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Controlled Synthesis of the Henry Reaction Products: Nitroalcohol Versus Nitrostyrene by a Simple Change of Amino-Groups of Aminofunctionalized Nanoporous Catalysts

Abhishek Anan · Rajyalakshmi Vathyam · Krishna K. Sharma · Tewodros Asefa

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Abstract A synthetic method for controlling the Henry reaction products from nitrostyrene to nitroalcohol in heterogeneous catalysis by a simple change of the catalytic sites in organoamine-functionalized mesoporous catalysts is reported. The synthesis resulted in either β-nitrostyrene or β-nitroalcohol by simple change of the types of amine functional groups in the amine-functionalized mesoporous catalysts from primary amines into secondary or tertiary.

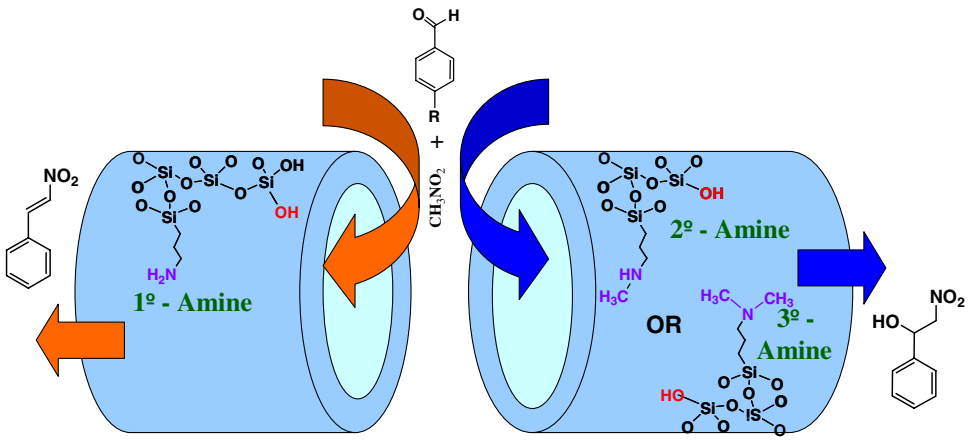
Keywords Henry reaction · Nitroaldol condensation · Amine-functionalized mesoporous materials · Nitrostyrene · Nitroalcohol

1 Introduction

The synthesis of efficient heterogeneous base catalysts for C–C bond forming reactions has been an intensively explored area of research [1]. Besides the possibility of recycling important and costly catalysts, success in the development of such catalysts provides for the efficient production of various synthetic molecules for pharmaceutical and industrial compounds, the selective catalysis of specific reagent(s) in a mixture of reactants, reduction of work-up procedures and minimization of environmental impacts of catalytic reactions. In this regard, solid-base catalysts [2] for the Henry reaction [3], Knoevenagel reaction [4], and Michael addition reactions [3, 4], which are among the most commonly employed C–C bond forming reactions, have been intensively sought and many new catalysts for these reactions have been recently published [5]. In particular amino-functionalized mesoporous materials via co-condensation and grafting synthetic methods have been developed [6] and the resulting materials have proved to catalyze these reactions [7]. The development of such mesoporous solid catalysts has drawn interest due to their large and easily modifiable surface areas conducive to high catalytic efficiency and their nanometer scale pore dimensions that allow for size-and shape-selectivity [8].

While our earlier work has shown that judicious choice of solvents and secondary functional groups to be grafted along with the organoamine in the post-grafting procedure can lead to a highly efficient solid-base heterogeneous catalyst exhibiting selectivity for reactants [9], selectivity over multiple products formed in the Henry reaction such as the β-nitroalcohol, β-nitrostryene and Michael addition products using a simple and versatile approach has been elusive. While our earlier work published in reference 9b explicitly deals with the synthesis of mesoporous catalysts containing only primary amines as the catalytic center, exhibiting selectivity for one of the reactants in a mixture of reactants (para-substituted benzaldehydes in this case) based on modification of the mesoporous materials to be hydrophobic or hydrophilic with the use of secondary functional groups such as methyl or ureidopropyl, the current work focuses on obtaining tunable selectivity over multiple products formed in nitroaldol condensation of p-nitrobenzaldehyde and nitromethane through use of primary, secondary or tertiary amines. A fair degree of control over the type of product with desired stereochemistry has been achieved in homogeneous medium by use of copper complexes [10], phosphine compounds [11], ionic liquids [12], KOH [13], potassium phosphate [14], and various other types of bases [15] and reaction conditions [16],

