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Scientific paper

N-Functionalized L-Proline Anchored MCM-41: A Novel Organic–Inorganic Hybrid Material for Solvent-Free Aminolysis of Styrene Oxide under Microwave Irradiation

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Abstract

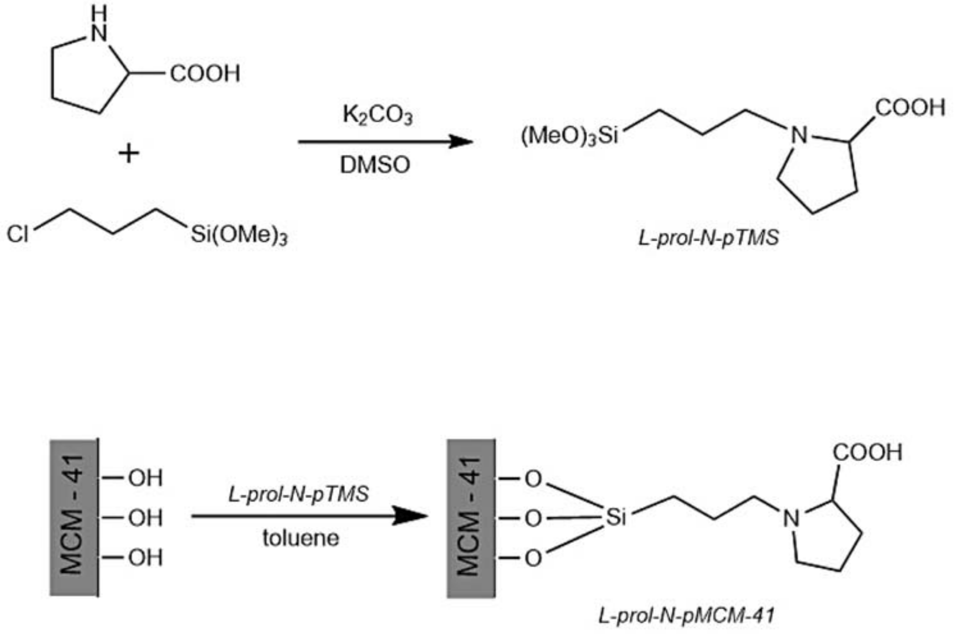
A novel organic–inorganic hybrid material, namely L-prol-N-pMCM-41, was synthesized via two steps by covalently anchoring N-functionalized proline derivative (L-prol-N-pTMS) into the pore channels of MCM-41 silica. The prepared material was characterized by X-ray diffraction (XRD), thermogravimetric analysis (TGA), nitrogen adsorption–desorption isotherm, Brunauer–Emmett–Teller (BET) surface area analysis, and Fourier Transform Infrared spectroscopy (FTIR). The immobilized catalyst demonstrated moderate to high catalytic activity and excellent regioselectivity for the ring opening of styrene oxide with aniline derivatives under microwave irradiation and solvent-free conditions. The catalyst could be rapidly separated from the reaction mixture and reused up to five runs with good conversion and high regioselectivity.

Keywords: Organic-inorganic hybrid material; Heterogeneous catalysis; Regioselectivity; β-Amino alcohols

1. Introduction

Design and synthesis of surface functionalized ordered mesoporous silica materials have attracted much attention in recent years, due to their applications in the fields of catalysis,[1] adsorption,[2] ion-exchange[3] and sensing.[4] Functionalization of mesoporous silicas with various organic groups has been implemented via post-synthesis grafting and organosiloxane/siloxane co-condensation. Rational design of these materials using suitable organic functionalities gives rise to smart mesoporous materials, which can have potential applications in many other frontier areas of science.[5] Indeed, hybrid materials with organic–inorganic character represents not only a new field of basic research but also offers prospects for many new applications (via their remarkable new properties and multifunctional nature) both from the academic and industrial vantage point.[6] One of the convenient approaches to synthesize organofunctionalized mesoporous material is to anchor the desired functionalities on high surface area silica matrices. The covalently anchored organic moieties due to the strong covalent bonding to the silica surface are expected to be more resistant to leaching of the active centers during the catalytic reactions; this can improve catalyst recycling.[7]

