_3$ = 200 and $SiO_2$/SDA = 2).

for industrial realization, a new two-step synthesis recipe was developed.

In the first step of this two-step procedure the silicate precursor, which also contains the SDA and the RUB-39 seed crystals (3–5% wt based on $SiO_2$), was prepared. The first crystallization step was conducted at 150 °C typically for durations between 12–48 hours. In the second step, the aluminium precursor was mixed with the silicate precursor obtained from the first step. The second crystallization step was performed at temperatures between 140–150 °C and the duration was between 24–48 hours. Detailed descriptions of typical synthesis procedures are available as ESI†; Powder XRD analyses before and after calcination, confirmed Al-RUB-39 and Al-RUB-41 topologies, respectively (Fig, S4, ESI†). The FE-SEM image of Al-RUB-41 presented in Fig. 2 depicts the typical platelet morphology observed for RUB-41. Local order and structural attributes of the new Al-RUB-41

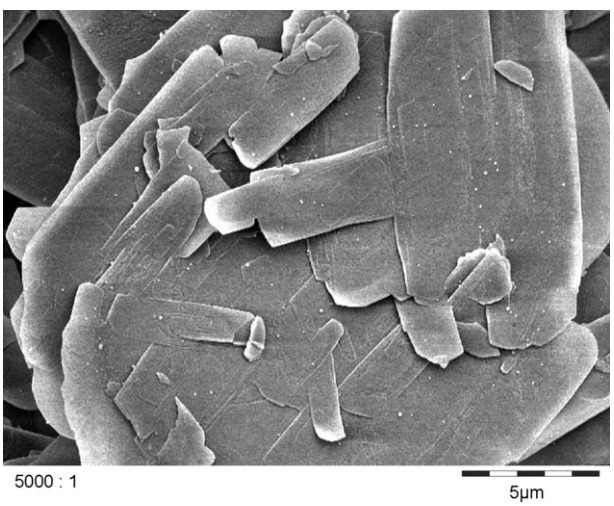


**Fig. 2** FE-SEM image of Al-RUB-41 obtained from the topotactic condensation of Al-RUB-39 prepared *via* the two-step crystallization route.

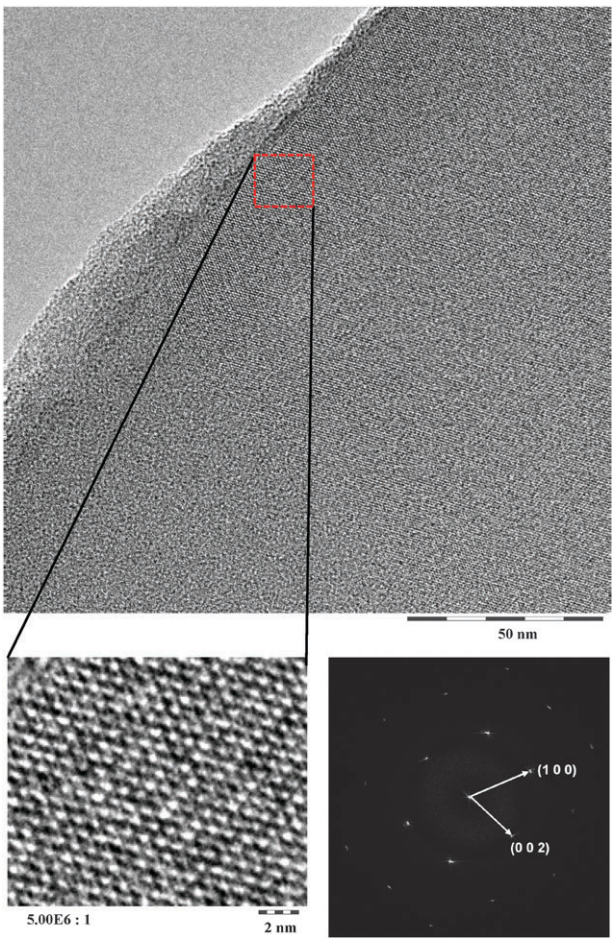


**Fig. 3** HR-TEM images (top and bottom-left) and ED pattern (bottom-right) of Al-RUB-41 obtained from the topotactic condensation of Al-RUB-39 prepared *via* the two-step crystallization route.

zeolite were also investigated using HR-TEM (Fig. 3). These findings suggest that Al incorporation did not markedly alter the textural and morphological features of the RRO-type material.