A. Anan · R. Vathyam · K. K. Sharma · T. Asefa (✉)
Department of Chemistry, Syracuse University, Syracuse, NY 13244, USA
e-mail: tasefa@syr.edu



Scheme 1 Different types of aminofunctionalized mesoporous catalysts for the synthesis of different products in the Henry reaction

however, a similar control over specific products of the Henry reaction has been hampered by intrinsic multiple products that are formed with heterogeneous catalysts and lack of an exhaustive relationship between type of active catalytic sites and the mechanism. For instance, while the relationship between the dielectric outer sphere and type of products formed with aminopropyl groups grafted on solid materials as basic sites has been investigated by Katz et al. [17], the relationship between different base catalytic sites in the materials and the products they form has not been known. The formation of β-nitrolalcohol or β-nitrostyrene in heterogeneous phase was previously achieved partially by using of Mg–Al hydrotalcites [18], by changing the substituents on reactants [13], and by controlling the silanol concentrations and dielectric atmosphere of the active site on silica gels as demonstrated by Katz and co-workers [17, 19]. Absolute control over both the products of the Henry reaction, i.e., β-nitrolalcohol or β-nitrostyrene, with a change in the type of base catalytic site anchored on MCM-41 type or related mesoporous materials itself has not been reported to date however. The latter is a more powerful approach as it precludes lengthy synthetic procedures and allows exclusive control over the mechanistic pathway leading to either ion-pair or imine intermediates [17] allowing exclusive control over the formation of β-nitroalcohol or β-nitrostyrene, i.e., product selectivity is determined at the mechanistic level and selectivity becomes an intrinsic property of the catalyst rather than being dependent upon the reaction conditions. Although a series of amine functionalized mesoporous materials consisting of primary, secondary and tertiary amine groups was synthesized previously [20] for the Henry reaction, they were all reported to produce exclusively β-nitrostyrene. Furthermore, the primary and secondary amine mesoporous samples were reported to result the β-nitrostyrene in higher yield while the tertiary amine mesoporous samples were reported to result in the β-nitrostyrene only in 5% yield over 1 h reaction time. The reason for the latter result was proposed to be the facile formation of imines, which lead to β-nitrostyrene in the presence of primary amines. However, possible ion-pair mechanisms, which are known to lead to nitroalcohols, in the case of the secondary and tertiary amine functionalized mesoporous silica, were not mentioned in the paper and no observation of nitroalcohols was reported. The formation of β-nitroalcohol was reported only for tertiary amine functionalized amorphous silica gel by the same authors [21].

Here we report a synthetic approach for controlling the selective formation of one of the products of the Henry reaction between aromatic aldehydes and nitroalkanes catalyzed by amine-functionalized mesoporous materials. Novelty of the process lies in the fact that by simply changing the type of amine group grafted on the mesoporous materials from primary into secondary or tertiary, which results in the change of the mechanism of the base catalyzed process from imine into ion-pair, the selectivity of the catalyst towards the formation of β-nitroalcohol or β-nitrostyrene almost exclusively in a reaction between *p*-nitrobenzaldehyde and nitromethane is observed (Scheme 1). The change of amine groups for the controlled synthesis of the Henry reaction product is simple and catalytically efficient as the product is obtained in a quantitative yield in a very short reaction time and is reported for the first time, to the best of our knowledge.

2 Experimental

2.1 Synthesis of the Mesoporous Silica

The mesostructured MCM-41 material used in this study was synthesized by following previously reported procedures [1, 2]. Briefly, 7 mL of 2.0 M NaOH solution was mixed with 480 g (26.67 mmol) of water and stirred for

10 min. This was followed by addition of 2 g of (5.49 mmol) cetyltriemthylammonium bromide (CTAB). The solution was stirred at 80 °C for 30 min. After adding 11.3 mL (50.6 mmol) tetraethoxysilane (TEOS) into it, the solution was stirred for 2 h at 80 °C. The solution was filtered while it was still hot and the precipitate was washed with copious amount of Millipore water and ethanol. The resulting precipitate was dried overnight at ambient conditions. The surfactant from the mesostructured material was extracted by stirring 1 g of the sample in a solution containing 0.5 mL HCl and 150 mL ethanol at 50 °C for 5 h. The CTAB-extracted mesoporous material was filtered and washed with copious amount of Millipore water and ethanol. The material was air dried and used for functionalization of the organoamines on it and to produce aminofunctionalized mesoporous catalysts.