The ring-opening reaction of epoxides with amines represents one of the most important and straightforward methods for preparing β-amino alcohols, which are versatile synthons in the synthesis of biologically active natural and synthetic products, unnatural amino acids and chiral auxiliaries.[8] Aminolysis of epoxides is an acid-catalyzed reaction. Among the catalysts reported for this type of reaction, Lewis acid catalysis is the most widely adopted method for epoxide ring openings with amines, e.g., $BiCl_3$,[9] VCl_3,[10] $ZrCl_4$,[11] $Al(OTf)_3$,[12] $Sc(OTf)_3$,[13] $Sm(OTf)_3$,[14] and $IrCl_3$.[15] However, the use of homogeneous Lewis acids could be problematic, because they may trigger undesired isomerization of the epoxides with formation of



Scheme 1. Synthesis of L-prol-N-pMCM-41.

carbonyl compounds.[16] Therefore, the search for new environmentally friendly, atom-efficient methods, which avoid the use of large amounts of condensing reagents, and activators should be beneficial and drawn increasing interest. Among heterogeneous catalysts used for the synthesis of β-amino alcohols, SBA-15-*pr*-SO_3H,[17] mesoporous aluminosilicate,[18] Ti-MCM-41,[19] zeolite NaY,[20] Fe–Zn cyanide complex,[21] cobalt complex/SBA-15,[22] MnO octahedral molecular sieves,[23] Hβ zeolite,[24] Fe (BTC) metal–organic framework,[25] and TiO_2–ZrO_2[26] have been reported.

Taking into account the importance of new catalytically active organic–inorganic hybrid materials,[27] this work focused on heterogenization of L-proline on mesoporous MCM-41 silica. We report here the preparation and characterization of L-proline functionalized MCM-41 silica (L-prol-N-pMCM-41) as a novel L-proline based solid catalyst (Scheme 1). The catalytic activity of L-prol-N-pMCM-41 was disclosed by testing it in the aminolysis of styrene oxide under microwave irradiation and solvent-free conditions.

2. Experimental

2. 1. Materials and Methods

Sodium silicate solution (7.5–8.5% Na_2O, 25.5–28.5% SiO_2, Merck-105621), cetyltrimethylammonium bromide (96%, Fluka-52370), 3-chloropropyltrimethoxysilane (98%, Merck-818816), potassium carbonate (99.5%, Merck-104924) and L-proline (99%, Merck-107434) were used as received. Substrates (aniline derivatives and styrene oxide) were commercially available and used as received without further purification (Merck, Fluka). All other chemicals (H_2SO_4, DMSO and organic solvents) were of analytical quality, and water was purified in an SG Water purification system (Germany).

Powder X-ray diffraction (XRD) patterns were recorded at room temperature from 1 to 70° (2θ) using a Bruker D8 Advance instrument with Cu Kα radiation (λ = 0.15406 nm). Thermogravimetric analysis (TGA) of MCM-41, L-prol-N-pTMS and L-prol-N-pMCM-41 were carried out in Perkin Elmer Pyris Diamond instrument from 25 to 600 °C, using heating rate of 10 °C/min under dry N_2. The nitrogen adsorption/desorption analyses were performed on BELSORP-miniII at 77 K. MCM-41 and L-prol-N-pMCM-41 were degassed at 120 °C for 1.5 h under inert gas flow prior analysis. Specific surface area, total pore volume, and pore diameter of samples were obtained by Brunauer–Emmett–Teller (BET) method using BELSORP analysis software. The FT–IR spectra of the samples were recorded using a Perkin Elmer Spectrum 65 FTIR spectrometer in a KBr matrix in the range of 4000–400 cm^{-1}.

