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Editor Choice Paper

Selective, efficient nanoporous catalysts for nitroaldol condensation: Co-placement of multiple site-isolated functional groups on mesoporous materials

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ABSTRACT

We recently reported the synthesis of efficient multifunctional catalysts for the Henry reaction by grafting aminopropyl groups on mesoporous silica with polar, protic solvents such as ethanol [K.K. Sharma, T. Asefa, Angew. Chem. Int. Ed. 46 (2007) 2879–2882]. Here we describe that the grafting of aminopropyl groups with secondary organic functional groups in polar solvents results in *selective* efficient nanoporous catalysts for hydrophilic or hydrophobic reactants in the Henry reaction. In the synthesis, a mixture of aminorganosilanes and secondary organosilanes containing ureidopropyl, 3-mercaptopropyl, or methyl groups was reacted with the silanol groups of mesoporous silica in *isopropanol*. While the 3-aminopropyl groups introduced solid-base catalytic sites, the secondary functional groups and the residual ungrafted silanols on the materials modified the catalyst's surface to either hydrophilic or hydrophobic. More importantly, by grafting the organosilanes in isopropanol, site-isolated multifunctional groups and high surface area mesoporous solid-base catalysts resulted, which afforded not only selectivity for hydrophilic or hydrophobic reactants but also high percentage conversion (~100%) of various *p*-substituted benzaldehydes within 15–30 min of the Henry reaction. Furthermore, the time to achieve the maximum selectivity for hydrophilic or hydrophobic reactants in mixtures of *p*-substituted benzaldehydes was obtained. These results are significant compared to examples of previously reported selective catalysts, which showed selectivity only for hydrophobic reactants with a maximum selectivity of 2.6:1.0, and a highest conversion of 50% in 24 h [J. Huh, et al., J. Am. Chem. Soc. 126 (2004) 1010–1011]. Our synthetic approach can be extended to other reactants and reactions by judiciously choosing and grafting multiple organic groups in polar, protic solvents.

1. Introduction

Many pharmaceutical and industrial catalytic processes involve multiple, similar reactants and competitive reactions, while only a product from one of the reactants or reactions is needed [1]. Obtaining specific products by selectively catalyzing a specific reactant or reaction in a mixture of similarly reactive compounds or from competitive reactions is often necessary for the efficient production of various fine chemicals and industrial materials [2]. Consequently, the development of selective and efficient catalysts for one specific reactant has remained an important research area in catalysis and materials science [3]; however, achieving the goal is often met with considerable challenges [4]. For instance, by exploiting the difference in the size and shapes of the reactants and their mass transport into the catalytic sites on solid zeolite porous supports [5], many selective catalysts have been synthesized [6]. However, due to the narrow pore-sizes of zeolites, selective catalytic reactions of only smaller molecules are possible [7].

Recent advances in the synthesis of organic- and organometallic-functionalized mesoporous metal oxides [8,9], periodic mesoporous organosilicas [10], imprinted polymeric [11], and imprinted metal oxide [12] nanostructured materials have opened up synthetic strategies to novel selective catalysts [13]. While the nanoporous structures in mesoporous materials enable size and shape selectivity as in zeolites [14], the higher pore diameters and the large surface areas in the former further allow surface immobilization of large number and many types of organic groups to tune the surface properties and pore-diameters of the materials [15] without severely clogging the pores as in zeolites [6,16,17]. Functionalization of these materials with organic groups of specific hydrophobicity or hydrophilicity [18,19] modifies the dielectric environment of the catalytic sites [20] and enables reactants of appropriate polarity to access the catalytic sites and undergo preferential catalytic reactions [21]. For instance, by co-assembling

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two organosilanes [22], Lin and co-workers [23] have synthesized bifunctional mesoporous organosilica materials that are selective for hydrophobic benzaldehydes in the nitroaldol reaction. These materials, however, achieved the required selectivity for only hydrophobic reactants and with a maximum conversion of 50% in over 24 h. Since co-condensation procedures in synthesis of mesoporous organosilica often result in poorly ordered mesostructures [24], this might be one of the reasons for low % conversion in nitroaldol condensation by these mesoporous materials. Very recently, Anwander and co-workers synthesized functionalized mesoporous silica with a two-step grafting method in non-polar solvent, cyclohexane, to engineer the pore-size of SBA-15 materials for size-selective catalytic transformations [25]. By using various sized long chain alkyl dimethylaminosilanes and organoaluminum compounds, they demonstrated aluminum-catalyzed Meerwein–Ponndorf–Verley reduction of aromatic aldehydes (benzaldehyde and 1-pyrenecarboxyaldehyde) [26,27] of varying size. Although selective catalysis was achieved by these materials, the selectivity was accompanied with low % conversion because of aggregated grafting of the catalytic sites and lower surface area of the materials, a result of grafting in non-polar solvents.

Here we describe the synthesis of efficient multifunctional mesoporous catalysts with tunable selectivity for hydrophilic or hydrophobic reactants in the Henry (nitroaldol) reaction [28]. The synthesis of the catalysts was achieved by rationally extending our recent successful synthetic approach to an efficient catalyst [29,30] for the Henry reaction. In the present study, the aminopropyl groups were grafted along with hydrophobic or hydrophilic secondary functional groups with different loadings in polar, protic solvents inside mesoporous materials to produce efficient and selective catalysts. While 3-aminopropyl groups introduced solid-base catalytic sites, the secondary functional groups, which consisted of ureidopropyl, 3-mercaptopropyl, or methyl groups, as well as the residual silanol groups allowed modification of the material's surface into hydrophilic or hydrophobic [19,23,31]. The choice of the secondary functional groups partially relied on the commercial availability of the corresponding organosilanes. Surface silanols and ureidopropyl groups modified the pores to be hydrophilic; mercaptopropyl provided an intermediate dielectric environment and methyl groups modified the pores to be hydrophobic. The catalytic properties of the resulting materials were investigated in the Henry (nitroaldol condensation) reaction between benzaldehydes of varying hydrophobicity by virtue of their *para*-substituents with nitromethane; either for each reactant individually or in a 1:1 mole ratio of reactant mixtures. These reactants included *p*-hydroxybenzaldehyde (*p*-OH), *p*-butoxybenzaldehyde (*p*-But) and *p*-tolualdehyde (*p*-methylbenzaldehyde, *p*-Me) [23]. The reactants were chosen and reactions were performed in a manner that allowed the comparison of both the effect of hydrophobicity and steric bulk of the reactants on selectivity. For example, *p*-Me and *p*-OH were construed to be hydrophobic and hydrophilic reactants, respectively, while *p*-Me and *p*-But as a pair of reactants with varying degrees of steric bulk. *p*-OH and *p*-But could also be used to provide the difference in steric bulk, but our choice of *p*-Me and *p*-But was based on approximately similar hydrophobicities of the latter aldehydes. Comparisons and conclusions were drawn based on % conversion per unit time of these reactants in the Henry reaction in the presence of various catalysts prepared from the same batch of MCM-41 as parent material by grafting in polar, protic solvent. Comparison based on individual reactants showed that samples containing 3-aminopropyl groups alone or along with the ureidopropyl groups catalyzed the hydrophilic reactant, *p*-OH, preferentially over a relatively more hydrophobic reactant, *p*-Me. Those samples containing mercaptopropyl groups showed no difference in % conversion per unit time for the two reactants. Methyl grafted samples, on the other hand, showed a clear preference for catalyzing *p*-Me over *p*-OH [Fig. 4(A)]. While a correlation in the hydrophobicity of mesopores and % conversion per unit time was observable in reactions performed individually, no significant difference in rate was found for reactions with 1:1 molar mixture of *p*-Me and *p*-OH reactants [Fig. 5(A)].

Therefore, to achieve selectivity in reactions performed with mixture of reactants, higher loading of methyl groups was obtained by grafting with 3:1 and 9:1 mole ratios of methyltrimethoxysilane:3-aminopropyltrimethoxysilane in isopropanol. These samples showed an increased selectivity for *p*-Me over *p*-OH when present together in a reaction mixture, probably due to further lowering of the dielectric environment of the mesopores. It is noteworthy that selectivity with our catalysts was accomplished in small reaction time (typically 15–30 min) with extremely high % conversion (~100% in many cases). For comparison, mesoporous selective catalysts reported by Huh et al. [23] give a maximum of 50% conversion over 24 h and moderate selectivity only for hydrophobic reactants. By a comparative study of MCM-41 [32] and SBA-15 [33] type materials functionalized with similar organic functional groups, we found that the size of the nanopores played no significant role in determining selectivity for our reactants. Furthermore, drying the catalysts before reactions was found to enhance their efficiency.

Control samples UDI-MCM, MEI-MCM and MPI-MCM containing ureidopropyl, methyl and mercaptopropyl, respectively, without catalytic amine groups were also prepared by stirring MCM-41 in the presence of the corresponding organosilanes in isopropanol. The Henry reaction performed with these samples showed no or trace product formation over a period of 60 min.

