

**MCM-41 Knoevenagel**

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**Knoevenagel reaction by MCM-41 functionalized with amino groups**Jung-Sik Choi, Wha-Seung Ahn\*

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**1. Introduction**

Numerous reactions such as isomerizations, additions, alkylations and cyclizations are carried out industrially by using liquid bases as catalysts. The replacement of liquid bases by solid base catalysts would have the advantages of decreasing corrosion and environmental problems, while allowing easier separation and recovery of the catalysts. Although relatively little attention has been devoted to solid base catalyst in comparison with solid acid catalysts, high activity and selectivity are often attained by solid bases for many kinds of reactions.

Knoevenagel reaction is one of the most important organic reactions available to the synthetic chemistry. It is also potentially one of the most environmentally friendly, having water as its co-product. The major drawback to the use of the Knoevenagel reaction in environmental terms has been the difficulty of finding suitable catalysts for some of the more demanding reaction partner. Solid base catalysts are easily poisoned by water or carbon dioxide. It is an intriguing problem to prepare water or carbon dioxide resistant solid bases. For example, creating basic sites in hydrophobic micropores may be of interest. When solid bases are applied to organic reactions in liquid phase, diffusion of reactants and products may limit the reaction rate especially in the case of porous catalysts, and the use of mesoporous support may offer an opportunity to avoid diffusion problems [1]. In this study, a series of amine functionalized MCM-41 catalysts were prepared and their catalytic performance in Knoevenagel reaction of selected substrates was investigated.

**2. Experimental**

**MCM-41 with enlarged pores :** MCM-41 with large pore size were prepared using a modified synthesis recipe of Lindlar et al [2]. For this purpose, a mixture of hexadecyltrimethylammonium chloride and dodecyltrimethylammonium bromide was employed as structure directing agent, and mesitylene as swelling agent. A silica solution was prepared by mixing 17.75 g colloidal silica (HS-40, Ludox), 2.82 g NaOH, and 0.7 g Cab-O-Sil M5 in demineralized water. This solution was stirred for 1 h at 333 K and was added to the nanoemulsion solution prepared by mixing 18.6 g hexadecyltrimethylammonium chloride (25% Fluka), 1.0 g dodecyltrimethylammonium bromide (Fluka purum.), and 5.23 g mesitylene (98%, Aldrich) in 10.8 g water. The molar composition of this

mixture was  $\text{SiO}_2$  /0.542 NaOH/ 0.116  $\text{C}_{16}\text{TMACl}$  /0.025  $\text{C}_{12}\text{TMABr}$ / 0.75 mesitylene /30.3  $\text{H}_2\text{O}$ . After the substrate mixture was stirred for 1 h at room temperature and aged 30 min., it was heated to 373 K. After 24 h hydrothermal heating in oven, the batch was cooled to room temperature and pH of this mixture was adjusted to  $11.0 \pm 0.1$  using acetic acid. The pH adjustment was repeated total of three times. After four days heating, the product was removed from the oven, cooled to room temperature, and washed with demineralized water and dried at 343 K under vacuum overnight. To remove the templates, the product was heated at a rate of  $5^\circ\text{C}/\text{min}$  to  $120^\circ\text{C}$  holding 3 h, followed by  $1^\circ\text{C}/\text{min}$  to  $550^\circ\text{C}$  holding 4 h.

**3-aminopropylsilane(APM) grafted MCM-41 :** Prepared MCM-41 was dried at 343 K under vacuum overnight. 1.5 g of the dried materials were added to 15 ml of toluene with stirring. 3-aminopropyltrimethoxysilane 5.0 mmol was then added to the mixture, stirred 6 h in room temperature, and refluxed 4 h at 383 K. The product was filtered and washed with ethanol and dried at 343 K under vacuum.

**Silylated 3-aminopropylsilane(SAPM) grafted MCM-41 :** A suspension of above material (0.5 g) in toluene (5 ml) was refluxed and stirred with excess trimethy-methoxysilane for 6 h. The product was filtered and washed with ethanol and extracted with diethyl ether–dichloromethane mixture using Soxhlet apparatus.