A laboratory microwave oven from Landgraf Laborsysteme HLL GmbH (model MW 3100, Langenhagen, Germany) equipped with a magnetic stirrer operating at 2450 MHz was used for all syntheses. Microwave heating was carried out using 420 W (70% of maximum power). To prepare L-prol-N-pTMS, the top of the reaction vessel (placed inside the microwave chamber) was attached to a water-cooled reflux condenser, located outside of the microwave chamber, for reflux purpose. A Fisons instruments gas chromatograph 8000 connected to a mass detector (Trio 1000) with 70 eV was used to analyze products.

2. 2. Preparation of MCM-41 Silica

MCM-41 silica was prepared through hydrothermal treatment following a methodology established by Gonçalves and co-workers.[28] In a typical experiment, 9.9 g sodium silicate solution were diluted with 30 mL deionized water and added slowly to a rapidly stirred solution of 8.12 g of cetyltrimethylammonium bromide in 80 mL deionized water. A precipitate formed immediately, which was stirred at the ambient temperature for 1 h. Dilute sulfuric acid (2 M) was then added dropwise to adjust the pH of the gel from 12.0 to 10.0. After stirring for a further 1 h, the pH was readjusted to 10.0. The mixture was then autoclaved at 373 K for two days in Teflon-lined stainless steel reaction vessels. The solid product was recovered by filtration, washed with hot water and air-dried at 333 K. Calcination was carried out at 813 K for 6 h to remove the surfactant.

2. 3. Synthesis of L-proline Functionalized MCM-41 Silica (L-prol-N-pMCM-41)

The procedure for synthetic of L-proline functionalized MCM-41 is illustrated in Scheme 1. The synthesis of L-proline derivative (L-prol-N-pTMS) was carried out by a methodology inspired from Islam and co-workers for the synthesis of anthranilic acid-functionalized polystyrene resin.[29] In a typical experiment, L-proline (2.3 g, 20.0 mmol) and K_2CO_3 (3.0 g, 21.7 mmol) were dissolved in 7 mL DMSO and vigorously stirred for 15 min at room temperature. The reaction mixture was irradiated four times (each time for 2 min with 1 min intervals) at 420 W in which the temperature raised to 180 °C to give a viscous liquid. Then 5 mL DMSO and 10.8 g (54.2 mmol) 3-chloropropyltrimethoxysilane were added to the cooled reaction mixture and irradiated once again four times (each time for 2 min with 1 min intervals) at 420 W in which the temperature raised to 170 °C. Then 100 mL deionized water was added to the cooled yellow precipitate, and the mixture was stirred vigorously for 4 h. Finally; the solid was filtered off under reduced pressure, and product was extracted in Soxhlet extractor with refluxing ethanol and dichloromethane separately for 4 h (L-prol-N-pTMS: 7.5 g).

For functionalization of MCM-41 mesoporous silica (5.2 g) and L-prol-N-pTMS (5.0 g) were refluxed in 100 mL toluene for 48 h. The solid was filtered and washed with copious amount of ethanol and dichloromethane to remove physisorbed organics on MCM-41 silica and make the acquired characterization more reliable. Finally, functionalized MCM-41 silica was dried under vacuum at 373 K for 7 h and 9.0 g product (L-prol-N-pMCM-41) was collected.

2. 4. General Procedure for Preparation of β-amino Alcohols under Microwave Irradiation

In a typical reaction, aniline (1.0 mmol), styrene oxide (1.2 mmol) and L-prol-N-pMCM-41 (0.1 g) were mixed thoroughly for a few minutes in order to ensure complete homogeneity. Then the mixture in an open vessel was inserted into the microwave chamber, and the reaction was carried out. The microwave power was maintained at 420 W (70% of maximum power) and mixture stirred for 15 min. Finally, the reaction mixture was washed with ethanol (2 mL) and the mixture was filtered. The organic medium was subjected to GC analysis in order to find out the conversion. The products were then analyzed by GC–MS and products identified by comparison of their mass spectra with authentic samples.