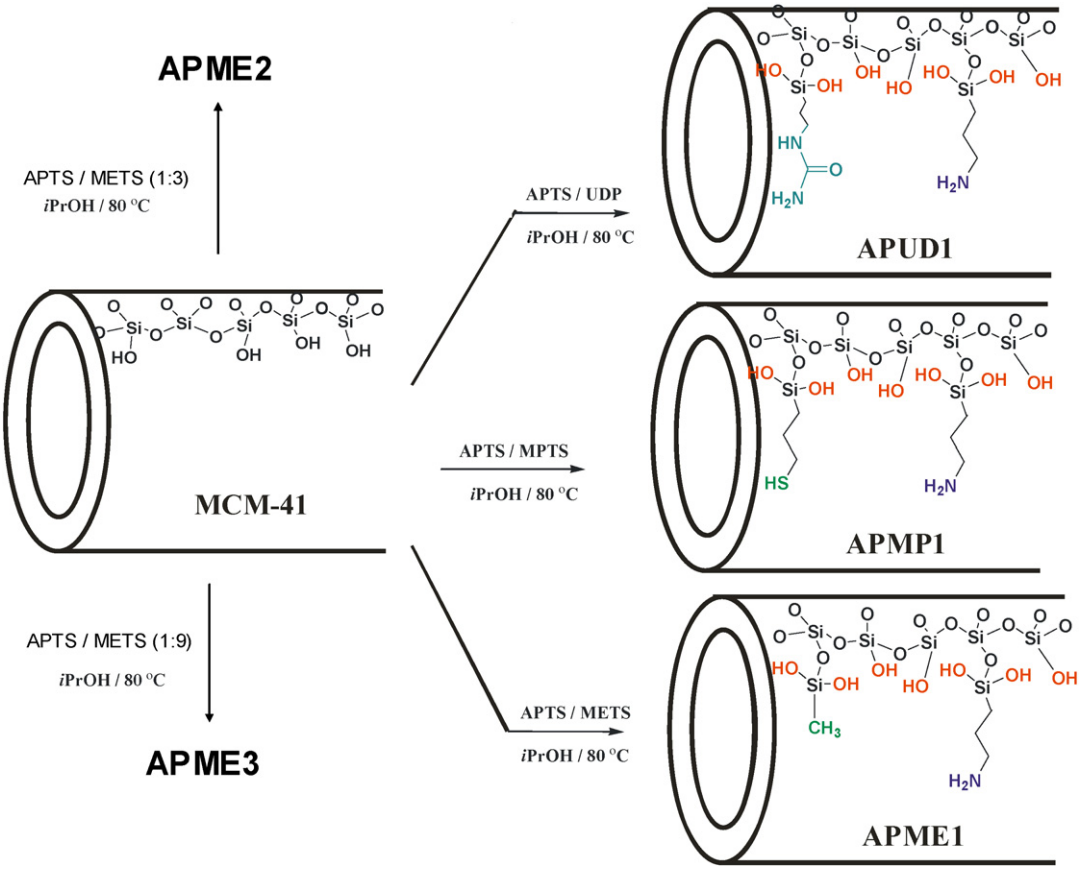
2. Experimental

2.1. Materials and reagents

p-Hydroxybenzaldehyde (*p*-OH), *p*-butoxybenzaldehyde (*p*-But), *p*-methylbenzaldehyde (*p*-Me), cetyltrimethylammonium bromide (CTAB), tetraethylorthosilicate (TEOS), 3-aminopropyltrimethoxysilane (APTS), poly(ethylene oxide)-*block*-poly(propylene oxide)-*block*-poly(ethylene oxide) (P123), and nitromethane were obtained from Sigma–Aldrich. 3-Mercaptopropyltrimethoxysilane (MPTS), ureidopropyltriethoxysilane (50% in methanol) (UDPS), and methyltrimethoxysilane (METS) were obtained from Gelest, Inc. Anhydrous toluene and isopropanol were purchased from Pharmco-AAEPR.

2.2. Grafting of two different functional groups onto mesoporous silica in polar solvents

Mesostructured MCM-41 and SBA-15 type materials were synthesized by following previously reported procedures [29,34,35] (See Supporting Materials for details). Two organosilanes consisting of 3-aminopropyl (AP) and a secondary organic group including ureidopropyl (UDP), mercaptopropyl (MP) or methyl (ME) were grafted onto MCM-41 (or SBA-15, see below) by stirring 1:1 mole ratio of APTS with UDPS, MPTS, or METS onto MCM-41 (or SBA-15) in isopropanol. Briefly, for example, 500 mg of the MCM-41 sample was stirred in a mixture of excess organosilanes containing 1.842 mmol of APTS and 1.842 mmol METS in 325 mL anhydrous isopropanol under reflux at ~80 °C for 6 h. The reaction mixture was filtered, washed with ethanol, and dried. The resulting material was labeled as APME-1. Similarly, other samples were prepared (see Scheme 1 and Table 1 for details). The resulting samples were labeled as APUD1, APMP1, and APME1 where "AP" stands for 3-



Scheme 1. Synthesis flowchart of selected multifunctional mesoporous samples containing various concentrations of 3-aminopropyl (AP) catalytic groups, residual silanols, and secondary organic groups [ureidopropyl (UD), 3-mercaptopropyl (MP), or methyl (ME)]. The compositions shown in the scheme were determined based on the various characterization results.

aminopropyl, "UD" for ureidopropyl, "MP" for 3-mercaptopropyl, and "ME" for methyl. A control catalytic sample was also prepared by grafting APTS alone (3.684 mmol) onto MCM-41 under reflux at ~80 °C in 325 mL isopropanol for 6 h. The resulting sample was labeled as API1. Additionally, three control samples namely UDI-MCM, MEI-MCM and MPI-MCM containing ureidopropyl, methyl and mercaptopropyl, respectively, without catalytic amine groups in them were also prepared by stirring MCM-41 in the presence of the corresponding organosilanes, UDPS, METS, and MPTS, respectively, in 325 mL isopropanol at 80 °C.

2.3. Grafting of MCM-41 with APTS:METS in 1:3 and 1:9 mole ratio in isopropanol

To prepare samples containing large concentrations of hydrophobic groups, MCM-41 was stirred in 1:3 and 1:9 mole

Table 1
Synthesis and structural data of multifunctional mesoporous materials and the control samples

Sample[a]	Substrate/organosilanes (solvent)[b]	Unit cell (Å)[c]	Pore width (Å)[d]	Wall thickness (Å)[e]	BET surface area (m^2/g)[f]	Pore volume (cm^3/g)
MCM-41	–	45	32	13	983	0.98
APUD1	MCM-41/1:1 APTS + UDPS, isopropanol	44	29	15	833	0.64
APMP1	MCM-41/1:1 APTS + MPTS, isopropanol	43	28	15	903	0.72
APME1	MCM-41/1:1 APTS + METS, isopropanol	44	27	17	896	0.70
API1	MCM-41/APTS, isopropanol	43	28	15	950	0.65
API1A	MCM-41/APTS, isopropanol, 12 h	43	27	16	960	0.66
SBA15	–	107	61	46	557	0.75
API1-SBA	SBA-15/APTS, isopropanol	113	62	51	356	0.63
APUD1-SBA	SBA-15/1:1 APTS + UDPS, isopropanol	108	59	49	372	0.63
APME1-SBA	SBA-15/1:1 APTS + METS, isopropanol	109	60	49	391	0.66
APMP1-SBA	SBA-15/1:1 APTS + MPTS, isopropanol	108	60	48	353	0.60

[a] The parent mesoporous silica and multifunctional mesoporous samples synthesized and studied.
[b] The synthesis of the multifunctional mesoporous samples were done by stirring MCM-41 or SBA-15 in the given organosilane(s) in isopropanol at 80 °C for 6 h, unless mentioned otherwise.
[c] Obtained from the sample's d-spacing on XRD (unit cell, $a_o = 2d_{100}/3^{1/2}$ for hexagonal P_{6mm} mesostructures).
[d] Obtained from the desorption branch of the N_2 gas adsorption isotherm.
[e] Wall thickness = unit cell – pore diameter.
[f] Obtained from the N_2 adsorption isotherm with the BET method [37].

ratios of APTS:METS in isopropanol at ~80 °C for 6 h. Briefly, a solution of 0.921 mmol of APTS and 2.763 mmol of METS was stirred with MCM-41 in 325 mL of anhydrous isopropanol at ~80 °C for 6 h. The reaction mixture was filtered, washed with ethanol, and dried under ambient conditions. The catalyst was labeled as APME2. Similarly, the catalyst prepared by stirring the 1:9 mole ratio of APTS and METS was labeled APME3.

2.4. Grafting of organosilanes onto SBA-15 in isopropanol

More samples were synthesized by stirring SBA-15 material with only APTS as well as in 1:1 mole ratio of APTS with METS, UDPS or MPTS. Typically 500 mg of SBA-15 was stirred in 3.684 mmol of APTS in 325 mL isopropanol under reflux at ~80 °C for 6 h resulting in API1-SBA-15. Stirring of 500 mg of SBA-15 in a mixture of 1.842 mmol of APTS and 1.842 mmol METS in 325 mL isopropanol resulted in APME1-SBA. Similarly, APUD1-SBA and APMP1-SBA were also synthesized (see Table 1).

