

Synthesis of Al-SBA-1 molecular sieve and its application in synthesis reaction of Coumarins

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Al-SBA-1 분자체의 합성과 Coumarins 합성반응에 촉매특성 연구

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Abstract

Aluminum containing mesoporous molecular sieves Al-SBA-1 ($n_{Si}/n_{Al} = 2, 5, 10, 15$) was synthesized with a one-step method, and the catalyst was characterized with powder X-ray diffraction (XRD), nitrogen adsorption-desorption, thermogravimetric analysis (TGA), scanning electron microscopy (SEM) and Fourier transform infrared spectroscopy (FT-IR). Finally, we studied the catalytic activities of Al-SBA-1 molecular sieves in Pechmann reaction of 3-methoxyphenol and Ethyl acetoacetate to get 7-methoxy-4-methyl coumarin. Four parameters reaction temperature, time, catalyst weight and reactants ratio were optimized.

Key words: Al-SBA-1, acid catalyst, coumarin synthesis.

1. Introduction

Coumarin is a fragrant chemical compound in the benzopyrone chemical class and occupies an important place in the realm of natural and synthetic organic chemistry [1], which can be found in many plants. Recent years, coumarins and its derivatives have attracted great interest because of their important chemical properties. They have been used as anticoagulants [2], additives in food and cosmetics [3], preparation of insecticides, optical brighteners [4], dispersed fluorescent and laser dyes [5]. Coumarins have been synthesized by several methods, such as Pechmann [6], Perkin [7], Knoevenagel [8], Reformatsky [9], Wittig [10] reactions and by flash vacuum pyrolysis [11]. The Pechmann reaction is one of the most widely applied method for the synthesis of coumarins and its derivatives because it involves the condensation of phenols

with β -ketonic esters in the presence of a variety of acidic condensing agents and gives good yields of 4-substituted coumarins [12,13].

In the last decade, Huo et al. reported the synthesis of SBA-1 under strongly acidic conditions employing a so-called S+X-I+ mechanism [14-16]. SBA-1 is a cubic phase, which possesses a three-dimensional cage-type structure. Pure silica mesoporous materials are limited to application in catalysis because they possess a neutral framework. In order to obtain materials with potential for catalytic applications, it is necessary to modify the nature of the amorphous walls by incorporation of hetero elements. Recently, several research groups have reported the incorporation of Fe, Cr, Cu and Mo into mesoporous silica SBA-1 in a highly acidic medium and studied their catalytic activities in various acidic and oxidation reactions [17-20].

The Al-SBA-1 molecular sieves were prepared by a direct synthesis in the present work and the catalytic activity was evaluated in the studied the catalytic activities of Al-SBA-1 molecular sieves in Pechmann condensation reaction of 3-methoxyphenol and ethyl acetoacetate.

2. Experimental

2.1 Preparation of the catalysts

Aluminum containing mesoporous molecular sieves Al-SBA-1 was synthesized under acidic conditions using cetyltriethylammonium bromide (C₁₆H₃₃(C₂H₅)₃NBr, CTEABr) as the template, tetraethylorthosilicate (TEOS) as the silica source and aluminium isopropoxide [Al(i-C₃H₇O)₃] as the aluminium source. The template CTEABr was synthesized by reaction of 1-bromohexadecane with an equimolar amount of triethylamine in ethanol under reflux conditions for two days. The resulting solid CTEABr was purified by recrystallization from a chloroform-ethylacetate mixture.

Al-SBA-1 catalyst was synthesized as following: solution A was prepared by adding 1.624 g of CTEABr to an aqueous solution of HCl. The solution obtained was cooled to 0 °C and homogenized for 30 min. TEOS and Al(i-C₃H₇O)₃ were precooled to 0 °C and then added to solution A under vigorous stirring and the stirring was continued for another 5 h at 0 °C. Thereafter, the reaction mixture was heated to 100 °C for 1 h. The solid product was recovered by filtration and dried in an oven at 100 °C overnight. A set of samples was prepared by changing the nSi/nAl ratio (nSi/nAl=2,5,10,15) in the gel. The molar composition of the gel was 1 TEOS: 0.033-0.25 Al₂O₃: 0.2 CTEABr: 10 HCl: 125 H₂O. Pure siliceous SBA-1 was synthesized with the same procedure (HCl/TEOS=56 and H₂O/TEOS=700) in the absence of aluminium. The as-synthesized materials were then calcined in air at 550 °C for 10 h to remove the organic template.