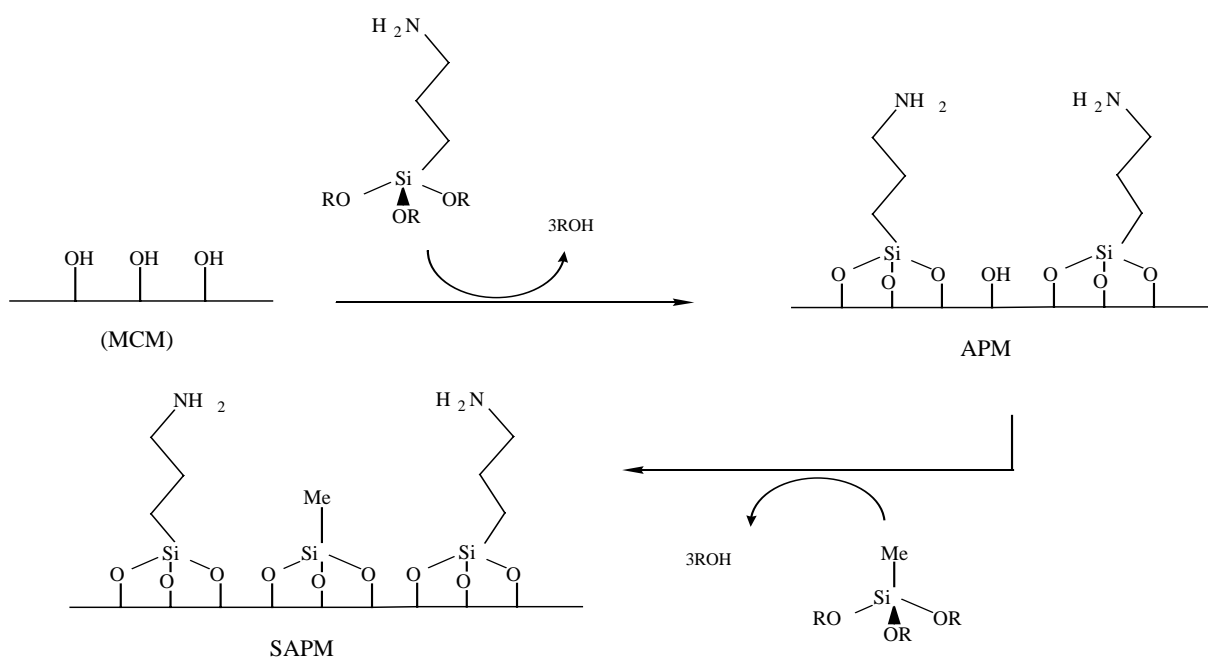
**Coated 3-aminopropylsilane(CAPM) on MCM-41 :** Support was dried at 343 K under vacuum overnight. 3.0 g of the dehydrated sample were refluxed for 3 h in 100 ml demineralized water. The mixture was cooled and filtered. Subsequently, the wet material was refluxed in 250 ml toluene and excess water was removed slowly using a Dean-stark trap. When the water remained on the sample reaches ca. 2 ml (approximately equal to four monolayers of water), the material became well dispersed. After cooling, 20 ml 3-aminopropyltrimethoxysilane was added to this suspension, stirred 8 h at room temperature, and refluxed 4 h at 383 K. Finally, the mixture was filtered and washed with 2-propanol several times.

**Characterization :** The product was dried under vacuum overnight to remove the solvent left. The crystallinity of the samples prepared was measured by X-ray diffraction using Ni-filtered  $\text{CuK}\alpha$  radiation (Philips, PW-1700), and those with the enlarged pores were measured using a X-ray diffractometer- WAXD/SAXD (Rigaku DMAX 2500). The specific surface area and average pore diameters were determined by  $\text{N}_2$  physisorption at liquid nitrogen temperature using a Micromeritics ASAP 2000 automatic analyzer. The surface area was determined by BET method and the pore size distribution was calculated by the Barrett-Joyner-Halenda (BJH) method using the desorption branch of the isotherm. Prior to the measurements, support materials were degassed at 373 K for 1 h and at 623 K for 4 h at a pressure less than 1.4 Pa. The organic-functionalized materials were degassed at 383 K. FT-IR spectra were recorded in air at room temperature on a Bomem MB104 spectrometer in KBr pellets. The loading and composition of the grafted materials were determined by using CHNS elemental analysis (CE instrument). Knoevenagel condensation was carried out in a round bottom flask containing an equimolar mixture (10mmol) of aldehyde and activated methylene compound. Amine functionalized catalyst (20mg) in 15ml toluene was added to the reactant and the mixture was vigorously stirred at 323K. n-Decane was used as internal standard. GC samples were taken at interval via a septum and analyzed on HP6890

