CHINESE JOURNAL OF CATALYSIS
Volume 32, Issue 4, 2011
Online English edition of the Chinese language journal

Cite this article as: Chin. J. Catal., 2011, 32: 532–535.

RESEARCH PAPER

Zr-MCM-41 Nanoreactors as Efficient and Reusable Catalysts in the Synthesis of New Aminonitriles by the Strecker Reaction

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Abstract: The synthesis and characterization of Zr-MCM-41 nanoreactors and their catalytic activity in the synthesis of new amino nitrile derivatives by the Strecker reaction in high yields and in short reaction times is reported.

Key words: Zr-MCM-41; Strecker reaction; aminonitrile; three component one-pot reaction

The three-component condensation of aldehydes, amines, and trimethylsilyl cyanide (TMSCN) in the Strecker reaction is an important reaction in organic synthesis. The products are α-aminonitrile derivatives, which are versatile intermediates that can be transformed into a variety of building blocks such as α-amino acids, 1,2-diamines, and nitrogen-containing heterocycles [1]. A variety of acid catalysts have been used in this reaction [2–8]. The tedious work-up procedure, long reaction time, toxic catalysts, and the use of an inert atmosphere are some of the drawbacks of these methods. For example, Al-MCM-41 has been used under an argon atmosphere [8].

New green legislation requires a decrease in waste creation and the use of more environmentally friendly alternative catalysts, which makes the current homogeneous organic reactions environmentally unacceptable [9].

Considerable attention has been given to M41S (Mobil Composition of Matter) mesoporous materials but particularly the MCM-41 family because of their unique properties [10–12]. They have high specific surface areas, high pore volumes, and tunable pore sizes with a narrow distribution. However, Si-based MCM-41 exhibits only mild acidity, which is much weaker than that of the microporous zeolites [13]. The incorporation of zirconium into the MCM-41 framework increases both the Lewis and Brönsted acidity [13].

Herein, we report a new approach toward the synthesis of Zr-MCM-41, its characterization, and its catalytic activity in a three-component one-pot synthesis of α-aminonitrile derivatives by condensing aldehydes, amines, and trimethylsilyl cyanide.

1 Experimental

1.1 Preparation of Zr-MCM-41

Fumed silica (8 g) was added to a solution of sodium hydroxide (2 g) in distilled water (150 ml) in a baker at 80 °C. The resulting mixture was continuously stirred until a clear solution was obtained. Cethyltrimethyl ammonium bromide (CTAB, 3 g) was slowly added to this solution under vigorous stirring at room temperature. The resulting gel was stirred for an additional 2 h. In the next stage zirconium (IV) oxide chloride octahydrate (5 g) was dissolved in distilled water (100 ml) by adding concentrated H_2SO_4 (2.5 ml) until a clear solution was obtained. This solution was added to the resulting gel in a dropwise manner over 2 h under vigorous stirring. The obtained gel was transferred into a Teflon-lined stainless steel autoclave for hydrothermal treatment at 100 °C over 3 d. The resulting solid product was recovered after filtration and washing several times with deionized water. The obtained white solid was dried in air at 100 °C for 5 h. Finally, the

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Received 1 November 2010. Accepted 15 December 2010.

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DOI: 10.1016/S1872-2067(10)60189-1

sample was calcined at 600 °C for 16 h in air. The heating rate was 1.5 °C/min and the molar ratio of Si/Zr was 8.

1.2 Characterization of Zr-MCM-41

X-ray diffraction (XRD) patterns were obtained using a Siefert 3003 PTS diffractometer with Cu K_α radiation (λ = 0.15406 nm). Fourier transform infrared (FT-IR) spectra were recorded using a Bruker Tensor 27 IR spectrometer and KBr pellets in a range of 400–4000 cm^{-1} under atmospheric conditions. Scanning electron micrographs (SEM) were obtained on a Holand Philips XL-30 microscope with an accelerating voltage of 25 kV. The sample was deposited on a sample holder with an adhesive carbon foil and sputtered with gold. Nitrogen adsorption studies were performed at liquid nitrogen temperature using a BELSORP-miniII.

1.3 Synthesis of α-aminonitrile derivatives

All solvents and reagents were purchased from Aldrich and Merck and were of high-grade quality, and used without any purification.