2.5. Henry reaction

The nitroaldol condensation reaction was carried out by using each of the organoamine-functionalized samples obtained above as catalysts for reactions between nitromethane and various *p*-substituted benzaldehydes [20,23,29]. The reactants *p*-OH, *p*-But, and *p*-Me were used either individually or as a 1:1 mmol mixture of two reactants in the reaction. Typically, 20 mg of the functionalized mesoporous sample was added to a solution of 1 mmol *p*-hydroxybenzaldehyde and 10 mL of nitromethane. The reaction was stirred at 90 °C under nitrogen. Aliquots of the reaction mixture were taken with a filter syringe and solvent was removed with rotary-evaporator under vacuum. The residue was dissolved in acetonitrile-d_3 or acetone-d_6 and characterized by solution ^{1}H NMR over the course of the reaction. Two different NMR solvents acetonitrile-d_3 and acetone-d_6 were used to characterize the reactions of 1:1 molar mixture of reactants and individual reactants, respectively. Use of acetonitrile-d_3 as the NMR solvent for a mixture of reactants led to resolved spectra conducive to easy characterization. For the 1:1 mmol mixtures, a mixture of two reactants (for example, 1 mmol *p*-OH and 1 mmol *p*-But) was used for reaction, and characterizations were carried out as above in acetonitrile-d_3. Resonances in acetone-d_6: *p*-hydroxy nitrostyrene (^{1}H NMR): δ 2.95 (1H, br, s), 6.97 (2H, d), 7.72 (2H, d), 7.84 (1H, d, J = 13.5 Hz)), 8.03 (1H, d, J = 13.5 Hz) and 9.84 (1H, s); *p*-butoxy nitrostyrene (^{1}H NMR): (^{1}H NMR): δ 7.98 (1H, d, J = 13.5 Hz), 7.87 (1H, d, J = 13.5 Hz), 7.78 (2H, d), 7.05 (2H, d), 4.13 (2H, t), 1.82 (2H, m), 1.55 (2H, m), 0.98 (3H, t); and *p*-methyl nitrostyrene (^{1}H NMR): δ 8.07 (1H, d, J = 13.5Hz), 7.93 (1H, d, J = 13.5Hz), 7.72 (2H, d), 7.33 (1H, d), 2.45 (3H, s); *p*-hydroxybenzaldehyde (^{1}H NMR): δ 9.85 (1H, s), 7.81 (2H, d), 7.02 (2H, d), 2.95 (1H, br, s); *p*-butoxybenzaldehyde (^{1}H NMR): δ 9.88 (1H, s), 7.86 (2H, d), 7.10 (2H, d), 4.13 (2H, t), 1.82 (2H, m), 1.55 (2H, m), 0.98 (3H, t): *p*-tolualdehyde 9.99 (1H, s), 7.82 (2H, d), 7.42 (2H, d), 2.44 (3H, s). Resonances in acetonitrile-d_3: *p*-hydroxy nitrostyrene (^{1}H NMR): δ 2.19 (1H, br, s), 6.90 (2H, d), 7.57 (2H, d), 7.68 (1H, d, J = 13.5 Hz), 8.00 (1H, d, J = 13.5) and 9.84 (1H, s); *p*-butoxy nitrostyrene (^{1}H NMR): δ 8.10 (1H, d, J = 13.5 Hz), 7.77 (2H, d), 7.71 (1H, d, J = 13.5Hz), 6.99 (2H, d), 4.06 (2H, t), 1.77 (2H, m), 1.52 (2H, m), 0.96 (3H, t); *p*-methyl nitrostyrene (^{1}H NMR): δ 8.07 (1H, d, J = 13.5Hz), 7.93 (1H, d, J = 13.5Hz), 7.71 (2H, d), 7.32 (1H, d), 2.43 (3H, s); *p*-hydroxybenzaldehyde (^{1}H NMR): δ 9.82 (1H, s), 7.63 (2H, d), 7.05 (2H, d), 2.19 (1H, br, s); *p*-butoxybenzaldehyde (^{1}H NMR): δ 9.85 (1H, s), 7.84 (2H, d), 7.05 (2H, d), 4.06 (2H, t), 1.77 (2H, m), 1.52 (2H, m), 0.96 (3H, t); *p*-tolualdehyde 9.99 (1H, s), 7.78 (2H, d), 7.39 (2H, d), 2.41 (3H, s).

2.6. Instrumentations

The powder X-ray diffraction (XRD) was measured using a Scintag powder diffractometer. The solid-state ^{13}C (75.5 MHz) and ^{29}Si (59.6 MHz) NMR spectra were acquired on a Bruker AVANCE 300 spectrometer. For ^{13}C CP-MAS NMR experiments, we employed 7.0 kHz spin rate, 5 s recycle delay, 1 ms contact time, $\pi/2$ pulse width of 5.2 μs, and 1000–3000 scans using TPPM ^{1}H decoupling. For the ^{29}Si CP-MAS NMR experiments, we employed 7.0 kHz spin rate, 10 s recycle delay, 10 ms contact time, $\pi/2$ pulse width of 5.6 μs, and 256–1024 scans using TPPM ^{1}H decoupling. The ^{29}Si MAS NMR experiments were done with 7.0 kHz spin rate, 100 s recycle delay, $\pi/6$ pulse width of 1.9 μs, and 700–4000 scans using high power CW ^{1}H decoupling. The solution ^{1}H NMR was measured by Bruker DPX-300 NMR spectrometer. The BET gas adsorptions were measured with Micromeritics Tristar 3000 adsorption analyzer at 77 K by following previously reported procedures [29,36,37]. The TEM images were taken by using a FEI Tecnai T-12 S/TEM transmission electron microscope working at 120 keV. The samples for TEM were prepared by sonicating the mesoporous samples in ethanol for 3 min, casting a drop of the solution on a formvar-carbon coated copper grid and letting it to dry under ambient conditions.

3. Results and discussion

3.1. Synthesis and characterizations

A series of multifunctional and selective mesoporous catalysts containing site-isolated AP groups, many residual silanols, and secondary organic functional groups, including UD, MP, or ME groups, were synthesized. The synthesis was carried out by grafting a mixture of the corresponding organosilanes in various proportions in isopropanol onto the channel walls of well-ordered mesoporous silica (MCM-41) sample (Scheme 1 and Table 1). Isopropanol was chosen as a solvent for grafting because we recently reported that grafting of 3-aminopropyltrimethoxysilane in isopropanol leads to optimum site-isolated AP groups for highly efficient solid-base catalyzed nitroaldol condensation reaction [29], and as other researchers also reported site-isolated catalytic sites often to be more efficient catalysts for other reactions as well [38]. Therefore, samples APUD1, APMP1, and APME1, which were synthesized by grafting 1:1 mole ratios of the corresponding two organosilanes in isopropanol, were anticipated to have site-isolated aminopropyl groups and be efficient catalysts. Control samples, containing only 3-aminopropyl groups, were also synthesized by stirring MCM-41 with APTS in isopropanol, resulting in API. To investigate the effect of size of nanopores on selectivity, similarly functionalized samples and control samples from parent SBA-15 material, whose pore diameter is approximately two times larger than that of MCM-41, were also synthesized. The latter samples were labeled as APUD1-SBA, APMP1-SBA, APME1-SBA, and API-SBA. All the samples synthesized and studied, and the procedures followed to prepare the samples are compiled in Table 1.

The original parent MCM-41 and SBA-15 materials, and all the functionalized mesoporous materials were characterized by XRD (Fig. 1), transmission electron microscopy (TEM) (Fig. 2 and Supporting Fig. S1), and N_2 gas adsorption (Supporting Fig. S2). The results indicated that all the samples had well-ordered mesoporous structures with unit cell dimensions of ~43–45 Å and ~107–113 Å, for those synthesized from MCM-41 and SBA-15, respectively (Fig. 1). The corresponding pore widths were obtained to be between 27–32 Å and 59–62 Å, respectively, while the BET surface areas ranged from 833 to 983 m^2/g and 353 to 557 m^2/g,