### **3. Results & Discussion**

Synthesis of the host mesoporous MCM-41 type silica was conducted following the Lindlar' method using colloidal silica, mesitylene as swelling agent, and cetytrimethylammoniumchloride-dodecyltrimethylammoniumbomide mixture as co-surfactant for enlarged pores in narrow pore size

distribution. The surfactant micelles, which template the hydrothermal condensation of silica, were subsequently eliminated by thermal degradation in air to liberate a monodispersed mesoporous system featuring regular hexagonal arrays of uniform channels. The surface silanol groups allow covalent linkage of functionalized organic moieties through Si-O-Si bonds by applying the usual methods of silica functionalization using APM. APM was subsequently treated with methyltrimethoxysilane at 383K in order to selectively remove the residual OH groups of the silica surface, yielding material SAPM. During the different modifications, no loss of the previously anchored chains or the regular porous structure was observed as confirmed by elemental analysis (see Table 2).



scheme 1. Functionalization procedure

Functionalization of propylamine groups to the surface of parent materials was also conducted by coating of a partially hydrated host material with a 3-aminopropyltrimethoxysilane layer. It was reported that the surface coverage of the monolayer was claimed to rise up to 76 % [3].

The catalytic activities and selectivities of the various solids were determined during the reaction of aldehyde with active methylene compound in toluene solution at 323K. The yield of product as a function of active methylene compound consumed were determined by G.C after reaction time 6 h as summarized in table 1.

Table 1. Conversion and TON of activated methylene compounds

		Conversion				TON		
		Parent	APM	SAPM	CAPM	APM	SAPM	CAPM
Benzaldehyde	ECA	0	88	94	92	2146	2632	1307
	DEM	0	10	13	11	243	364	156
Butyraldehyde	ECA	0	94	100	96	2292	2800	1364
	DEM	0	33	35	34	807	968	483

The activity of grafted amino groups toward the catalytic production is revealed by comparison with the inactivity of corresponding parent material. It should be noted that the conversion using SAPM catalyst is higher than other catalysts. The higher efficiency of the SAPM over other catalysts is owing to the water-repelling and removal of residual silanol groups. Knoevenagel reaction is very dependent on the efficient removal of water, which leads to faster reaction rates and much higher conversion. The effect of removing water was reported by D. J. Maquarrie et al[4]. In reactions where water was continuously removed by Dean-stark trap the rate, conversion and yield all increase significantly. This effect is general, over the range of ketones studied, and increases the conversion from, typically, 50-70% to almost quantitative. Residual silanol can also reduce the basic strength of the amine grafted via hydrogen bond with N.

This phenomenon, which was higher in SAPM than APM grafted catalysts can be explained by repulsion of hydrophobic catalyst to water even though this reaction was carried out without a Dean-stark trap. Catalyst modified with methyltrimethoxysilane separates water from grafted amine groups.

Table 2. Elemental analysis of catalysts.

Sample Name	Nitrogen	Carbon	Mmol/g (N)	mmol/g (C)	C/N (mol%)
APM	2.87	8.77	2.05	7.31	3.57
SAPM	2.50	9.50	1.79	7.92	4.43
CAPM	4.93	15.89	3.52	13.24	3.77

CAPM have almost twice the amount of the active N site comparison with SAPM in shown Table 2. However, reaction conversion is low rather than SAMP. In the case of the catalyst prepared by coating method, excess of aminopropyltrimethoxy-silane was introduced into mesoporous materials and a cross-linked monolayer of aminopropylsilane is formed, covalently bound to and closely packed on the pore surface of MCM-41. Therefore amine groups were not isolated between them and bonded by hydrogen force, which resulted in the lower basicity of the N group.

#### **4. Conclusions**

Water resistant and catalytically active amine grafted MCM-41 was prepared after silylation using methyltrimethoxysilane. Hydrogen bonding with surface silanol was effectively suppressed and led to high TON. Amine functionalized MCM-41 prepared by coating produced high conversion, but its TON was much lower than the amine grafted with silylation. Amine groups were not isolated and large portion of them may be bonded by hydrogen force, which resulted in the reduction in the strength of basicity of the N group.

#### **5. Resferences**

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