2.2 Catalyst characterizations

Powder X-ray diffraction (XRD) patterns were recorded using a Rigaku D/Max 2200+Ultima diffractometer with Cu-K α radiation (λ =0.154 nm). The diffraction data were recorded in the 2 θ range 0.9-10 ° at step of 0.02/s. The nitrogen adsorption-desorption isotherms were measured at 77 K on a BEL-Belsorp II volumetric adsorption analyzer. Prior to each adsorption measurement the samples were evacuated at 398 K under vacuum (p <10⁻⁵mbar) for 6 hours in the degas port. Thermogravimetric analysis (TGA) was performed by Scinco TGA N-1000 thermo gravimetric (TG) analyzer, the sample was heated from room temperature to 800 °C under N₂ at a heating rate of 10 °C/min. FT-IR spectroscopy was performed on a Nicolet IR 200 instrument with the wavenumber range of 4000-400 cm⁻¹. SEM images were captured on JEOL JSM 5600 scanning electron microscope.

2.3 Catalytic study

The catalyst was activated at 100 °C for at least 4 h prior to experiments, so as to maintain the dry conditions. In a typical run, a mixture of 3-methoxyphenol, ethyl acetoacetate and a freshly activated catalyst was taken in a round bottom flask separately fitted with a condenser, N₂ gas flow tube and a septum. The mixture was continued stirring for 20 h at 150 °C in N₂ gas atmosphere. In order to optimize the reaction conditions, the temperature (100, 130, 150, 180 °C), time (16, 18, 20, 22, 24 h), weight of catalyst (0.03, 0.05, 0.07, 0.1, 0.15 g) and reactants ratio 3-methoxyphenol/ethyl acetoacetate (1:1, 1:2, 1:3, 1:4, 1:5) were investigated. The resulted product samples were analyzed with a gas chromatograph.

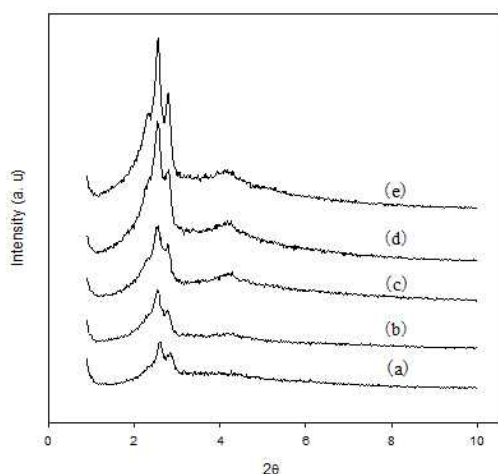
3. Result and discussions

3.1 Catalysts characterization

3.1.1 XRD

Fig. 1 shows the XRD patterns of parent SBA-1 and Al-SBA-1 molecular sieves. In the Al-SBA-1 samples (Fig. 1 a-d) characteristic

patterns with reflections (200, 210, 211)) were observed in the range of $2\theta=1.5-3^\circ$. The characteristic XRD patterns exhibited by the three-dimensional cubic structure (pm3n space group) matches well with those reported in the literatures [21-23]. As displayed in Fig. 1, the intensity of the reflections increase with the increasing the nSi/nAl ratio, which suggested that higher amount of aluminum incorporation in the mesoporous material SBA-1 was probable to reduce the structure order. The position of the patterns in Al-SBA-1(2) was slightly shifted to higher 2θ which was caused by the higher aluminum content.

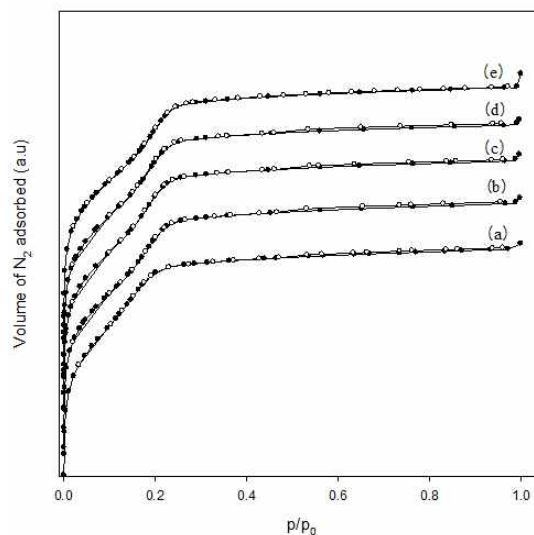


[Fig. 1] XRD patterns of the various calcined samples:
(a) Al-SBA-1(2), (b) Al-SBA-1(5), (c) Al-SBA-1(10),
(d) Al-SBA-1(15), (e) SBA-1

3.1.2 BET

The nitrogen adsorption-desorption isotherms of various Al-SBA-1 and SBA-1 samples are presented in Fig.2. All samples displayed type IV isotherm, a signature characteristic of mesoporous materials. The structural properties of the catalysts are summarized in Table 1. There was only little difference in pore diameter and pore volume for the aluminum contained silica materials compared to silica SBA-1, indicating the structural properties of the silica materials was not changed by the aluminum grafting process. A slight decrease in surface area was found for the

Al-SBA-1 sample which was caused by the incorporation of aluminum, which can be explained by some destruction of the pore structure of Al-SBA-1 materials, this is in agreement with the results of XRD displayed in Fig.1.



