Journal of Catalysis 278 (2011) 246–252

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Shape-selective synthesis of methylamines over the RRO zeolite Al-RUB-41

Bart Tijsebaert [a], Bilge Yilmaz [b], Ulrich Müller [b], Hermann Gies [c], Weiping Zhang [d], Xinhe Bao [d], Feng-Shou Xiao [e], Takashi Tatsumi [f], Dirk De Vos [a,*]

[a] Centre for Surface Chemistry and Catalysis, K.U.Leuven, Kasteelpark Arenberg 23, 3001 Leuven, Belgium
[b] BASF AG, GCC/Z M 301, Ludwigshafen, Germany
[c] Institute für Geologie, Mineralogie und Geophysik, Ruhr-Universität Bochum, Germany
[d] State Key Laboratory of Catalysis, Dalian, China
[e] State Key Laboratory of Inorganic Synthesis and Preparative Chemistry, Jilin University, Changchun, China
[f] Tokyo Institute of Technology, Yokohama, Kanagawa, Japan

ARTICLE INFO

Article history:
Received 10 September 2010
Revised 8 December 2010
Accepted 16 December 2010
Available online 28 January 2011

Keywords:
Methylamine synthesis
Amination
Catalysis
Zeolite
Synthesis
Layered materials
Monomethylamine
Dimethylamine
Ammonia

ABSTRACT

Aluminum was incorporated into the layered silicate RUB-39, which is transformed by calcination into RUB-41. This new zeolite with RRO topology contains 8- and 10-ring pores, and the acid sites in the aluminated material catalyze the synthesis of methylamines, in particular mono- and dimethylamine, by amination of methanol. Owing to the shape-selective catalytic properties of (H)Al-RUB-41, low selectivity to the thermodynamically favored trimethylamine product is obtained in comparison with results on RUB-39 or non-shape-selective materials. Both activity and selectivity are highest for RUB-41 catalysts with a high Si to Al ratio. Silylation reduces the number of unselective sites and results in a further suppression of trimethylamine formation. The introduction of acidity in the intact RUB-41 structure is supported by Al-MAS NMR and NH_3-TPD data. Additional characterization by XRD and SEM is provided.

1. Introduction

Zeolites are widely used as heterogeneous catalysts in the chemical industries for the production of petrochemicals, fine chemicals, etc. Their high surface area, well-defined pore structure, and tunable acidity constitute an appropriate basis to catalyze a broad scope of transformation processes. As each process requires different types of catalysts and because of the permanent quest for more sustainable catalytic processes, there are constant efforts to develop new zeolite materials with improved catalytic properties, for example, resulting in higher product selectivities [1].

Recently, innovative synthesis pathways have been developed wherein layered silicates are transformed into three-dimensional silicate frameworks. For example, zeolites like MWW [2], EU-20b [3], CDS-1 [4], Nu-6(2) [5], and RWR [6] were synthesized by conversion of the layered silicates ERB-1 [2], EU-19 [3], PLS-1 [4], Nu-6(1) [5], and RUB-18 [6]. Similar research led to the development of the all-silica RUB-41 zeolite with RRO topology starting from the layered material RUB-39. After the topotactic layer condensation to RUB-41, a two-dimensional pore system is created in between the layers. The pore system comprises intersecting 8- and 10-membered ring pores. From structure analysis, their dimensions are determined as 5.8 Å × 4.1 Å (8MR) and 5.9 Å × 4.1 Å (10MR) [7]. In previous work, we demonstrated the selective adsorption of 2-butenes out of a mixture of the four butene isomers on such an all-silica RUB-41 zeolite. *Trans*-2-butene, with a critical diameter of 0.431 nm, and *cis*-2-butene, with a critical diameter of 0.494 nm, were preferred in the adsorption over 1-butene and isobutene. This selectivity was ascribed to the distorted 10-rings present in RUB-41 [8] and suggests that the effective diameter of these 10-rings is hardly larger than that of the 8-ring windows.