3. Results and Discussion

3. 1. Characterization of L-prol-N-pMCM-41

Due to insolubility of L-prol-N-pMCM-41 in all common organic solvents, its structural investigations were limited only to its physicochemical properties, i.e. X-ray diffraction (XRD), thermogravimetric analysis (TGA), differential thermogravimetric (DTG), nitrogen adsorption–desorption, Brunauer–Emmett–Teller (BET), and Fourier transform infrared (FT-IR) spectroscopy.

3. 1. 1. XRD

The XRD patterns of the MCM-41 and L-prol-N-p-MCM-41 are presented in Figure 1. The XRD pattern of MCM-41 shows four reflections, a very intense peak (1 0 0) and three additional high-order peaks (1 1 0), (2 0 0) and (2 1 0) with lower intensities. These results are in accordance with the hexagonal pore structure. The (1 0 0) reflection of L-prol-N-pMCM-41 with decreased intensity was remained intact after functionalization, while the (1 1 0), (2 0 0) and (2 1 0) reflections became weak and diffuse, which

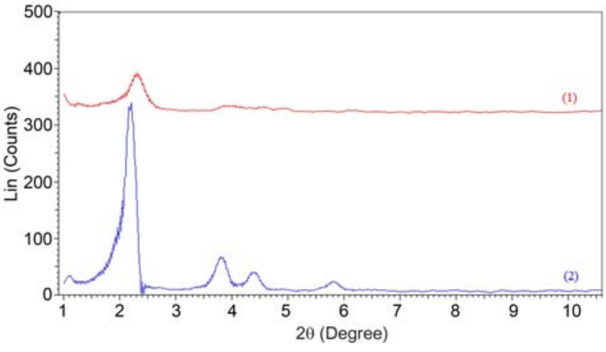


Figure 1. XRD patterns of the parent (1) L-prol-N-pMCM-41 and (2) MCM-41.

could be due to contrast matching between the silica framework and organic moieties which are located inside the mesoporous channels of MCM-41 silica. In other words, the attachment of the organic functional groups to the surface of the mesoporous channels tend to reduce the scattering power (or scattering contrast) of the silicate wall.[30]

3. 1. 2. TGA-DTG

The organic content of L-prol-N-pTMS and L-prol-N-pMCM-41 was measured using DTG and TGA (Figure 2). TGA analysis curve of L-prol-N-pMCM-41 showed a 23% weight loss from 25 to 600 °C. The weight loss up to 220 °C (2.5 wt%), refers to removal of physically adsorbed water and unreacted organic molecules. The DTG analysis data of L-prol-N-pMCM-41 showed a second weight loss (9.9 wt%) between 220 to 450 °C due to the decomposition of L-proline moiety from the surface of silanols. A third weight loss (10.6 wt%) was observed between 450 to 600 °C associated with the decomposition of propyl moiety from the surface of silanols. The thermal analysis of L-prol-N-pMCM-41 showed about 0.86 mmol g^{-1} L-proline grafted on MCM-41 silica.

3. 1. 3. Nitrogen Adsorption–Desorption Isotherms

Adsorption–desorption of nitrogen was used to measure surface area of mesoporous MCM-41 silica before and after functionalization with L-proline. BET surface area, pore size and pore volume of MCM-41 and L-prol-N-pMCM-41 are presented in Table 1. Naturally, MCM-41 showed higher surface area compared to L-prol-N-pMCM-41. Apparently, the surface area of MCM-41 silica was significantly decreased by functionalization with L-proline. This can be attributed to the pore blocking by L-proline loading. The pore volume of MCM-41 silica showed the same trend as that of surface area, while the average pore diameter of L-prol-N-pMCM-41 is slightly higher than that of MCM-41 silica (Table 1). Using the BJH equation along with the desorption isotherm, the pore diameter of L-prol-N-pMCM-41 is calculated to be 1.2 nm. The thickness of the silicate wall of L-prol-N-pMCM-41 is estimated around 2 nm (Table 1) by combining the results of XRD and nitrogen adsorption–desorption.