2.2 Synthesis of Amino-Functionalized Mesoporous Catalysts

The surfactant extracted mesoporous silica (MCM-41) was heated at 80 °C for 4 h before being grafted with various orgnoamines consisting of primary, secondary and tertiary amine groups. Briefly, 500 mg of the MCM-41 was stirred with 3.684 mmols of 3-aminopropyltrimethoxysilane (APTS), 3-(N-methylaminopropyl)trimethoxysilane (MAPS), or 3-(N, N-dimethylaminopropyl)trimethoxysilane (DMAPS) (Gelest) in 250 mL of anhydrous isopropanol or toluene (Pharmco-AAEPR) at 80 °C for 5 h. The resulting material was filtered while it was still hot and washed with ethanol, followed by dichloromethane and finally ethanol. The samples obtained from APTS, MAPTS, and DMAPTS in isopropanol were labeled as API, MAPI, and DMAPI, respectively while the samples obtained from APTS, MAPTS, and DMAPTS in toluene were labeled as APT, MAPI, MAPT, and DMAPT, respectively.

2.3 Henry (Nitroaldol) Reaction

The Henry reaction was performed by using the amino-functionalized materials above as catalysts. Typically, 20 mg of the aminofunctionalized mesoporous samples, pre-heated for 4 h in oven at 80 °C was added into a mixture of 151 mg (1 mmol) *p*-nitrobenzaldehyde and 10 mL of nitromethane. The reaction mixture was stirred at 90 °C under nitrogen and aliquots of the reaction product were taken with a filter syringe and characterized by solution ^{1}H NMR spectroscopy. The percent yield and conversion were determined by using ^{1}H NMR spectra measured in deutrated acetonitrile. Resonances in Acetonitrile-d_3: 4-Nitrobenzaldehyde: δ 10.13 (1H, s), δ 8.36 (2H, d), δ 8.11 (2H, d); 1-nitro-4-[(1E)-2-nitroethenyl]-Benzene: δ 8.28 (2H, d), δ 8.12 (1H, d, J = 13.8 Hz), δ 7.88 (2H, d), δ 7.87 (1H, d, J = 13.8 Hz); 1-(4-Nitrophenyl)-2-nitroethanol: δ 8.22 (2H, d), δ 7.67 (2H, d), δ 5.53 (1H, m), δ 4.63 (2H, m), δ 4.30 (1H, br, s); 1-nitro-4-[2-nitro-1-(nitromethyl)ethyl]-Benzene: δ 8.23 (2H, m), δ 7.60 (2H, d), δ 4.95 (2H, m), δ 4.85 (2H, m), δ 4.46 (1H, m).

3 Results and Discussion

3.1 Synthesis and Characterizations of Aminofunctionalized Mesoporous Catalysts

A series of aminofunctionalized solid-base catalysts containing primary, secondary, and tertiary amine catalytic sites by grafting different organosilanes in isopropanol and

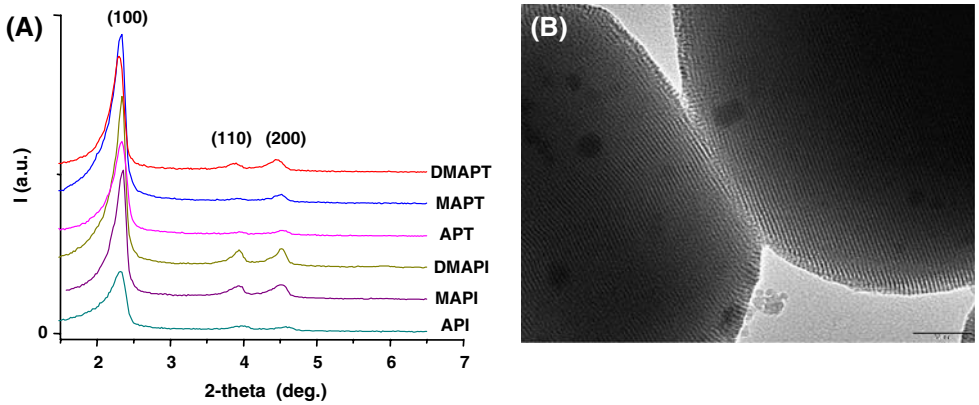


Fig. 1 (**a**) Powder X-ray diffraction patterns of various aminofunctionalized mesoporous samples. The samples were synthesized by grafting 3-aminopropyltrimethoxysilane (APTS), 3-(N-methylaminopropyl) trimethoxysilane (MAPS), or 3-(N,N-dimethylaminopropyl)trimethoxysilane (DMAPS) onto MCM-41 in isopropanol or toluene under reflux. (**b**) Representative transmission electron microscopy (TEM) image of amino-functionalized sample, MAPI