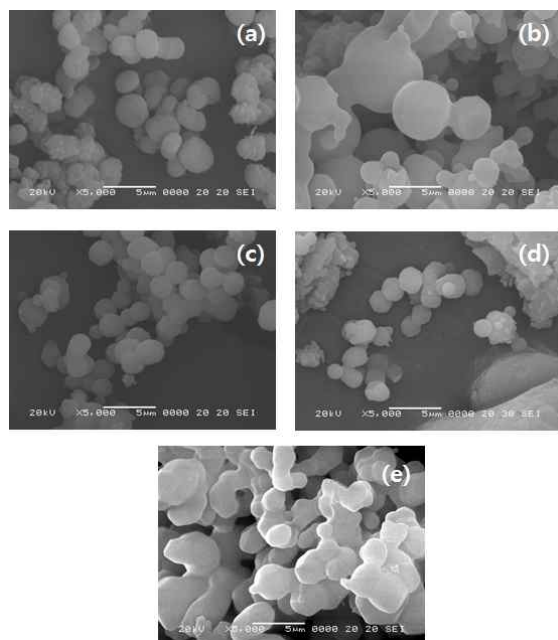
[Fig. 2] Nitrogen adsorption-desorption isotherms of the various calcined samples:
(a) Al-SBA-1(2), (b) Al-SBA-1(5),
(c) Al-SBA-1(10), (d) Al-SBA-1(15), (e) SBA-1

[Table 1] Structural properties of various Al-SBA-1 samples

Catalysts	n_{Si}/n_{Al} (in gel)	BET surface area (m^2/g)	Pore volume (cm^3/g)	Pore size (nm)
SBA-1	-	1431.4	0.7291	2.2724
AlSBA-1(2)	2	1321.0	0.7140	2.1621
AlSBA-1(5)	5	1243.1	0.7302	2.3498
AlSBA-1(10)	10	1335.3	0.7450	2.2317
AlSBA-1(15)	15	1257.4	0.7339	2.3348

3.1.3 SEM

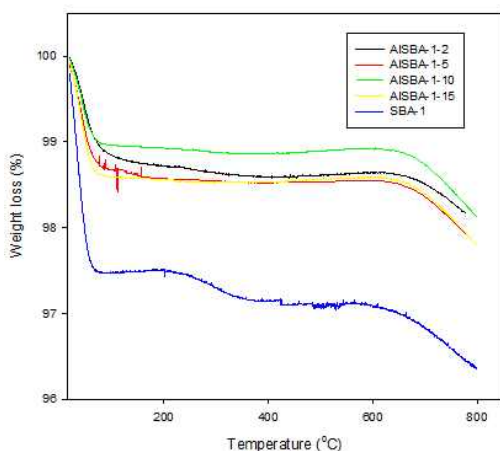
Fig.3 displays the SEM images of various Al-SBA-1 and SBA-1 samples. All the samples presented spherical morphology with different particle size, which was in well agreement with previous reports [23]. As shown in Fig. 3 (a-d), the particles of the Al-SBA-1 samples were slightly smaller than that of mesoporous silica molecular sieve SBA-1. The size of Al-SBA-1 samples were found to be 150~500 nm.



[Fig. 3] SEM images of the various calcined samples:
 (a) Al-SBA-1(2), (b) Al-SBA-1(5), (c) Al-SBA-1(10),
 (d) Al-SBA-1(15), (e) SBA-1

3.1.4 TGA

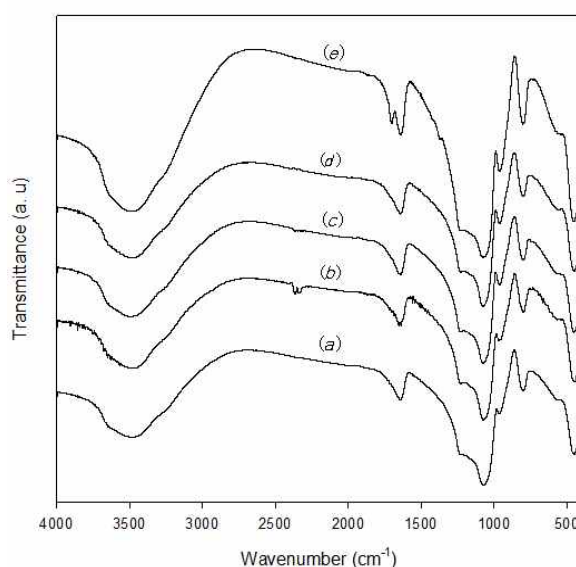
The TGA curves of various Al-SBA-1 and SBA-1 are presented in Fig. 4. There was a slight weight loss for both Al-SBA-1 and SBA-1 at the temperature of 100 °C, caused by the loss of moisture content and physisorbed gases. No obvious weight change was found at 200~800 °C illustrating complete absence of the template after calcination and high thermal stability of the catalysts making them suitable for high temperature reactions.