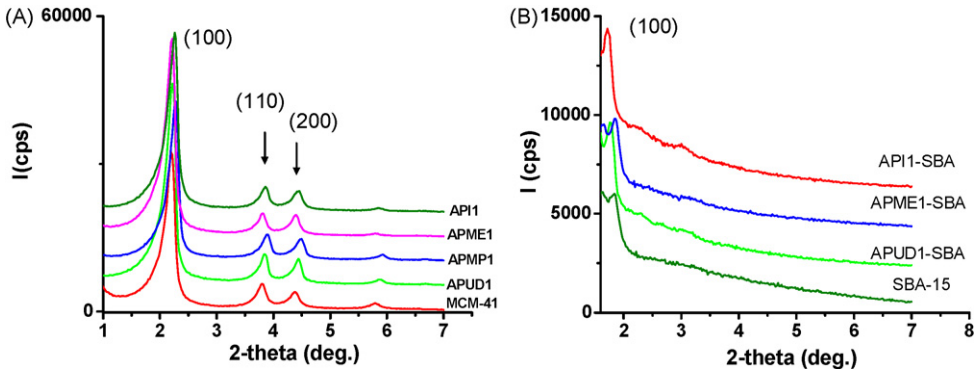


Fig. 1. (A) Powder X-ray diffraction patterns of MCM-41 compared with the corresponding selected multifunctional mesoporous catalysts prepared by one-step grafting in isopropanol: APUD1, APMP1, APME1, and API1. (B) Powder X-ray diffraction patterns of SBA-15 compared with corresponding selected multifunctional mesoporous catalysts prepared by one-step grafting in isopropanol: APUD1-SBA, APME1-SBA, and API1-SBA.

respectively. Samples with relatively higher % of grafted organic groups typically showed lower surface areas. This is consistent with other functionalized mesoporous materials synthesized by grafting organosilanes in toluene, which are reported in the literature [39] (see Table 1). The grafting procedures did not cause a loss of the mesostructures other than a slight decrease in unit cell dimensions, pore diameters and surface areas of the materials (Fig. 1 and Table 1). The presence of well-ordered mesostructures in the sam-

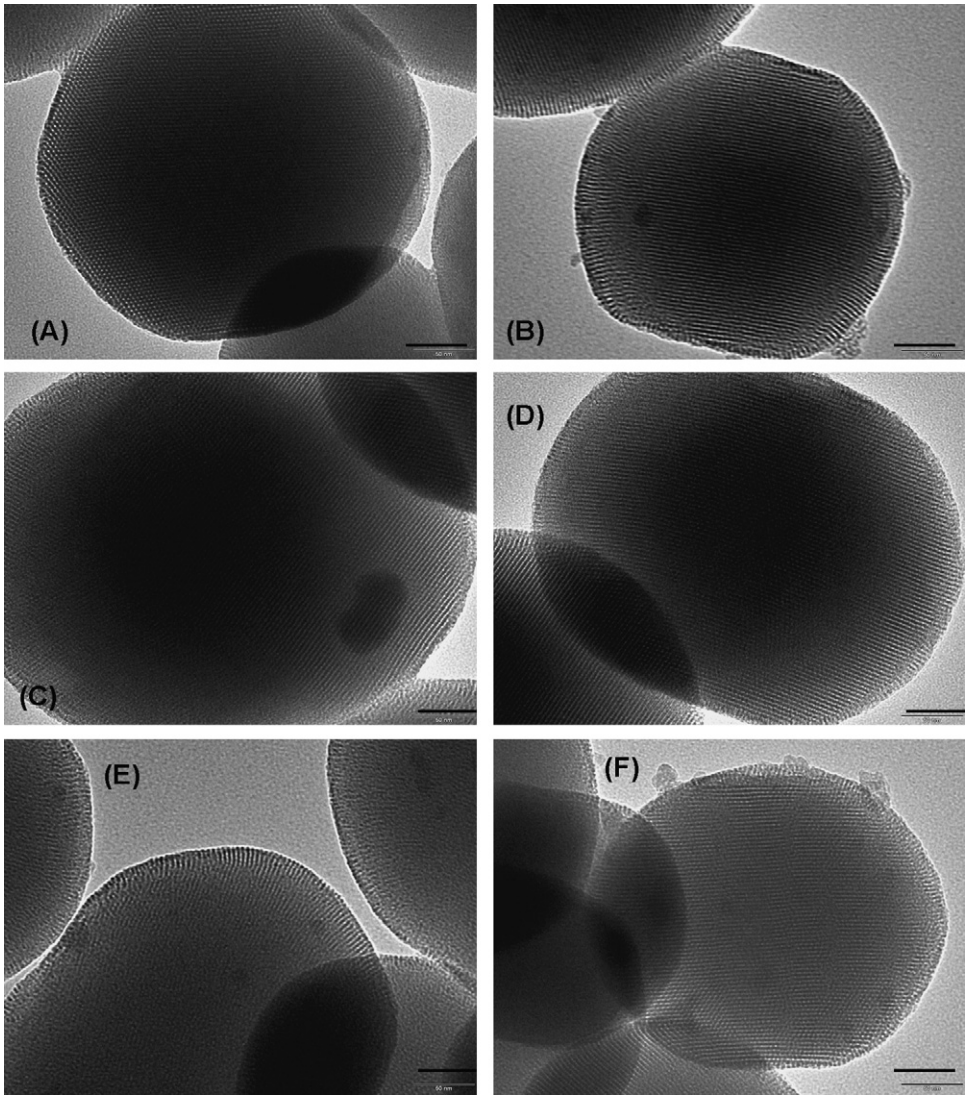


Fig. 2. TEM images of (A) MCM-41 and selected multifunctional mesoporous catalysts (B) APMP1, (C) APME1, (D) APMP2, (E) APME2, and (F) API1. Scale bar = 50 nm in all images.

Table 2
Relative catalytic efficiency of various mesoporous catalysts synthesized from MCM-41 by grafting, in the individual Henry reactions of *p*-hydroxybenzaldehyde (*p*-OH), *p*-butoxybenzaldehyde (*p*-But), and *p*-tolualdehyde (*p*-Me) with nitromethane[a] as substrate and solvent

Sample	N, EA[b] (wt.%)	Maximum ratio of % conversion, *p*-OH/% *p*-But (time, min)[c]	Maximum ratio of % conversion, % *p*-Me/% *p*-OH (time, min)[c]	Maximum ratio of % conversion, % *p*-Me/% *p*-But (time, min)[c]	% conversion *p*-OH: % conversion *p*-But at Maximum ratio[d]	% conversion *p*-Me:% Conversion *p*-OH at Maximum ratio[d]	% conversion of *p*-Me:% conversion *p*-But at Maximum ratio[d]
MCM-41	–	–	–	–	–	–	–
API1	1.02[e]	2.4 ± 0.1 (12)	0.6 ± 0.1 (16)	1.5 ± 0.1 (12)	82:34	61:95	51:34
APUD1	1.64	1.6 ± 0.1 (21)	0.8 ± 0.1 (19)	1.3 ± 0.1 (28)	86:54	61:78	94:73
APMP1	2.11 (0.83)	2.2 ± 0.1 (16)	1.2 ± 0.1 (8)	2.1 ± 0.1 (15)	86:40	48:38	81:38
APME1	2.50	1.7 ± 0.1 (21)	1.3 ± 0.1 (12)	2.2 ± 0.1 (12)	93:55	69:54	69:32

[a] The reaction was performed at 90 °C by using nitromethane as reactant and solvent unless mentioned otherwise.
[b] The wt. % N from elemental analysis, EA. The numbers in bracket indicate % S obtained from Ref. [28b].
[c] The maximum ratio of % conversion of the two reactants or the maximum selectivity, which was determined from the ratio of % conversion versus time of one reactant with that of the other, from the reactions done individually.
[d] The % conversion of the two reactants at the time the maximum ratio was obtained (See Fig. 4).
[e] From Ref. [30].

ples was also corroborated by TEM images (Fig. 2 and Fig. S1) and the type IV isotherms obtained on the N_2 gas adsorption experiments (Supporting Fig. S2). The structural data for the characterized samples are compiled in Table 1.

By using elemental analysis (Table 2) and ^{13}C and ^{29}Si solid-state NMR spectroscopy (Fig. 3), the presence and concentrations of the functional groups have been analyzed. Elemental analysis was also used to quantify the wt.% N (or % NH_2) and wt.% S (or % thiol) groups in the samples (Table 2). The elemental analysis data indicated that the grafting of 1:1 mole ratio of APTS:UDPS resulted in less % N than those corresponding samples grafted with 1:1 mole ratio of APTS:MPTS and APTS:METS. Due to the hydrophilic nature of APTS and UDPS and their tendency to form hydrogen bonding with isopropanol and among themselves, these molecules have less tendency to go to the surface silanols to graft in polar solvents [9]. Detailed study on the correlations between solvents and concentrations of grafted groups was reported recently [30]. The elemental analysis data also revealed that the grafting of 1:3 and 1:9 APTS:METS resulted in even lower % N (or –NH_2 groups), i.e., wt. % N of 1.46 for APME2 and wt. % N of 1.07 for APME3, which was probably due to relatively lower concentrations of APTS used in these cases.

The ^{13}C CP-MAS NMR spectra of all the samples grafted with APTS containing solutions showed peaks at 9.4, 24.4 and 43.6 ppm.