The nitrogen adsorption–desorption isotherm of the functionalized mesoporous silica is shown in Figure 3. L-prol-N-pMCM-41 exhibits a type IV isotherm, feature a sharp adsorption increase at relative pressure $P/P_0 = 0.3$, characteristic of the mesoporous materials.[31] A linear increase of adsorbed volume at the low pressure followed by a noticeable increase in the adsorbed volume of nitrogen and finally by a slow increase at high pressure is observed. The adsorption at low relative pressure, P/P_0, is occurred from the monolayer adsorption of nitrogen on the walls of the mesopore and it does not show the presence of any micropores. The inflection at $P/P_0 = 0.3$ in the adsorption isotherm of L-prol-N-pMCM-41 suggests the filling of the mesopore system. Nitrogen adsorption in the mesopore region is saturated at $P/P_0 = 0.4$ and larger pores are filled at higher P/P_0.

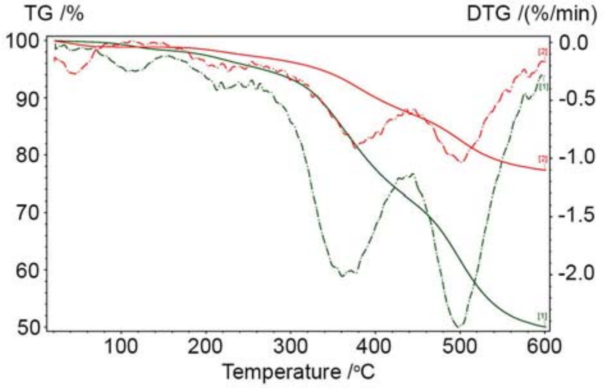


Figure 2. Thermogravimetric (TGA–solid line) and differential thermogravimetric (DTG–dash-dot line) curves of (1) L-prol-N-p-TMS and (2) L-prol-N-pMCM-41 samples.

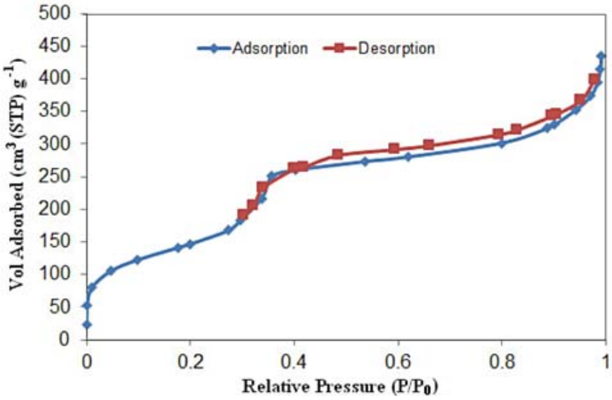


Figure 3. N_2 adsorption–desorption isotherm of L-prol-N-pMCM-41 at 77 K.

Table 1. Surface characteristics of ordered mesoporous solids

Sample	d_{100} (nm)	α_0 (nm)^a	BET surface area (m^2/g)	Total pore volume (cm^3/g)	Average pore diameter (nm)	WTH (nm)
MCM-41	4.02	4.64	1275	1.24	3.88	2.20
L-prol-N-pMCM-41	3.83	4.42	669	0.651	3.89	2.00

^{a}Unit cell parameter: $\alpha_0 = 2d_{100} / \sqrt{3}$, ^{b}Wall thickness: WTH = $\alpha_0 - \Phi_{BJH}$