In Fig. 4 results of the methanol amination reaction on the H-form of the Al-RUB-41 catalyst obtained from the two-step crystallization route are presented. These preliminary reaction tests were performed at 340 °C with a $NH_3/CH_3OH$ ratio of 2, and demonstrated that the Al-RUB-41 catalyst is highly active and shape-selective. After one hour methanol conversion was 83%, and the product selectivities were 49% monomethylamine (MMA), 40% dimethylamine (DMA) and 11% trimethylamine (TMA). In methanol amination thermodynamics favor TMA formation, and under these reaction conditions the thermodynamic equilibrium results in 20% MMA, 27% DMA and 52% TMA.[6] Using the shape-selective Al-RUB-41 catalyst, a much more favorable product distribution is obtained since the worldwide demand for MMA and DMA is significantly higher than the TMA demand.[4]

Shape selectivity was also evidenced by using Pt-loaded Al-RUB-41 (0.5 wt% Pt) as a bifunctional catalyst for decane hydroconversion (WHSV = 2252 kg s $mol^{-1}$, $H_2$ pressure = 4.5 bar, $H_2$/decane = 300). A maximum isomerisation selectivity of 19% was obtained at 230 °C at

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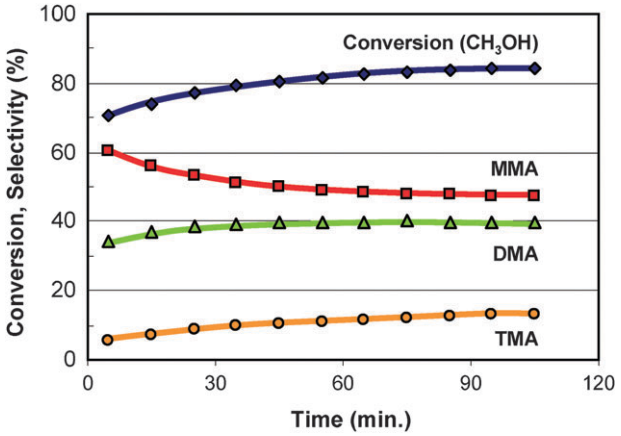


**Fig. 4** Synthesis of methylamines at 340 °C with a $NH_3/CH_3OH$ ratio of 2 on Al-RUB-41 catalyst obtained from the two-step crystallization route.

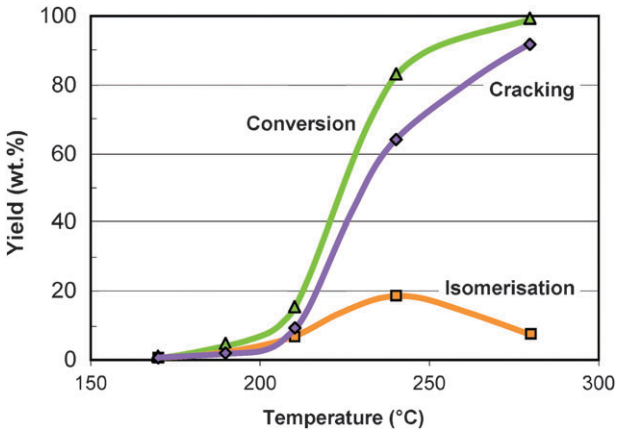


**Fig. 5** Results of hydroconversion of decane experiments on Al-RUB-41 loaded with 0.5 wt% Pt (Al-RUB-41 obtained from the two-step crystallization route).

83% decane conversion (Fig. 5). The methylnonane isomer distribution gives an insight on the spaciousness of the pore structure (Fig. 6). If methylnonane formation from decane were statistical, one would obtain the following distribution: 2-$MeC_9$ 17%, 3-$MeC_9$ 33%, 4-$MeC_9$ 33%, 5-$MeC_9$ 17%.[7] In zeolites with smaller cavities and 10-membered ring pores, the formation of 2-$MeC_9$ is favored at the expense of especially 4- and 5-$MeC_9$. The ratio 2-$MeC_9$/5-Me-$C_9$ for ZSM-5 is between 6.8–9.4, for zeolite Beta between 1.4–2.9 and for Mordenite 1.8. The ratio for Al-RUB-41 is around 4, clearly demonstrating the shape-selective properties of this catalyst.

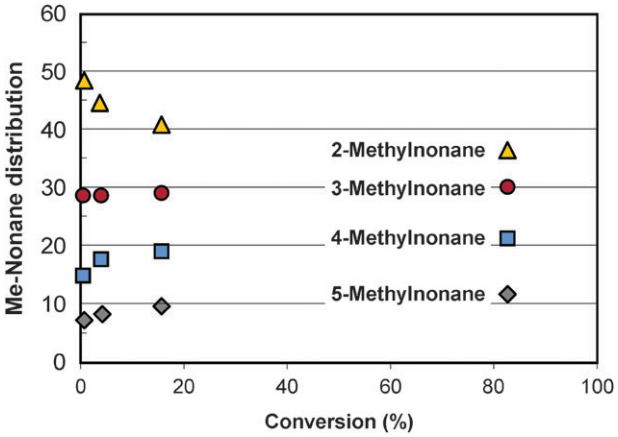


**Fig. 6** Methylnonane distribution at various decane conversion levels on Al-RUB-41 loaded with 0.5 wt% Pt (Al-RUB-41 obtained from the two-step crystallization route).

In conclusion, we have synthesized Al-RUB-41 for the first time. We have also demonstrated the use of this new zeolite as a catalyst in methanol amination and decane hydroconversion. It was verified that Al-RUB-41 is a highly active, stable and shape-selective catalyst. Additional experimental work on synthesis of methylamines is being performed using Al-RUB-41 catalysts with varying Si/Al ratios. Incorporation of other functional T-atoms such as Ga, Zn, B and Ti into the RUB-41 framework is also being carried out. Findings from these investigations will be reported in detail elsewhere.

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