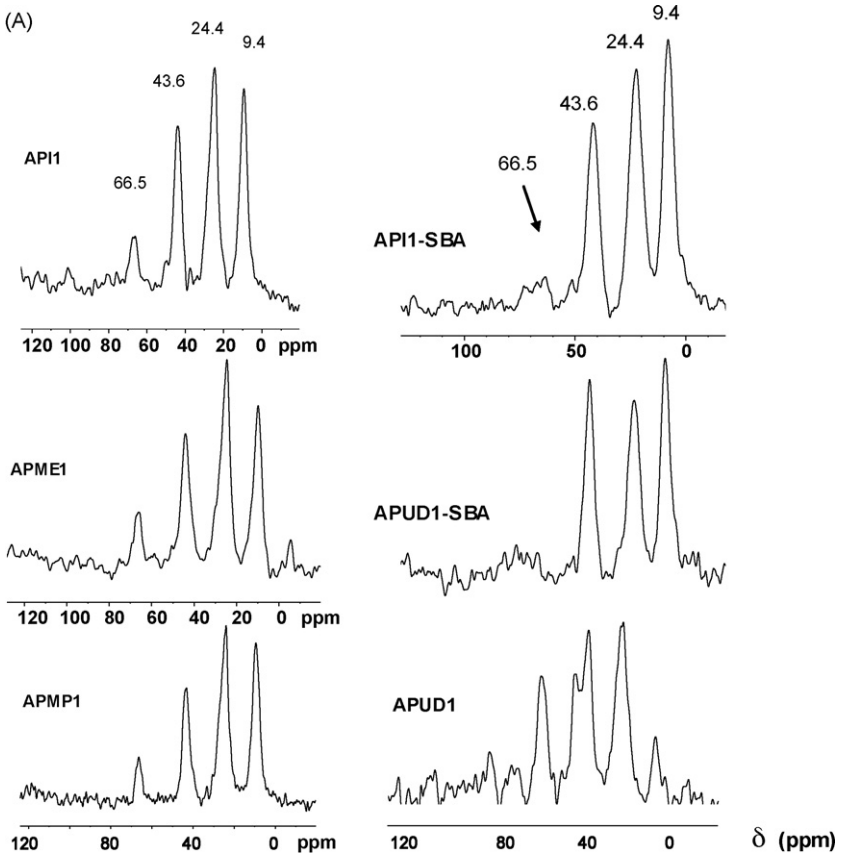


Fig. 3. (A) ^{13}C CP-MAS solid-state NMR spectra of various multifunctional mesoporous catalysts (API1, APME1, APMP1, API1-SBA, APUD1-SBA, and APUD1) and (B) ^{29}Si MAS solid-state NMR spectroscopy of MCM-41, and various multifunctional mesoporous catalysts (API1, APME1, APMP1, API1-SBA, APUD1-SBA, and APUD1).

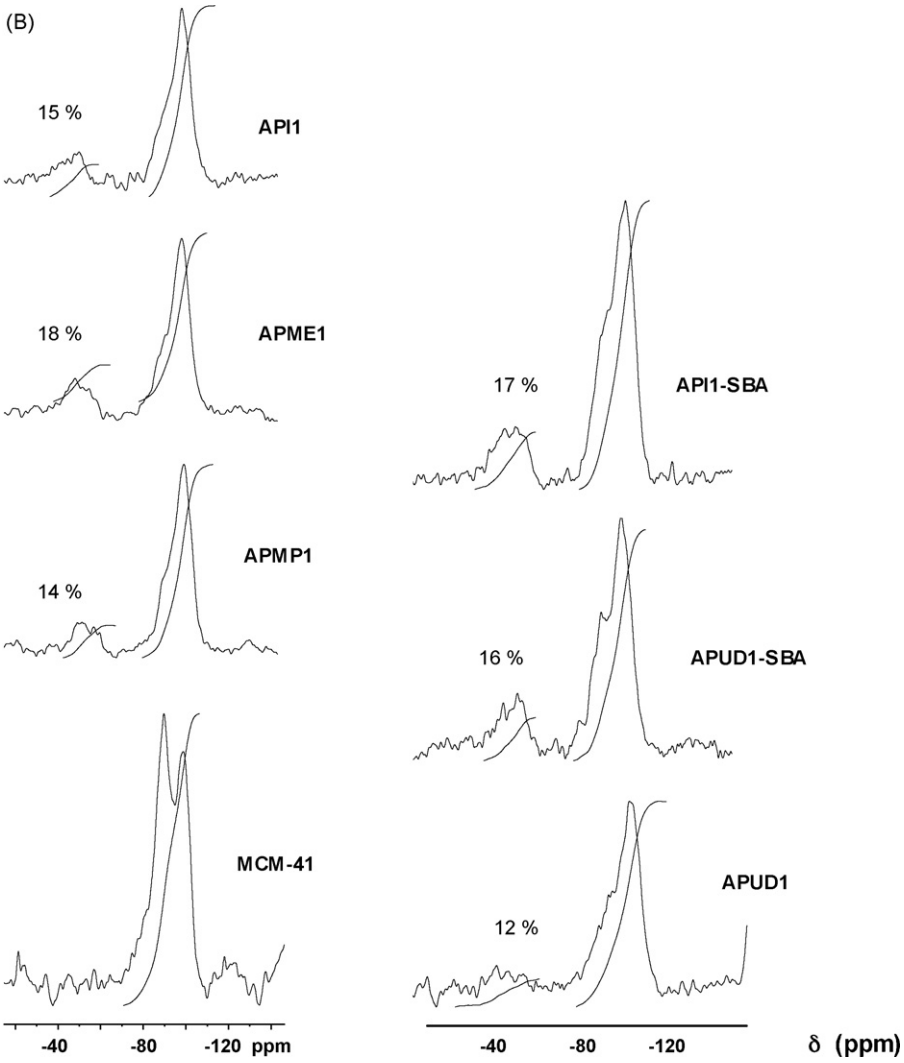
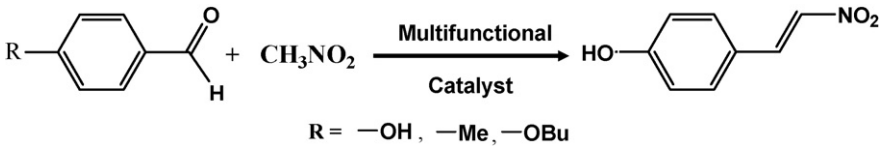


Fig. 3. (*Continued*).

These broad peaks correspond to the α, β, and γ carbons, respectively, of AP group. Coincidently, the peaks for the secondary functional groups, namely UD, or MP groups also appear around the same chemical shift position as those of APTS, also reported in previous studies [23,40,41]. The weak peak at −6 ppm in samples APME1 corresponds to the carbon atoms of ME groups [42]. The peak observed at 66 ppm corresponds to isopropoxide [$(CH_3)_2CHO$–] carbons, from isopropanol solvent used for grafting. Such alkoxide peaks often appear in ^{13}C CP-MAS solid-state NMR spectra of functionalized mesoporous samples synthesized by grafting, either due to reactions of the polar, protic solvents with silanol groups or their chemisorption [43]. After grafting of the organosilanes onto the mesoporous silica, the Q3 and Q2 peaks corresponding to $SiO_{1.5}(OH)$ and $SiO(OH)_2$ groups of the silica decreased while the T peaks corresponding to $RSi(O)_x(OH)_y$ groups increased (Fig. 3B). Due to the overlap of T peaks corresponding to different organic groups, we did not attempt to quantify the organic groups by ^{29}Si NMR and we solely relied on elemental analysis results. Nevertheless, quantification was difficult for the ME groups based on elemental analysis of C due to the presence of residual isopropoxide groups, which also contain carbon atoms.

3.2. Selective catalytic properties and selective catalysis

Comparative studies on the selective catalytic properties and efficiency of each material for various *p*-substituted benzaldehydes including *p*-OH, *p*-But and *p*-Me either individually or in a reaction mixture in the Henry (nitroaldol condensation) reaction were investigated (Scheme 2). As reported previously [29,30] for samples grafted in polar protic solvents, all multifunctional mesoporous catalysts containing 3-aminopropyl groups and secondary functional groups grafted in isopropanol reported here catalyzed



Scheme 2. The catalysis of different *p*-substituted benzaldehydes with nitromethane in a mixture of two reactants by a selective multifunctional catalyst.

the nitroaldol condensation very efficiently. Relative catalytic efficiency based on % conversion per unit time for different reactants was observed to be dependent on the type and relative concentration of secondary functional groups. It is also worth noting that these reactions resulted in *p*-substituted nitrostyrene products exclusively, unlike some catalysts reported in the literature where a mixture of nitroalcohol and nitrostyrene [44] was observed.