3. 1. 4. FT-IR

The FT-IR spectrum of L-prol-N-pMCM-41 is shown in Fig. 4. The characteristic band at 1000–1250 cm^{-1} is due to the Si-O stretching vibration of Si–O–Si in MCM-41 silica mesoporous structure. The spectrum also showed the starching and bending vibrations of adsorbed water and hydroxyl group at 3200–3680 cm^{-1} and 1837 cm^{-1}, respectively. The asymmetric starching vibration bands of carboxylic acid and the propyl chain appeared at 1744 and 2957 cm^{-1}, respectively. Notably, N–H bending vibration band, which usually appears around 1544 cm^{-1}, is not observed (Figure 4).[32]

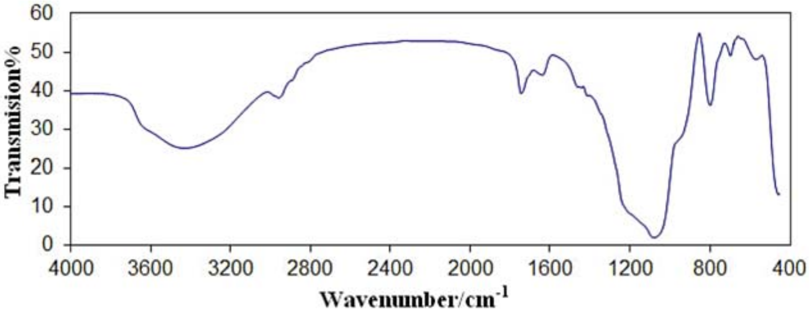


Figure 4. FT-IR spectrum of L-prol-N-pMCM-41.

3. 2. Catalytic Activity of L-Prol-N-pMCM-41

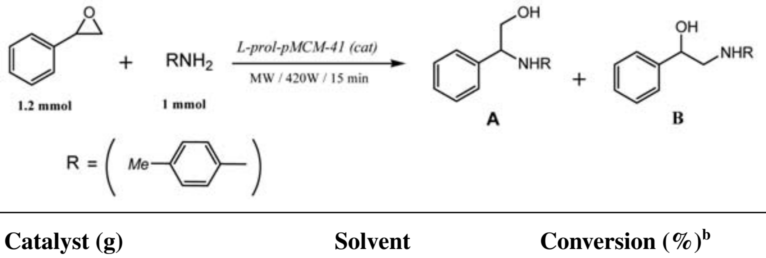
3. 2. 1. Optimization of the Model Reaction

The role of L-prol-N-pMCM-41 as a catalyst for the microwave-induced reaction of styrene oxide (1.2 mmol) with 4-methylaniline (1 mmol) in ethanol, water and solvent-free conditions was investigated, and the results are shown in Table 2. While in the absence and presence of solvent excellent conversions were obtained, the regioselectivity of **A** to **B** remains significantly superior under solvent-free conditions (Table 2, entries 1–3).

To investigate the role of L-prol-N-pMCM-41, the same reaction was carried out in the absence or presence of catalyst. In the absence of catalyst, low yield of product was obtained, which indicates that the catalyst is obviously necessary for the reaction (Table 2, entry 5). A remarkable yield for product was observed (75%) with high regioselectivity (89%) when the reaction was carried out under catalytic influence of L-proline (Table 2, entry 7), indicating the prominent role of L-proline as the catalyst. In contrast, heterogeneous L-prol-N-pMCM-41 proved to be more effective compared with L-proline itself (Table 2, entries 2–4, 7). Therefore, the remarkable efficiency of L-prol-N-pMCM-41 can be explained by the existence of multiple catalytic centers.

The effect of relative amounts of the catalyst on the outcome of the model reaction was also studied (Table 2, entries 3–4). The optimum amount of L-prol-N-pMCM-41 was found to be 0.1 g of catalyst containing 0.086 mmol of L-proline per one mmol of substrate (Table 2, entry 3).

