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Hydroxyalkylation of *p*-Cresol to 2,2′-Methylenebis(4-methylphenol) Using Sn/Si-MCM-41 Catalysts

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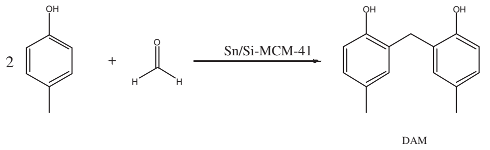
Sn/Si-MCM-41 has exhibited an excellent catalytic activity [70% product yield with 88% selectivity to 2,2′-methylenebis(4-methylphenol)] for the selective hydroxyalkylation of *p*-cresol. At equal level of Sn loading, Sn/Si-MCM-41 prepared by direct hydrothermal synthesis showed higher activity than Sn-impregnated Si-MCM-41 catalyst.

Developing eco-friendly and efficient catalysts are highly desirable for an industrially important hydroxyalkylation reaction of phenols to give bisphenols.[1] Hydroxyalkylation based on the use of conventional catalysts like HCl, H_3PO_4, and oxalic acid in the stoichiometric amount leads to serious environmental and operational problems.[2] In order to overcome these drawbacks, several solid acid catalysts were reported for the hydroxyalkylation of phenols.[3–8] Among such solid acid catalysts, zeolites were found to give better activity for the hydroxyalkylation of phenols, however they suffer from a serious problem of fast deactivation due to pore blockage by trimers and oligomers formed during the reaction.[8] Although larger surface areas and variety of unique structures make mesoporous materials useful in various catalytic reactions involving larger molecules, tuning of their acidity and hydrothermal stability is necessary for their application to a specific reaction. By virtue of higher electronegativity, atomic size and stronger acidity, the incorporation of tetrahedral Sn(IV) in silica-based mesoporous materials not only enhances the overall acidity but also the structural stablility.[9] Sn-containing mesoporous materials have exhibited excellent catalytic activity in hydroxylation of phenol and 1-naphthol, epoxidation of norbornene, Mukaiyama-type aldol condensation, Baeyer–Villiger and Meerwein–Ponndorf–Verley reactions.[10–14]

Here we report for the first time a very high product yield with 88–90% selectivity to 2,2′-methylenebis(4-methylphenol) (DAM) for the hydroxyalkylation of *p*-cresol (Scheme 1) using Sn/Si-MCM-41 catalyst prepared by two methods viz. direct hydrothermal synthesis and post-synthesis modification by impregnation of Sn on Si-MCM-41.

Sn-free MCM-41 and Sn-containing MCM-41 were prepared hydrothermally by following a reported procedure and designated them as Si-MCM-41 and Sn/Si-MCM-41(A) respectively.[12] Since calcined Sn/Si-MCM-41(A) has shown molar SiO_2/SnO_2 ratio of 110, a third catalyst possessing nearly identical composition was prepared differently by wet impregnation using Si-MCM-41 as a substrate having molar ratio of $SiO_2/SnO_2 = 110$. After drying for 2 h at 373 K, it was then calcined at 673 K for 6 h and labeled as Sn/Si-MCM-41(B). The characteristics of the prepared material matched very well with those reported.[12] The specific BET surface areas and the concentration of acid sites (mmol NH_3 desorbed/g) measured using NH_3-TPD profiles were obtained from a Quantachrome CHEMBET 3000 instrument.[3]



Scheme 1. Hydroxyalkylation of *p*-cresol to DAM.

The hydroxyalkylation of *p*-cresol with formaldehyde was carried out in a magnetically stirred glass reactor (Capacity 50 mL) fitted with a reflux condenser and an arrangement for temperature control. In a typical experiment, *p*-cresol (42 mmol), formaldehyde (8.4 mmol), toluene (108 mmol), and catalyst (0.04 g cm^{-3}) were added to the reactor, then heated to 363 K for 2 h. The product yield and DAM selectivity were determined using a HP6890 series GC System (Hewlett Packard) coupled with FID detector and HP-1 capillary column (30 m length × 0.32 mm i.d.). The products were identified by ^{1}H NMR, ^{13}C NMR, and by GC-MS.

Although Sn/Si-MCM-41(A) and Si-MCM-41 were prepared by following the same hydrothermal synthesis route, Sn/Si-MCM-41(A) exhibited higher specific BET surface area (1215 m^2 g^{-1}) compared to Si-MCM-41 (1070 m^2 g^{-1}). This may be attributed to the changes in synthesis periods, unit cell parameters and wall thicknesses caused by the difference in the initial gel composition. Sn/Si-MCM-41(B) has shown specific BET surface area of magnitude 955 m^2 g^{-1} which is marginally lower than Si-MCM-41 indicating no structural damage due to the post-synthesis treatments such as impregnation/calcination.

Figure 1 shows the typical UV–vis diffuse reflectance spectra of these three samples. Si-MCM-41 did not show any absorption band relevant to charge transitions from O^{2-} to Sn^{4+} in tetrahedral coordination. Sn/Si-MCM-41(B) exhibited a broad absorption at 280 nm which may be assigned to

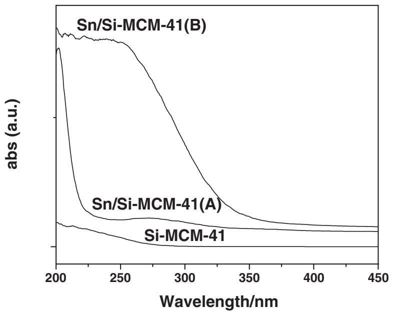


Figure 1. Diffuse reflectance UV–vis spectra of Si-MCM-41, Sn/Si-MCM-41(A), and Sn/Si-MCM-41(B).