In the present work, aluminum was introduced into the RUB-41 structure via various routes, which results in a catalytically active aluminosilicate material. As a test reaction, (H)Al-RUB-41 was employed in the synthesis of methylamines from methanol and ammonia. Methylamines are widely used intermediates in the synthesis of fine and specialty chemicals, for instance in the synthesis of pharmaceuticals (e.g., theophylline), pesticides, or surfactants. In the methanol amination reaction, monomethylamine (MMA), dimethylamine (DMA), trimethylamine (TMA), and water are the typical reaction products [9]. The thermodynamic equilibrium

---

[*] Corresponding author.
E-mail address: dirk.devos@biw.kuleuven.be (D. De Vos).

0021-9517/$ - see front matter © 2010 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2010.12.010

and thus product distribution are controlled by the ratio of ammonia versus methanol as well as by the reaction temperature. For thermodynamic reasons, TMA is predominantly formed, but the demand for monomethylamine and dimethylamine is much higher. Therefore, an ammonia excess and a recycle of undesired TMA are often applied in the process. However, this approach requires expensive purification steps, also because of the azeotropic mixtures intermediately formed. To overcome these limitations, shape-selective catalysts have been introduced [10].

The first commercially available shape-selective catalysts were applied by Nitto and consisted of a mordenite treated with tetraethoxysilane to enhance the selectivity to the mono- and dialkylated amines [11]. A large body of further work focused on the shape-selective properties of small pore zeolites containing typically cages that can be accessed via 8-membered ring pore windows [12–19]. Active and selective amination catalysts are for instance H-Rho, H-chabazite, and H-levyne zeolites. The windows of the cages in these materials are sufficiently small to prevent the egress of trimethylamine.

In this work, we report on the activity and shape-selective properties of (H)Al-RUB-41 in methanol amination. As is apparent from the literature background, this reaction is a sensitive one to detect even minor amounts of non-selective sites. Important questions are whether the RUB-41 pore system of 8-rings and distorted 10-rings may allow shape-selective methanol amination and whether the Al-siting can be controlled so as to mostly generate active sites only in a shape-selective environment. The effect of aluminum content on selectivity and conversion and the influence of post-synthesis modification by a silylating agent will also be investigated.

2. Experimental

2.1. Catalyst preparation

Different Al-RUB-41 materials with varying Al content were synthesized. Typically, the molar composition of the synthesis gel in the first step was 1 SiO_2: 0.5 SDA: 0–0.08 NaOH: 2–10 H_2O. Dimethyldipropylammoniumhydroxide was used as structure-directing agent (SDA). After aging of the gel for 1 h at room temperature, it was kept in Teflon-lined stainless steel autoclaves and stirred at a temperature of 140 or 150 °C at 15 rpm for 2–4 days. Seeding crystals of RUB-39 were added to shorten crystallization times. After this first stage, the synthesis mixture was cooled, and a minute amount of Al isopropoxide or $NaAlO_2$ was added to the gel. This was carried out using synthesis mixtures with SiO_2/Al_2O_3 = 30–200 and SiO_2/SDA = 2.

Crystallization was continued for another 2–4 days. The as-synthesized, layered Al-RUB-39 material was converted to Al-RUB-41 by slow heating at 1 °C/min until 520 °C in a furnace under static air. After 12 h at this temperature, heating was continued until 560 °C for 4 h.

To eliminate any Na^+ that could be present as a residue from the synthesis, samples were three times ion-exchanged in a solution of 0.5 M NH_4NO_3 at 80 °C for 24 h and washed with distilled water. Next, these samples were dried at 70 °C and calcined for 6 h in a furnace under static air with a constant temperature increase of 1 °C/min from 20 °C to 450 °C. Silylation was performed with a hexamethyldisilazane (HMDS) treatment. One gram of the calcined(H)Al-RUB-41 catalyst was dried at 200 °C and added to a solution of 0.38 g HMDS in 10 g toluene. The resulting mixture was refluxed under N_2 atmosphere at 120 °C for 2 h. The silylated sample was filtered, abundantly washed with toluene, and subsequently dried at 70 °C [20]. A sample designation list can be found in Table 1. Al-RUB-41 could be synthesized with different Si/Al ratios. Samples A1–A4 were synthesized using aluminum isopropoxide; sample B was synthesized using sodium aluminate.