Table 2. Aminolysis of styrene oxide by 4-methylaniline (**6**) in the presence of L-prol-N-pMCM-41 as catalyst under microwave irradiation.[a]



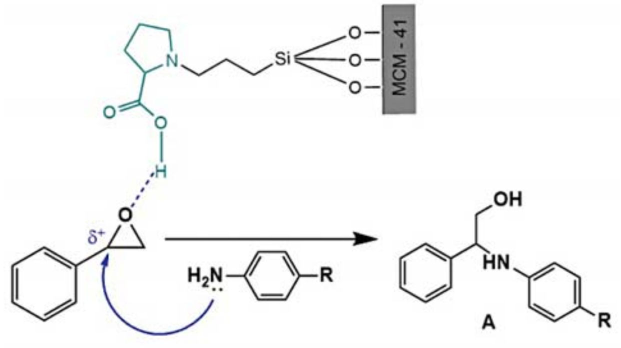
Entry	Catalyst (g)	Solvent	Conversion (%)[b]	Product selectivity[c] A	Product selectivity[c] B
1	L-prol-N-pMCM-41 (0.10)	H_2O (1 mL)	100	81	19
2	L-prol-N-pMCM-41 (0.10)	C_2H_5OH (1 mL)	99	87	13
3	L-prol-N-pMCM-41 (0.10)	–	100	94	6
4	L-prol-N-pMCM-41 (0.05)	–	90	91	9
5	–	–	25	80	20
6	MCM-41 (0.10)	–	20	69	31
7	L-proline (0.12)	–	75	89	11

[a]Microwave irradiation: 420 W/15 min, [b]Conversions were determined by GC, [c]Selectivities were determined by GC–MS.

3. 2. 2. Evaluation of the Reaction Scope

To expand the generality of this novel catalytic method, various aromatic primary amines were tested under the optimized conditions, and the results are presented in Table 3. In all cases, the reactions proceeded under microwave irradiation, although the yields were highly dependent on the substrate used. Despite the poor activity of aromatic amines substrates bearing a strong electron-withdrawing group such as NO_2 (Table 3, entries 6–8), excellent selectivity for all products was observed.

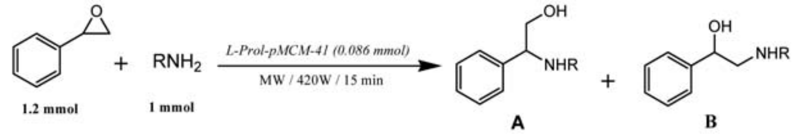
The turnover frequency (TOF) for this catalytic process, which is defined as moles of converted substrate (primary amine) per mole of catalyst per hour, is listed in Table 3. In most cases, turnover frequency values (as a measure of catalyst activity) were in range of 10–47 h^{-1}.

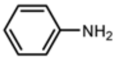
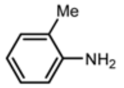
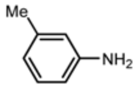
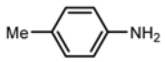
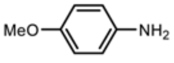
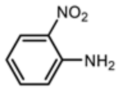
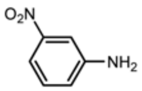
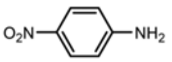
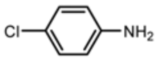


Scheme 2. Proposed mechanism for L-prol-N-pMCM-41 catalyzed regioselective aminolysis of styrene oxide.

A plausible mechanism for the L-prol-N-pMCM-41 catalyzed ring opening of styrene oxide with aniline is given in Scheme 2. Nucleophilic epoxide ring opening is assumed to occur by activation of the epoxide through complexation to the COOH group of L-prol-N-pMCM-41 followed by attack with aniline.[21]

Table 3. Synthesis of β-Amino alcohols by the ring opening of styrene oxide with aniline derivatives over (L-prol-N-pMCM-41) catalyst.



Entry	amine	Conversion (%)[a]	TOF (h^{-1})[b]	Product selectivity[c]	
				A	B
1		96	44.7	97	3
2		98	45.6	95	5
3		97	45.1	96	4
4		100	46.5	94	6
5		100	46.5	95	5
6		34	15.8	100	0
7		9	4.2	100	0
8		22	10.2	100	0
9		73	34.0	96	4

[a]Conversions were determined by GC, [b]TOF: turnover frequency = moles of converted substrate (aniline)/(moles of catalyst × reaction time in h), [c] Selectivities were determined by GC–MS.