In a general procedure, a solution of an aromatic aldehyde (1 mmol), a primary amine (1.2 mmol), TMSCN (1 mmol), and Zr-MCM-41 (0.03 g) in CH_3CN (5 ml) was stirred under reflux conditions for an appropriate time. After reaction completion (monitored by TLC) the catalyst, which is not soluble in boiling acetonitrile, was easily filtered off and the mixture was cooled to room temperature. The solid products were collected by filtration, washing with water and aqueous ethanol, and purified by recrystallization from ethanol. For the oily products the reaction mixture was poured into distilled water (15 ml) and the product was extracted with chloroform (20 ml × 2) and dried over $MgSO_4$. The solvent was removed under reduced pressure and crude product was purified by column chromatography over silica gel (hexane–Et_2O). Compounds 1, 2, and 3 are new products (Scheme 1) and the other products are known compounds, and their physical and spectroscopic data have been reported in the literature. Melting points were measured using the capillary tube method with an electrothermal 9200 apparatus. ^1H NMR spectra were recorded on a Bruker AQS AVANCE-300 MHz or a 500 MHz spectrometer using TMS as an internal standard ($CDCl_3$ or DMSO-d_6 solution).

Compound 1: 2,2'-(1,4-phenylene)bis(2-(4-methylbenzylamino)acetonitrile). ^1H NMR (300 MHz, $CDCl_3$): δ 1.86 (2H, br. s, 2NH), 2.03 (6H, s, 2Me), 3.86 (4H, s, $2CH_2$), 6.92 (4H, d, J = 9 Hz, $4CH_{Ar}$), 7.33 (4H, d, J = 9 Hz, $4CH_{Ar}$), 7.60 (4H, s, $4CH_{Ar}$). Mass: 395.3, 373.4. Anal. Calcd (%): C, 79.16; H, 6.64; N, 14.20; Found: C, 78.76; H, 6.44; N, 14.50.

Compound 2: 2-(4-chlorophenyl)-2-(4-morpholinophenylamino)acetonitrile. ^1H NMR (300 MHz, $CDCl_3$): δ 3.06–3.09 (4H, m, $2CH_2$), 3.85–3.88 (4H, m, $2CH_2$), 5.36 (1H, d, J = 9, CH), 6.77 (2H, d, J = 9 Hz, $2CH_{Ar}$), 6.92 (2H, d, J = 9 Hz, $2CH_{Ar}$), 7.44 (2H, d, J = 9 Hz, $2CH_{Ar}$), 7.57 (2H, d, J = 9 Hz, $2CH_{Ar}$).

Compound 3: 2-(2-(1H-imidazol-4-yl)ethylamino)-2-(4-chlorophenyl)acetonitrile. ^1H NMR (300 MHz, $CDCl_3$): δ (2H, t, J = 6, CH_2), 2.96–3.09 (2H, m, CH_2), 4.81 (1H, s, CH), 6.84 (1H, s, CH_{Ar}), 7.35–7.46 (4H, m, $4CH_{Ar}$), 7.56 (1H, s, CH_{Ar}). Mass (m/z): 260, 254, 234. Anal. Calcd (%): C, 59.89; H, 5.03; Cl, 13.60; N, 21.19; Found: C, 59.95; H, 5.13; N, 21.19.

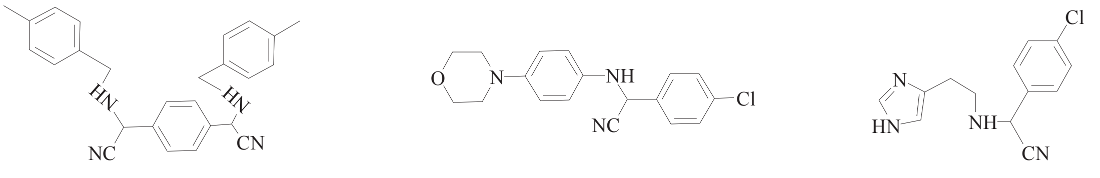
1.4 Recycling the catalyst

The catalyst is not soluble in boiling acetonitrile and it was removed by hot filtration after reaction completion. In the synthesis of 2-(4-chlorophenyl)-2-(4-methylbenzylamino) acetonitrile the catalyst was recovered three times, washed with diethyl ether, and reused in a similar reaction.

2 Results and discussion

Mesoporous silicate materials contain a chemically inert silicate framework. To induce specific catalytic activity researchers have tried to incorporate a variety of metals into the mesostructure by either direct synthesis/ion-exchange or impregnation. Among the transition metals, zirconium is considered to be important because of the possible strong polarization of the $Si–O^{-\delta}\cdots Zr^{+\delta}$ linkages [14].

The surface acidity of the mesoporous solids is significantly influenced by the incorporation of zirconium ions into the framework. The addition of zirconium creates Brönsted acid sites and also enhances the acid strength of both the Lewis and Brönsted acid sites. The diameter of Zr^{4+} is much larger than that of Si^{4+} and when smaller Si^{4+} ions are replaced by larger Zr^{4+} ions in the framework of the solid the bond length of Zr–O–Si clearly differs from that of Si–O–Si. This must lead to the deformation of some structures and the generation of mi-



Compound 1 Compound 2 Compound 3

Scheme 1. Structure of compound 1, 2, and 3.