Table 1
Overview of Al-RUB-41 samples employed.

	Al source	Si/Al	BET (m^2/g)	NH_3 mmol g^{-1} adsorbed
A1	Al isopropoxide	19	69	0.413
A2	Al isopropoxide	25	412	0.285
A3	Al isopropoxide	51	350	0.156
A4	Al isopropoxide	163	323	0.062
B	Sodiumaluminate	20	270	0.218

ZSM-5 CBV 2314 was obtained from ZEOLYST and has a Si/Al ratio of 20. A chabazite sample (Si/Al = 16) was obtained from BASF Ludwigshafen. XRD showed the pattern of pure and fully crystalline chabazite (checked as-synthesized and after ion exchange). FE-SEM analysis showed the typical cube morphology. Al-MCM-41 (Si/Al = 10) was synthesized according to a modified Stoeber method [21].

2.2. Characterization

^{27}Al MAS NMR spectra of the samples were acquired on a Varian Infinity Plus-400 spectrometer at 104.2 MHz using a 4 mm MAS NMR probe head with a spinning rate of 10 kHz. Chemical shifts were referenced to $(NH_4)Al(SO_4)_2{\cdot}12H_2O$ at −0.4 ppm as a secondary reference. All spectra were accumulated for 12,000 scans with a $\pi/4$ flip angle and a 2-s pulse delay. The X-ray powder diffraction analysis was carried out with a Siemens 5000D diffractometer using CuKα radiation (λ = 0.15401 nm). Nitrogen adsorption isotherms were determined by physisorption of nitrogen at 77 K on a Coulter Omnisorp 100 CX. Prior to measurements, the samples were outgassed under vacuum at 473 K overnight. SEM micrographs were recorded using a Philips XL30 FEG. The temperature-programmed desorption of ammonia (NH_3-TPD) experiments were performed using a Micromeritics AutoChem II 2920 automated chemisorption analysis unit with a thermal conductivity detector (TCD) under helium flow. The sample was heated with a temperature ramp of 20 °C/min–500 °C under He flow. After staying at that temperature for 10 min, it was cooled down to 100 °C in He atmosphere. Ammonia saturation was carried out at 100 °C using a 10% NH_3–He gas mixture. After saturation, excess ammonia was purged from the chamber under flowing He at 100 °C for 1 h. The desorption step was performed with a temperature ramp of 10 °C/min up to 500 °C under He flow. Desorbed species were observed with the on-line mass spectroscopy unit, which confirmed that the TCD signal indeed corresponded to ammonia desorption.

2.3. Catalytic experiments

Catalytic experiments were performed in a continuous flow fixed-bed reactor. Prior to reaction, 200 mg of calcined zeolite sample in the H^+-form was pelletized. Pelletizing was done by pressing the catalyst between 2 iron bolts at 200 bar followed by sieving to obtain the 250–500 μm fraction. Then, the catalyst was pretreated in the reactor at 400 °C under a helium flow of 5.6 mL/min. Thereafter, the reactor was cooled to reaction temperature (300 or 340 °C). The reaction was carried out by feeding the reactor with a 1:1 or a 2:1 mixture (on mole basis) of ammonia and methanol diluted in helium. Methanol was fed to the reactor by passing a helium flow through a methanol-filled saturator. Mass flow controllers enabled to adjust the ammonia to methanol ratio. Typically, the gas flow of a 2:1 mixture contained 1.6 mL/min NH_3 and 5.6 mL/min MeOH+He, or reactant partial pressures of 22.5 kPa NH_3 and 11.25 kPa MeOH, which resulted in a WHSV of 0.66 g_{feed} $g^{-1}_{catalyst}$. For a 1:1 mixture, gas flows of 0.8 mL/min NH_3 and