Table 4. Literature results for the ring opening of styrene oxide with aniline under various heterogeneous conditions.

Method	Catalyst	Conditions	Conversion (%)	Product selectivity	Reference	
					A	B
1	SBA-15-*pr*-SO_3H	25 °C / 4 h	38	90	10	17
2	Mesoporous aluminosilicate	25 °C / 24 h	68	80	20	18
3	Ti-MCM-41	35 °C / 4 h	81	94	6	19
4	Zeolite NaY	35 °C / 8 h	90	92	8	20
5	Fe–Zn cyanide complex	60 °C / 4 h	95	98	2	21
6	Cobalt complex / SBA-15	27 °C / 12 h	77	89	11	22
7	MnO octahedral MS[a]	110 °C /24 h/toluene	76	100	0	23
8	Hβ zeolite	MWI[b](900 W)/3min	88	74	26	24
9	Fe (BTC) MOF[c]	80 °C / 24 h	72	98	2	25
10	TiO_2-ZrO_2	25 °C /80 min /water	86	92	8	26
11	L-prol-N-pMCM-41	MWI (420 W)/15min	96	97	3	This work

[a]MS: Molecular sieves, [b]MWI: Microwave irradiation, Metal-Organic-Faramwork

Table 4 shows the comparison of present catalyst to other catalysts reported in literature for the same reaction under heterogeneous conditions. As it can be seen, there are promising features of this protocol in terms of reaction rate, product conversion and regioselectivity.

3. 2. 3. Recycling of the Catalyst

The reusability of catalyst was also examined. As shown in Table 5, the catalyst was recycled for five subsequent runs. It was found that the catalyst remains active even in fifth run with a gradual decrease in activity while high regioselectivity is still maintained. The recovery of catalyst was very easy. Substrates and product are soluble in ethanol, while the catalyst remains insoluble. After completion of the reaction, ethanol was added to the reaction mixture. The catalyst was simply filtered from the resulting mixture, dried at 100 °C for 2 h and reused in the subsequent runs without adding fresh catalyst.

Table 5. Recyclability of L-prol-N-pMCM-41 for aminolysis of styrene oxide with 2-methylaniline.

Run	Conversion (%)	Product selectivity	
		A	B
1st	98	95	5
2nd	89	93	7
3rd	80	90	10
4th	71	90	10
5th	58	90	10

4. Conclusion

The results of the present study clearly establish a novel method for the anchoring of L-proline onto the mesoporous MCM-41 silica through simple two-step reaction method assisted by microwave heating. This economically viable organic–inorganic hybrid material showed remarkable catalytic activity in terms of regioselectivity and recyclability for the ring opening of styrene oxide with aniline derivatives under microwave irradiation in a short period of time.

5. References

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Povzetek

Nov organsko-anorganski hibridni material L-prol-N-pMCM-41 smo sintetizirali s kovalentno vezavo N-funkcionaliziranega derivata prolina (L-prol-N-pTMS) v pore silikata MCM-41. Material smo karakterizirali z rentgensko praškovno difrakcijo (XRD), termogravimetrično analizo (TGA), dušikovo adsorpcijsko desorpcijsko izotermo, analizo specipične površine (BET) in infrardečo spektroskopijo (FTIR). Tako pripravljen katalizator je pokazal srednje do veliko katalitično aktivnost in odlično regioselektivnost za reakcijo odprtja obroča v stiren oksidu z derivati anilina, ki je potekala brez topila pod vplivom mikrovalov. Katalizator lahko tudi hitro ločimo od reakcijske zmesi in ponovno uporabimo (do pet krat) s še vedno dobro aktivnostjo in visoko regioselektivnostjo.