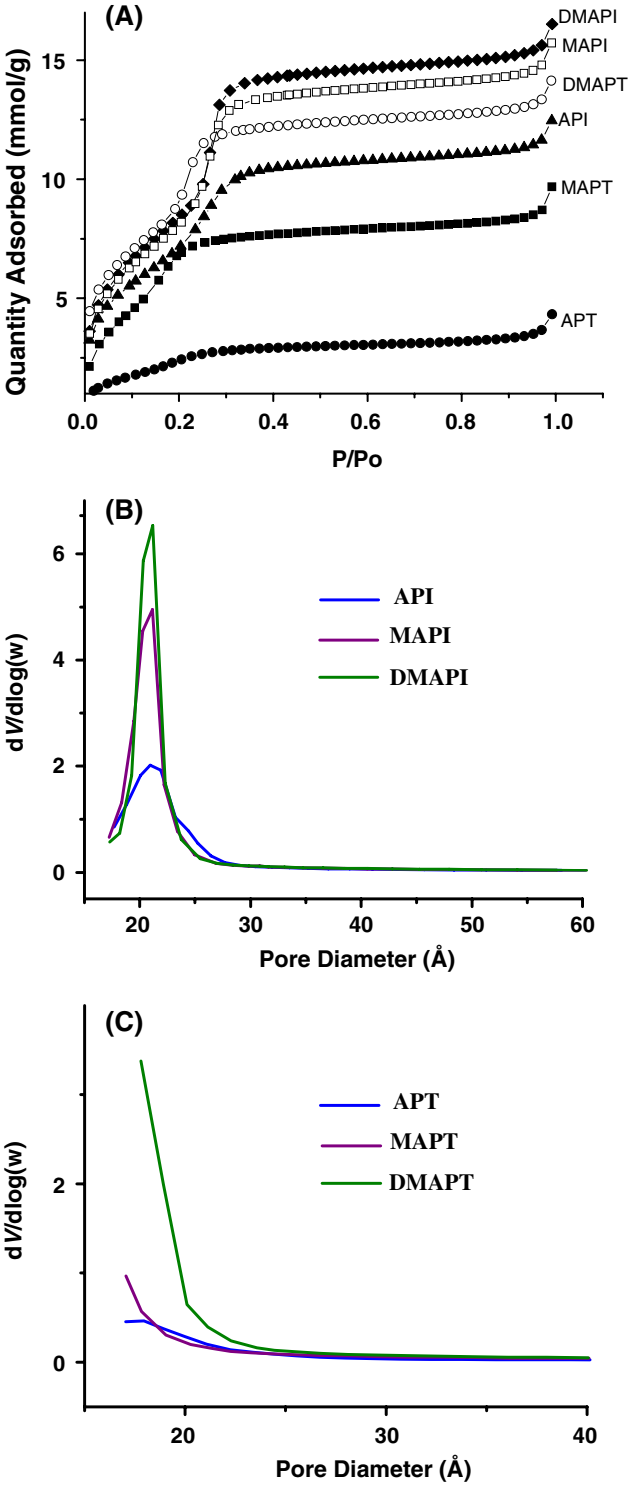


Fig. 2 N_2 gas adsorption isotherms (**a**) and pore size distributions (**b** and **c**)

toluene were synthesized and used as catalysts to demonstrated selective catalytic reactions in the Henry reaction. The aminofunctionalized materials were synthesized by stirring mesoporous silica (MCM-41) [22] with 3-APTS, 3-MAPS, or 3-DMAPS in isopropanol or toluene under reflux for 5 h. This produced samples labeled as API, MAPI, and DMAPI, respectively, for isopropanol or samples labeled as APT, MAPT and DMAPT, respectively, for toluene. The structures of the resulting materials were found to be mesoporous as characterized by powder X-ray diffraction (XRD) and transmission electron microscopy (TEM) (Fig. 1) and N_2 gas adsorption (Fig. 2). The XRD patterns of all the samples showed a sharp peak corresponding to (100) Bragg reflection as well as at least two more peaks corresponding to (110) and (200) reflections indicating that the materials have hexagonally ordered mesostructures. The unit cells of the materials were 4.3–4.4 nm. The TEM images of the samples further corroborated the mesoporous structures of the materials. N_2 gas adsorption indicated the materials to have Type IV isotherms. The BET surface areas were found to be 692, 865 and 889 m^2/g for API, MAPI, and DMAPI, respectively, and 214, 607, and 714 m^2/g for APT, MAPT and DMAPT, respectively (Table 1).