Fig. 4(A–C) shows % conversion versus time graph of nitroaldol condensation of individual reactions of *p*-OH, *p*-Me and *p*-But with nitromethane. These reactants were so chosen to allow a systematic study of the dependence of efficiency and selectivity of reactants in the nitroaldol condensation reaction on differences in size and hydrophobicity [23]. Selectivity of different catalysts towards the reactants was compared based on

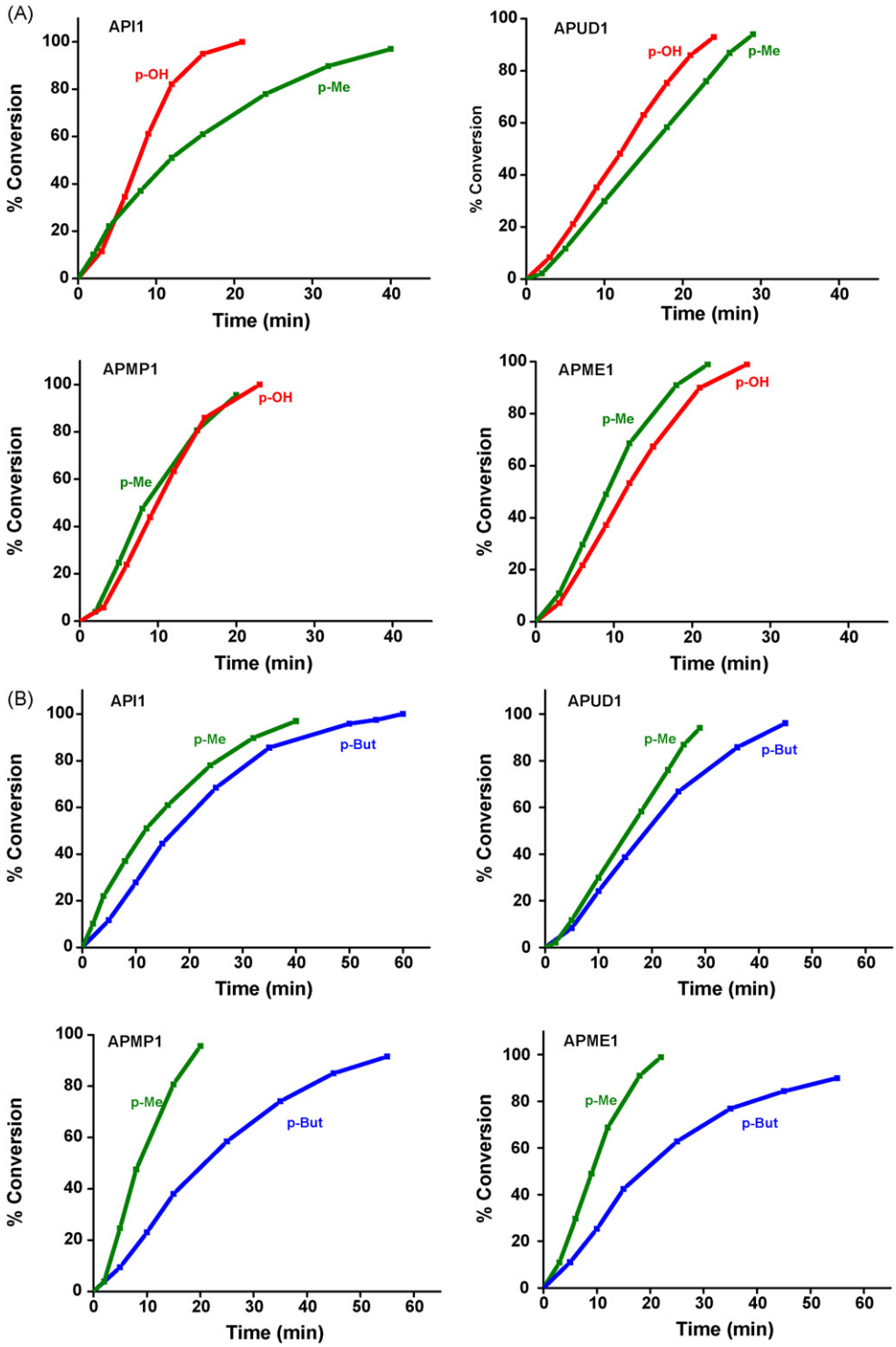


Fig. 4. % conversion vs. time plots for the Henry reaction of individual reactants (A) *p*-hydroxybenzaldehyde and *p*-tolualdehyde and (B) *p*-tolualdehyde and *p*-butoxybenzaldehyde (C) *p*-hydroxybenzaldehyde and *p*-butoxybenzaldehyde catalyzed by mesoporous catalysts API1, APUD1, APMP1, and APME1 synthesized from parent MCM-41 in presence of nitromethane.

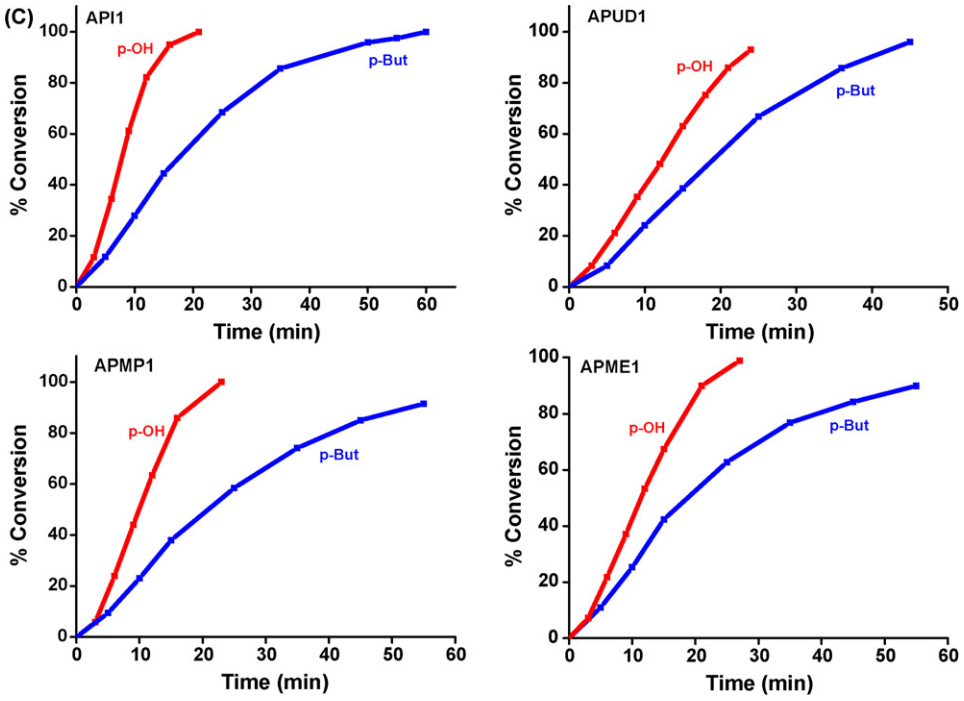


Fig. 4. (*Continued*).

differences in the ratio of % conversion per unit time for both the individual and mixture of reactants. The time and % conversion at which maximum selectivity was obtained were also determined.

A comparison of the ratio of % conversion of the two reactants *p*-Me and *p*-OH catalyzed individually with different catalysts showed interesting differences. While control experiments performed with the APTS precursor as in homogeneous phase in nitromethane (Fig. S3) showed the reaction rates in order *p*-OH ≫ *p*-Me > *p*-But, all the mesoporous catalysts synthesized showed variable reaction rates for the three reactants based on the type and concentration of secondary functional groups grafted. Based on the similarity in size of *p*-Me and *p*-OH, the differences that arise from one catalyst to other must be due to variable hydrophobicity of the mesopores achieved by grafting of different secondary functional groups or the differences in the rate of diffusion of the two reactants into the mesopores [45]. Confirming this, Fig. 4(A) shows the rate of *p*-Me relative to *p*-OH increasing with increasing hydrophobicity of the catalyst. The catalysts containing significantly hydrophilic ureidopropyl groups, APUD1, or no secondary functional groups, API1, show preference for the more hydrophilic reactant *p*-OH with a ratio of % conversion *p*-Me/*p*-OH values of 0.8 ± 0.1 and 0.6 ± 0.1, respectively (Table 2). APMP1, within limits of experimental error, shows no preference towards *p*-Me (Fig. 4A). The hydrophobic catalyst APME1, on the other hand, shows a preference for catalyzing *p*-Me over *p*-OH with values of 1.3 ± 0.1 (Table 2). While this trend was true for reactions catalyzed individually, no significant difference in rates were found for *p*-Me and *p*-OH when present together in a reaction mixture with the aforementioned catalysts (Figs. 5A and 6A). Although initial selectivity values of 1.2 ± 0.1 (Table 3) were obtained with most catalysts, it dropped rapidly to 1.0 as reactions progressed (Fig. 6A). We succeeded in obtaining selectivity for *p*-Me over *p*-OH when present together in a reaction mixture by increased loading of methyl groups in catalysts APME2 and APME3. A selectivity value of 1.8 ± 0.1 for *p*-Me/*p*-OH (Table 3) was obtained for both catalysts. It is also noteworthy that although all the catalysts showed a selectivity >1.0 initially for *p*-Me/*p*-OH (at low % conversions), only APME3 maintained a selectivity >1.0 even at 75% conversion for both of the reactants (Fig. 6A).