[Fig. 4] TGA curves of various calcined Al-SBA-1 and SBA-1 samples.

3.1.5 FT-IR

The FT-IR spectra of calcined siliceous SBA-1 and various Al-SBA-1 samples are shown in Fig. 6. The broad peaks at 3480 cm^{-1} in all of sample are due to the defective of -OH groups. The intensity of the peaks decreased with the increase in aluminum content in the catalysts. The peaks at 1077 and 802 cm^{-1} corresponds to asymmetric and symmetric vibrations of Si-O-Si linkage, The asymmetric stretching vibrations at about 802 cm^{-1} in the Al-SBA-1 samples decreased with increase in aluminium content..



[Fig. 5] FT-IR spectra of the various calcined samples:
 (a) Al-SBA-1(2), (b) Al-SBA-1(5), (c) Al-SBA-1(10),
 (d) Al-SBA-1(15), (e) SBA-1

3.2 Catalytic study

The aluminum incorporated SBA-1 mesoporous materials were studied for the reaction of 3-methoxyphenol and ethyl acetoacetate under a solvent free condition. The effect of temperature effect, time, reactant ratio and catalyst weight were investigated in the reaction in order to obtain high 3-methoxyphenol conversion and coumarin derivative selectivity. This work is under progress in our lab now.

References

- [1] Fang D., Cheng J., Gong K., Shi Q. R, Liu Z. L, *Catal Lett*, 121 (2008) 255.
- [2] L.A. Singer, N.P. Kong, *J. Am. Chem. Soc.* 88, (1966) 5213.
- [3] O. Kennedy, R.D. Thornes, *Coumarins: Biology, Applications and Mode of Action*, Wiley and Sons, Chichester, 1997.
- [4] M. Zahradnik, *The Production and Application of Fluorescent Brightening Agents*, Wiley and Sons, 1990.
- [5] R.D.H. Murray, J. Mendez, S.A. Brown, *The Natural Coumarins: Occurrence, Chemistry and Biochemistry*, Wiley and Sons, New York, 1982.
- [6] von Pechmann H, Duisberg C. *Chem Ber.* 17 (1884) 929.
- [7] Johnson J.R. *Org React.* 1 (1942) 210.[8]. Jones G. *Org. React.* 15 (1967) 204.
- [9] Shriner R.L. *Org React.* 1 (1942) 1.
- [10] Narasimahan N.S., Mali RS, Barve MV *Synthesis.* (1979) 906.
- [11] Cartwright G.A., McNab W. *J. Chem Res (S).* (1997) 296.
- [12] Sethna, S., Phadke, R. *Org. React.* 7 (1953) 1.
- [13] Russell, A.; Frye, J. R. *Org. Synth.* (21) 1941 22.
- [14] Q. Huo, D.I. Margolese, U. Ciesla, D.G. Demuth, P. Feng, T.E. Gier, P. Sieger, A. Firouzi, B.F. Chmelka, F. Schuth, G.D. Stucky, *Chem. Mater.* 6 (1994) 1176.
- [15] Q. Huo, R. Leon, P.M. Petroff, G.D. Stucky, *Science.* 268 (1995) 1324.
- [16] Q. Huo, D.I. Margolese, G.D. Stucky, *Chem. Mater.* 8 (1996) 1147.
- [17] A. Vinu a, T. Krithiga, N. Gokulakrishnan, P. Srinivasu, S. Anandan, K. Ariga, V. Murugesan, V.V. Balasubramanian, T. Mori. *Micropor. Mesopor, Mater.* 100 (2007) 87.
- [18] X. H. Zhao, X. L. Wang. *J. Mol. Catal. A: Chem.* 261 (2007) 225.
- [19] S. Li, Gl. Li, Q. Li. *Chem. Res. Appl.* 23 (2011) 4.
- [20] S. Che, Y. Sakamoto, H. Yoshitake, O. Terasaki, T. Tatsumi, *J. Phys. Chem. B* 105 (2001) 10565.
- [21] Q. Huo, D.I. Margolese, U. Ciesla, D.G. Demuth, P. Feng, T.E. Gier, P. Sieger, A. Firouzi, B.F. Chmelka, F. Schuth, G.D. Stucky, *Chem. Mater.* 6 (1994) 1176.
- [22] Q. Huo, D.I. Margolese, G.D. Stucky, *Chem. Mater.* 8 (1996) 1147.
- [23] K. Venkatachalam, M. Palanichamy, V. Murugesan, *Catal. Commun.* 12 (2010) 299.