Table 1 Characterization results of the functionalized mesoporous materials and the structural data

Catalyst	Unit cell, Å[a]	Pore width, Å[b]	Wall thickness, Å[c]	Surface area, m^2/g[d]	Pore volume, m^3/g
API	44	22	22	692	0.39
APT	43	21	22	214	0.09
MAPI	43	21	22	865	0.67
MAPT	43	–	–	607	0.14
DMAPI	43	–	–	889	0.67
DMAPT	44	–	–	714	0.41

[a] Obtained from the sample's d-spacing on XRD (unit cell, $a_o = 2\ d_{100}/3^{1/2}$ for hexagonal $P6_{mm}$ mesostructures)

[b] Obtained from the desorption branch of the N_2 gas adsorption isotherm

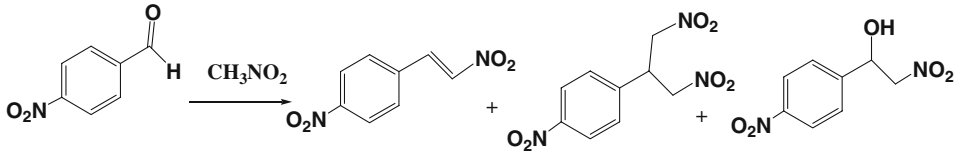
[c] Wall thickness = Unit cell − Pore diameter

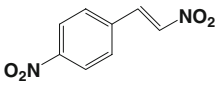
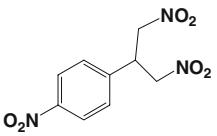
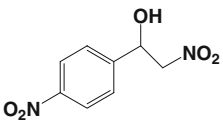
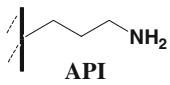
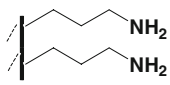
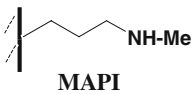
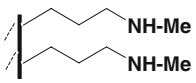
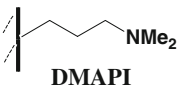
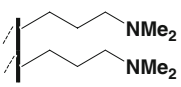
[d] Obtained from the N_2 adsorption isotherm with the BET method

3.2 Catalysis

Product selectivity in the Henry reaction by the different organoamine (primary, secondary, or tertiary) functionalized mesoporous catalysts was exhibited that was in agreement with their corresponding mechanisms. While primary amine functionalized samples have been shown to follow imine mechanism preferentially to yield *β*-nitrostyrene almost exclusively [17, 18, 22], it was proposed that amines incapable of undergoing the imine mechanism would proceed exclusively via the classical ion-pair mechanism to yield *β*-nitroalcohol [17]. It is worth noting that this hypothesis with respect to Henry reaction was not

Table 2 Catalysis results by different organoamine-functionalized mesoporous materials in the Henry reaction[a]



Entry		%Conversion[b]			
1	 API	~100[c]	(76%)	(15%)	(9%)
2	 APT	~100[d]	(48%)	(24%)	(29%)
3	 MAPI	93[e]	(4%)	(19%)	(77%)
4	 MAPT	92[e]	(0.2%)	(12%)	(88%)
5	 DMAPI	96[f]	(1.2%)	(9%)	(90%)
6	 DMAPT	92[f]	(11%)	–	(89%)

[a] The catalytic tests were carried out with the Henry reaction between p-nitrobenzaldehyde and nitromethane as reported previously [9]

[b] % Conversion (or total% conversion) based on the limiting reactant, p-nitrobenzaldehyde, (nitromethane is also the solvent)

[c] Reaction time = 45 min

[d] Reaction time = 6 h

[e] Reaction time = 10 min

[f] Reaction time = 2 h

considered in Ref. [20] and there was no mention of ion-pair mechanism as well as β-nitroalcohol product in that article.