Comparison of catalysis of *p*-Me and *p*-But over the multifunctional catalysts also showed interesting differences when compared to the corresponding homogeneous reactions (Fig. S3). While all the catalysts preferentially catalyzed *p*-Me over *p*-But partially due to faster kinetics of *p*-Me evident in homogeneous catalysis (Fig. S3), far greater selectivity than that observed in homogeneous phase was obtained with the hydrophobic catalysts. In the individual

Table 3
Mesoporous catalysts and control samples synthesized by grafting in various solvents and their catalytic efficiency in a reaction containing 1:1 mole mixtures of various *p*-substituted benzaldehydes with nitromethane[a]

Sample	Maximum selectivity or [% *p*-Me/% *p*-OH] (time, min)[b]	% conversion *p*-Me:% conversion *p*-OH at maximum selectivity[b]	Maximum selectivity or [% *p*-Me/% *p*-But] (time, min)[b]	% conversion *p*-Me:% conversion *p*-But at maximum selectivity[b]
API1	1.2 ± 0.1 (5)	6:2	–	–
APUD1	1.2 ± 0.1 (5)	6:5	–	–
APMP1	1.2 ± 0.1 (5)	8:7	–	–
APME1	1.2 ± 0.1 (5)	9:7	2.7 ± 0.1	17:6
APME2	1.8 ± 0.1 (5)	7:4	3.2 ± 0.1	10:3
APME3	1.8 ± 0.1 (5)	6:3	4.2 ± 0.1	7:2

[a] The reaction was performed at 90 °C using nitromethane as the reactant and the solvent.
[b] The maximum ratio of % conversion of one reactant versus the other with respect to time, in a reaction mixture containing 1:1 mole ratio of both reactants.

reactions of *p*-Me and *p*-But with various catalysts, no significant difference between reactions catalyzed by APUD1 and API1 compared to homogeneous phase was found (Fig. 4B). Small ratios of % conversion of *p*-Me/*p*-But with values of 1.5 ± 0.1 for catalyst API1, and 1.3 ± 0.1 for catalyst APUD1 were observed (Table 2). Relatively hydrophobic catalysts APMP1 and APME1 showed marginally increased values of 2.1 ± 0.1 and 2.2 ± 0.1, respectively (Table 2). The selectivity of *p*-Me over *p*-But was more pronounced in reactions performed with a 1:1 molar mixture of reactants (Figs. 5B and 6B). Hydrophobic catalysts prepared by grafting of methyl groups showed large selectivities of 2.7 ± 0.1, 3.2 ± 0.1 and 4.2 ± 0.1 for APME1, APME2 and APME3, respectively (Table 3). If it is assumed that the methyl and amine groups are grafted in similar concentration as present in the grafting solution of MTMS and APTS organosilanes in isopropanol, then the order of selectivity values from APME1 to APME3 is concomitant with increase in methyl concentration. All APME*i* samples ($i = 1$–3) showed a decrease in selectivity with the progress of reaction; however, this decrease again was proportional to the methyl concentration, where samples with higher methyl concentrations exhibited lower decreases in selectivity over time (Fig. 6B). It is noteworthy that selectivity of *p*-Me over *p*-But was greater than 2.0 even at 40% conversion of reactants for APME2 and APME3.

A comparison of the reactions of *p*-OH and *p*-But with heterogeneous catalysts showed no significant difference compared to corresponding reactions conducted in homogeneous phase (Fig. S3). In both cases, selectivity for a more hydrophilic reactant *p*-OH over a more hydrophobic reactant *p*-But was obtained. The only apparent advantage our heterogeneous catalyst had with *p*-OH and *p*-But was heterogeneity accompanied by an appreciable selectivity for hydrophilic reactant *p*-OH over *p*-But. Further, *p*-OH showed faster kinetics than *p*-But with all the catalysts [42] with marginal variations among the different catalysts. These minor variations, however, also corresponded to the relative hydrophobicity of the samples (Fig. 4C). For example, a comparison of the ratio of % conversion of *p*-OH over *p*-But for reactions catalyzed individually by hydrophilic catalyst API1 and hydrophobic catalyst APME1 showed higher values of 2.4 ± 0.1 and 1.7 ± 0.1, respectively (Table 2). Since *p*-But is bulkier than *p*-OH on account of its *para*-butoxy substituent, in an effort to increase its mass transport into

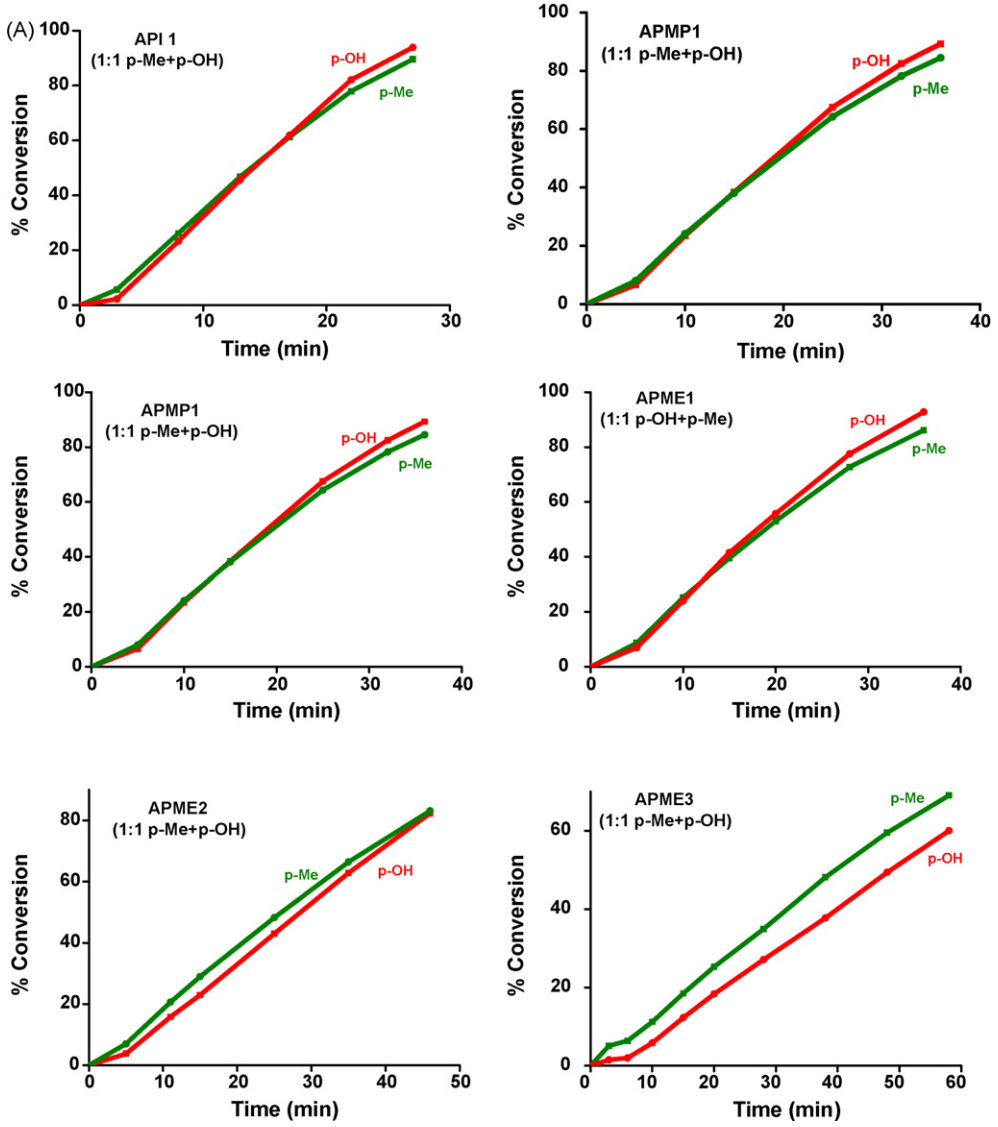


Fig. 5. % conversion versus time plots for the Henry reaction of 1:1 mole mixture of (A) *p*-hydroxybenzaldehyde and *p*-tolualdehyde with catalysts API1, APUD1, APMP1, APME1, APME2, and APME3 and (B) *p*-tolualdehyde and *p*-butoxybenzaldehyde with hydrophobic catalysts APME1, APME2 and APME3 catalyzed by various selected multifunctional mesoporous catalysts prepared from parent MCM-41.