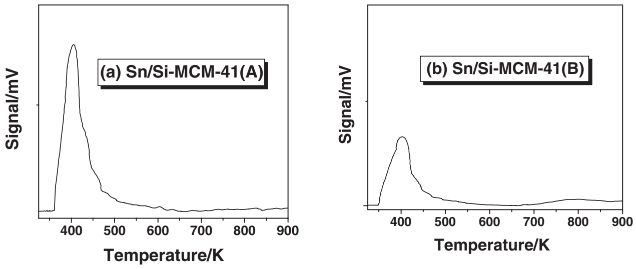


Figure 2. NH_3-TPD profile of (a) Sn/Si-MCM-41(A) and (b) Sn/Si-MCM-41(B).

hexacoordinated polymeric Sn–O–Sn species.[10,14] The spectrum of Sn/Si-MCM-41(A) revealed the absorption at 208 nm suggesting the presence of Sn^{4+} in tetrahedral coordination in the silica framework.[10,14] This implies that any differences in the catalytic behavior of these materials can be attributed to the differences in the acidity originating from the intrinsic differences in Sn location.

Figure 2 presents the NH_3-TPD profiles of Sn/Si-MCM-41(A) and Sn/Si-MCM-41(B) catalysts. Parent Si-MCM-41 showed only one desorption peak of ammonia in the low temperature region (375–525 K) having acid site concentration of 0.3 mmol g^{-1} NH_3. In the case of Sn/Si-MCM-41(B), the concentration of acid sites enhanced from 0.3 to 2.6 mmol g^{-1} NH_3 upon impregnation of SnO_2 (2.2 wt %) on Si-MCM-41. Interestingly, Sn/Si-MCM-41(A) prepared by direct hydrothermal synthesis showed the highest acidity (7.8 mmol g^{-1} NH_3) in the low (375–525 K) temperature region.

The catalyst activity results for the hydroxyalkylation of *p*-cresol to DAM are presented in Figure 3a. Among the solid acid catalysts screened for the hydroxyalkylation of *p*-cresol, the least acidic Si-MCM-41 (0.3 mmol g^{-1} NH_3) showed negligible activity, while Sn/Si-MCM-41(A) showed the highest catalyst activity (70% product yield with 88% selectivity to DAM, turn over frequency, 171 h^{-1}). The highest activity with Sn/Si-MCM-41(A) was due to its high acidity (7.8 mmol g^{-1} NH_3) which facilitates the formation of DAM. Compared to Sn/Si-MCM-41(A), Sn/Si-MCM-41(B) showed lower acidity (2.6 mmol g^{-1} NH_3) and lower activity (34% product yield with 90% selectivity to DAM, turn over frequency 88 h^{-1}).

The effect of reaction time on the product yield and DAM selectivity are presented in Figure 3b. It was observed that product yield and DAM selectivity increased from 11 to 70% and from 80 to 88%, respectively, with increase in the reaction time from 30 to 120 min. Interestingly, predominant formation of carbinol (20%) was observed after 30 min which further converted into DAM with increase in reaction time from 30 to 120 min.

The reusability of the Sn/Si-MCM-41(A) was assessed by catalyst recycle experiments. After the reaction, the catalyst was separated from the reaction mixture by filtration, washed several times with methanol, dried at 383 K for 2 h and reused for the hydroxyalkylation of *p*-cresol. The catalyst Sn/Si-MCM-41(A) was found to give 68% product yield after the 3rd recycle experiment as compared to 70% product yield for the fresh catalyst while the selectivity to DAM was constant at 88%. The slight decrease in product yield from 70 to 68% was due to handling losses of the catalyst during the recycle experiments.

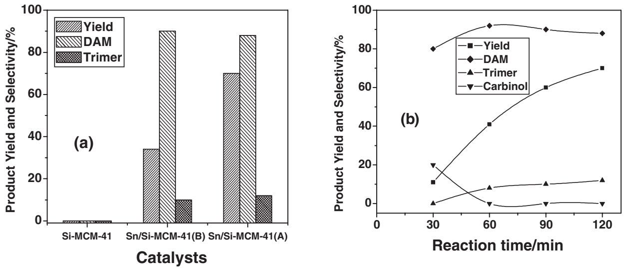


Figure 3. (a) Catalyst screening and (b) effect of reaction time on product yield and selectivity. Reaction conditions: *p*-cresol, 42 mmol; formaldehyde, 8.4 mmol; *p*-cresol to formaldehyde, 5; catalyst concentration, 0.04 g cm^{-3}; temperature, 363 K; toluene, 12 cm^3; catalyst, Sn/Si-MCM-41(A).

In summary, Sn/Si-MCM-41(A) catalyst prepared by direct hydrothermal synthesis showed higher catalyst activity (70% product yield with 88% selectivity to DAM, turn over frequency, 171 h^{-1}) than Sn/Si-MCM-41(B) prepared by the impregnation of Sn on Si-MCM-41. The higher activity with the former was due to its higher acidity (7.8 mmol g^{-1} NH_3) as evidenced by NH_3-TPD results.

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