As the mechanism suggests, our primary amine functionalized samples gave β-nitrostyrene as the major product while secondary and tertiary amines produced β-nitroalcohol in high

Table 3 Catalysis results by different organoamine-functionalized mesoporous materials in the Henry reaction[a]

Entry	Catalyst	%Conversion[b]	A/(S + M)[c]	M/S	Catalyst loading,% N[d]
1	API	~100[e]	0.1	0.2	2.58
2	APT	~100[f]	0.4	0.5	4.27
3	MAPI	93[g]	3.4	4.7	2.44
4	MAPT	92[g]	7.3	53.9	3.60
5	DMAPI	96[h]	9.3	7.2	1.87
6	DMAPT	92[h]	7.9[i]	–	2.81

[a] The catalytic tests were carried out with the Henry reaction between p-nitrobenzaldehyde and nitromethane as reported previously [9]

[b] % Conv. or total% conversion based on the limiting reactant, p-nitrobenzaldehyde, (nitromethane is also the solvent)

[c] mol ratio, $A = \beta$-nitroalcohol, $S = \beta$-nitrostyrene, $M =$ 1,3-dinitroalkane (Michael product)

[d] Based on elemental analysis

[e] Reaction time = 45 min

[f] Reaction time = 6 h

[g] Reaction time = 10 min

[h] Reaction time = 2 h

[i] No β-nitrostyrene product observed

selectivity (Tables 2, 3). Furthermore, the percent conversion for the β-nitroalcohol product (entries 3–4, Tables 2, 3) is the highest in the given reaction time reported so far in the literature for such mesoporous solid-bases and *p*-nitrobenzaldehyde as the reactant. The basicity order of the secondary and tertiary amine is consistent with basicities in polar solvents, i.e., secondary > tertiary and is reflected in the larger reaction time required to achieve approximately 90% yield with DMAPS functionalized samples as compared to MAPS ones (entries 5–6, Tables 2, 3). Furthermore, slow reaction rate for *p*-nitrobenzaldehyde with AP functionalized samples (i.e., API and APT) as compared to *p*-hydroxybenzaldehyde with similar samples as reported in our previous work [9] is explained by the destabilization inherent in the iminium [17] intermediate of *p*-nitrobenzaldehyde relative to *p*-hydroxybenzldehyde.

To understand the effect of active base concentration on the reaction rate and selectivity, all the organoamines were also grafted in toluene. Toluene is known to provide much higher catalytic loading compared to isopropanol [9], which was corroborated by the elemental analysis results (Table 3). Surprisingly, the catalytic efficiency was found to be independent of amino-group loading for both the MAPS and DMAPS functionalized samples as approximately similar percentage conversion in a given time was obtained for MAPI versus MAPT and DMAPI versus DMAPT samples.

On the other hand, the APTS functionalized samples showed a large variation in catalytic efficiency with varied aminopropyl loading reflected in eight-fold reaction time required to obtain 100% conversion for APT compared to API. This is consistent with previous observation [9] that organoamine is grafted at the expense of the acidic surface silanol groups, which play a pivotal role in base catalysis as both imine formation and the subsequent nucleophilic attack by the nitromethane are acid-catalyzed [17]. The type of amine group grafted along with the solvent used had a pronounced effect in determining the degree of selectivity towards β-nitroalcohol or β-nitrostyrene for all the samples. Of all the amines, tertiary amine functionalized samples, DMAPI and DMAPT, showed the highest selectivity towards β-nitroalcohol. In general, all the toluene grafted samples showed higher selectivity towards the β-nitroalcohol compared to the corresponding isopropanol grafted samples, with DMAPT being the only exception. Since grafting in toluene markedly reduces the surface silanol concentration and increases the base loading, the increased selectivity in toluene for the formation of β-nitroalcohol could be a combined effect of both factors. The formation of nitrostyrene was favored in bases (primary amines) where imine formation is kinetically or otherwise was unfavorable. The cause of variation in the relative ratio of the β-nitrostyrene and β-nitroalcohol product with change in the type of amine and the catalytic loading along with silanol concetration is under investigation and will be reported in due course.

4 Conclusions

In summary, we have described the efficient synthesis of either β-nitrostyrene or β-nitroalcohol by simple change of the types of amine functional groups in amine functionalized mesoporous catalysts from primary amines into secondary or tertiary. The latter allows the change in

mechanism by which the base catalyzed process in the Henry reaction proceeds, namely imine mechanism which results in nitrostyrene versus nitroalcohol. Such synthetic strategies would allow the development of systematic selective catalysts for the production of specific products by simple, rational design of heterogeneous catalytic sites based on understanding of the reaction mechanisms involved.

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