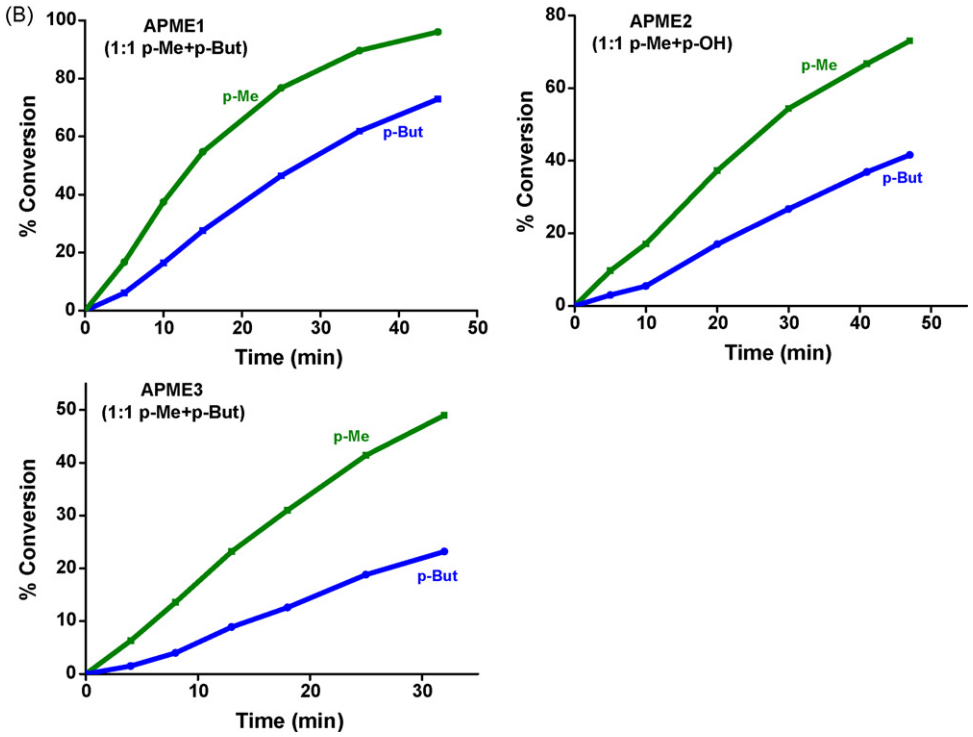


Fig. 5. (*Continued*).

the channels and achieve selectivity for *p*-But we prepared catalytic samples with SBA-15 that has twice the pore diameter of MCM-41. The functionalized samples from SBA-15 were prepared with similar secondary functional groups. Results are compiled in supporting information (Fig. S4 and Table S1). An increase in the pore diameter did not appear to have any difference on the selectivity of *p*-OH over *p*-But as values similar to the catalysis done with MCM-41 were observed. For reactions performed with a 1:1 molar mixture of *p*-OH and *p*-But with API1-SBA, APUD1-SBA and APMP1-SBA, the highest selectivity *p*-OH/*p*-But values obtained were 2.1 ± 0.1, 2.1 ± 0.1 and 2.0 ± 0.1, respectively. Hydrophobic catalysts APME1 showed a marginally decreased value of 1.7 ± 0.1. Based on these results, it can be noted here that the variations obtained in the differences in the rates of reactions between *p*-OH and *p*-But among the different catalysts was principally due to the intrinsic lower reaction rate of *p*-OH than *p*-But. However, in the smaller channel pore MCM-41 materials, the sizes and the hydrophobicity appeared to have played roles in causing the differences amongst the catalysts.

All the catalysts reported here catalyzed the nitroaldol condensation reaction very efficiently with a high % conversion in smaller reaction time. Despite the low % conversion obtained for *p*-But compared to other reactants, the efficiency for the latter was still much higher than that obtained previously by Lin and co-workers [23], which is 50% in 24 h for the same reaction. The generally low % conversion observed for *p*-But with all the catalysts was found to be due to electronic effects of the *para*-butoxy substituent and its bulkier size compared to the others.

Samples that contained a higher loading of organic functional groups generally showed lower efficiency for most of the reactants indicating correlation between catalytic efficiency and relative crowding of the catalytic sites, or their site-isolation within the mesopore channels. Furthermore, the catalytic efficiency of one reactant over another (or the relative ratio of % conversions individually obtained for two reactants by the same catalyst in a give time) correlates with the type of functional groups and their concentrations (Fig. 4). It is also worth noting that sample API1 showed much higher efficiency even for the hydrophobic reactant, *p*-But, com-

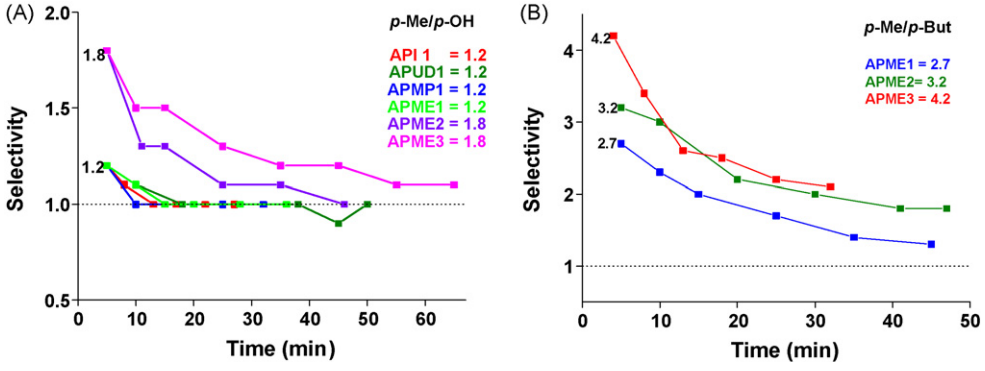


Fig. 6. Selectivity (or ratio of % conversion reactants) versus time plots for the Henry reaction of 1:1 mole mixture of (A) *p*-hydroxybenzaldehyde and *p*-tolualdehyde with catalysts API1, APUD1, APMP1, APME1, APME2 and APME3 and (B) *p*-tolualdehyde and *p*-butoxybenzaldehyde with hydrophobic catalysts APME1, APME2, and APME3.

Table 4
Effect of drying multifunctional mesoporous catalysts on their catalytic efficiency in the Henry reaction of *p*-hydroxybenzaldehyde with nitromethane as demonstrated by catalysts prepared from API1[a]

Sample	% conversion of *p*-OH in 10 min
API1-A[b]	61
API1-B[c]	61
API1-C[d]	65
API1-D[e]	78
API1-E[f]	79

[a] The reaction was performed at 90 °C using nitromethane as substrate and solvent by using various derivatives of API1 as catalysts. API1 was first stirred in water for 30 min, filtered and washed with ethanol and samples API1-A through API1-E were prepared from it as follows.
[b] API1-A was prepared by vacuum drying API1 for 1.5 h.
[c] API1-B was prepared by vacuum drying API1 for 12 h.
[d] API1-C was prepared by oven drying at 80 ° for 1 h.
[e] API1-D was prepared by oven drying API1at 80 °C for 4 h.
[f] API1-E was prepared by oven drying API1 in oven at 80 °C for 24 h.

pared to 3-aminopropyl containing samples previously reported [23].

For comparative purposes, we repeated the work carried by Huh et al. [23] but monitored the reaction's % conversion over time. With a similar catalyst we have obtained ~100% conversion of the reactants within 6 h. Furthermore, all the catalysts showed selectivity towards *p*-OH over both *p*-But and *p*-Me. Also we found that after the reaction was completed in 6 h, the nitrostyrene formed started to convert into the Michael product ^{1}H NMR [46,47].

The effect of drying the catalysts on the rate of reaction of *p*-hydroxybenzaldehyde was investigated (Table 4). Heating of the catalyst before the reactions were performed was found to be absolutely crucial for obtaining a good % conversion. For example, for catalyst API1, the optimum heating time was found to be 4 h for *p*-OH (Table 4). Removal of H_2O and CO_2 by heating has been reported to increase the strength of basic sites of solid-base catalysts for nitroaldol condensation [48] and removal of surface physisorbed water may be the reason for increased catalytic efficiency of our dried samples. The presence of small amounts of water has also been reported to cause a dramatic effect on the nitroaldol reaction catalysis, particularly those reactions proceeding with ion-pair mechanisms [19].

4. Conclusions

We have described the synthesis of multifunctional mesoporous catalysts containing multiple site-isolated functional groups for selective catalysis of either hydrophilic or hydrophobic reactants in the Henry reaction. This was demonstrated in the reaction between various *p*-substituted benzaldehydes differing in size, hydrophobicity and electronic properties, and nitromethane. While site-isolation of organoamine and silanol functional groups on multifunctional mesoporous materials rendered high efficiency in the reaction, judiciously chosen secondary organic functional groups inside mesoporous channels provided the materials with suitable surface properties to allow preferential reaction of hydrophilic or hydrophobic reactants. Further, selective catalytic properties for a mixture of some of the reactants were found to be time dependent. It is worth noting that the reaction products by these catalysts were exclusively *p*-substituted nitrostyrene. By stopping the reaction at a specific time and removing the catalysts as reported for other catalysts [49], higher concentration of selective reaction product from one reactant could be achieved. The synthetic approach employed here is simple and versatile and can be adopted for a number of other catalytic reactions and mixtures of reactants. For the first time, multifunctional mesoporous catalysts with efficient selectivity by grafting synthesis in polar, protic solvents for both hydrophilic and hydrophobic reactants are reported. Our design of catalysts significantly improves the relative efficiency of all the reactants in the Henry reaction by manifold, and better selectivity is obtained for hydrophilic and hydrophobic reactants, both when they are reacted individually and in a mixture. The resulting materials would potentially be useful for many reactions that are commonly employed for the synthesis of various chemical products.

Acknowledgements

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.molcata.2008.03.027.

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