Preparation of the Novel Mesoporous Solid Acid Catalyst UDCaT-4 *via* Synergism of Persulfated Alumina and Zirconia into Hexagonal Mesoporous Silica for Alkylation Reactions

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Received: November 20, 2003; Accepted: March 5, 2004

Abstract: A novel mesoporous solid acid catalyst named UDCaT-4 was designed by loading persulfated alumina and zirconia (PAZ) into highly oredered, hexagonal mesoporous silica (HMS). UDCaT-4 was characterized by XRD, BET surface area and pore size analysis which revealed that neither pore blocking nor structure collapse of HMS had occurred. NH_3-TPD and FTIR were used to determine the acid strength and nature of the sulfate ion retained on the surface of UDCaT-4. It is known that HCl and water have detrimental effects on the activity of the zirconia-based catalyst. Hence, the activity of UDCaT-4 was evaluated in comparsion with that of bulk PAZ in the liquid-phase alkylation of toluene with benzyl chloride and also in the vapour-phase alkylation of mesitylene with isopropanol, where acid and water are generated *in-situ*, respectively, as co-products. The superior catalytic acivity of UDCaT-4 is atributed to the uniform dispersion of the superacidic centers of PAZ into HMS *vis-à-vis* bulk PAZ. Reusability and time on-stream studies reveal that UDCaT-4 is a robust and reusable catalyst even in the presence of HCl and H_2O.

Keywords: alkylation; alumina; mesoporous material; persulfation; silica; zirconium

Homogeneous catalysis is widely used in several industries which produce wastes to the tune of 10–100 kg/kg product depending on the number of stages used and type of industry. Alkylation, acylation, nitration, esterification, hydration, dehydration, condensation, oligomerization and polymerization are some of the important reactions which are acid catalyzed. Use of homogeneous acid catalysts leads to several problems such as loss of conversion, yield and selectivity, presence of impurities, corrosion of equipment, hazards of handling corrosive acids and neutralization of the resulting reaction mass leading to the generation of large quantities of dilute dissolved salts. Since the prices of fine chemicals are very high and volumes low, no serious attempts were made until recently to recover the catalysts or change the processes. There are a large number of well studied solid acids available as replacements for liquid acids, amongst which zeolites have emerged as a promising alternative. Unfortunately, the slow diffusion of reactants through the zeolitic microporous structure makes them relatively poor catalysts and their stability is questionable in reactions where acids are generated (e.g., anhydrous HCl as a co-product), which may remove aluminum species from the framework of the zeolite. Furthermore, zeolites are found to deactivate at high temperatures due to coke formation.[1–7] Mesoporous materials with tailored catalytic centers will be most suitable for reactions of bulky molecules. Hexagonally ordered, mesoporous silicates such as FSM-16, HMS (hexagonal mesoporous silica) and MCM-41, possessing large surface areas ($>800\ m^2/g$) and highly ordered mesopores (2–10 nm) can be functionalized to extend their applications to a variety of areas.[8–13]

Among many solid acid systems other than zeolites and clays, sulfated zirconia has received much attention due to its superacidity.[14] A number of attempts have been made to improve the acidity of zirconia-based catalysts by incorporating different transition metals[15] but they suffer from deactivation at high temperatures. The stability of sulfated zirconia can be improved by incorporating alumina in zirconia followed by treatment with ammonium persulfate.[16] *Persulfated alumina zirconia (PAZ)* exhibits excellent catalytic activity and better stability towards coke formation than sulfated zirconia but its low surface area and non-uniform pore size limits its potential applications. Thus, in the current work, use of hexagonal mesoporous silica (HMS)[8] was perceived as a catalyst support for persulfated alumina and zirconia (PAZ) in order to make a new catalyst called UDCaT-4 with enhanced catalytic activity and ordered mesoporosity to minimize the diffusion resistance for the reaction of bulky molecules. *The abbrevia-*

DOI: 10.1002/adsc.200303212

tion UDCaT-4 is used to denote the series of solid acid catalysts developed in this laboratory, which was formerly known as the University Department of Chemical Technology (UDCT). Liquid-phase benzylation of toluene with benzyl chloride and vapour-phase isopropylation of mesitylene were used as test reactions to evaluate the stability and robustness since HCl and water are formed as co-products, respectively.

Catalyst Characterization

BET Surface Area and Pore Size Analysis: The textural characterizations of HMS and UDCaT-4 were carried out by nitrogen BET surface area and pore size analysis (Table 1). Both HMS and UDCaT-4 display characteristic type IV adsorption isotherms (Figures 1A and 1B) with well-defined steps in the N_2 adsorption and desorption isotherms and hysteresis in the desorption isotherm at relative pressures (p/p_0) in the range of ~ 0.45 – 0.8 (p/p_0). This behaviour is indicative of a uniform mesopore size distribution, which is filled spontaneously due to capillary condensation in both HMS and UDCaT-4 and this explanation is in accordance with IUPAC classification.[17] Furthermore, the average pore diameter of UDCaT-4 calculated by the Barrett–Joyner –Halenda (BJH) method is reduced marginally from 36 Å of HMS to 30 Å. The reduction in the BET surface area and pore volume of UDCaT-4 are much more remarkable since nanoparticles of alumina and zirconia are generated *in situ* and persulfated thereafter; some large particles can block a few pore junctions thereby reducing accessibility of some channels of HMS. Thus, there is a reduction in surface area and pore volume of UDCaT-4; however, both these values are far greater than those of bulk unsupported PAZ. The results are in consonance with earlier literature reports.[18]

X-Ray Diffraction Studies: The structural integrity of the HMS as well as of UDCaT-4 was determined with X-ray diffraction. One diffraction peak in the low angle region (2θ = 1 – 10°) is visible indicating that HMS has a long-range hexagonal ordering (Figure 1D). The struc-

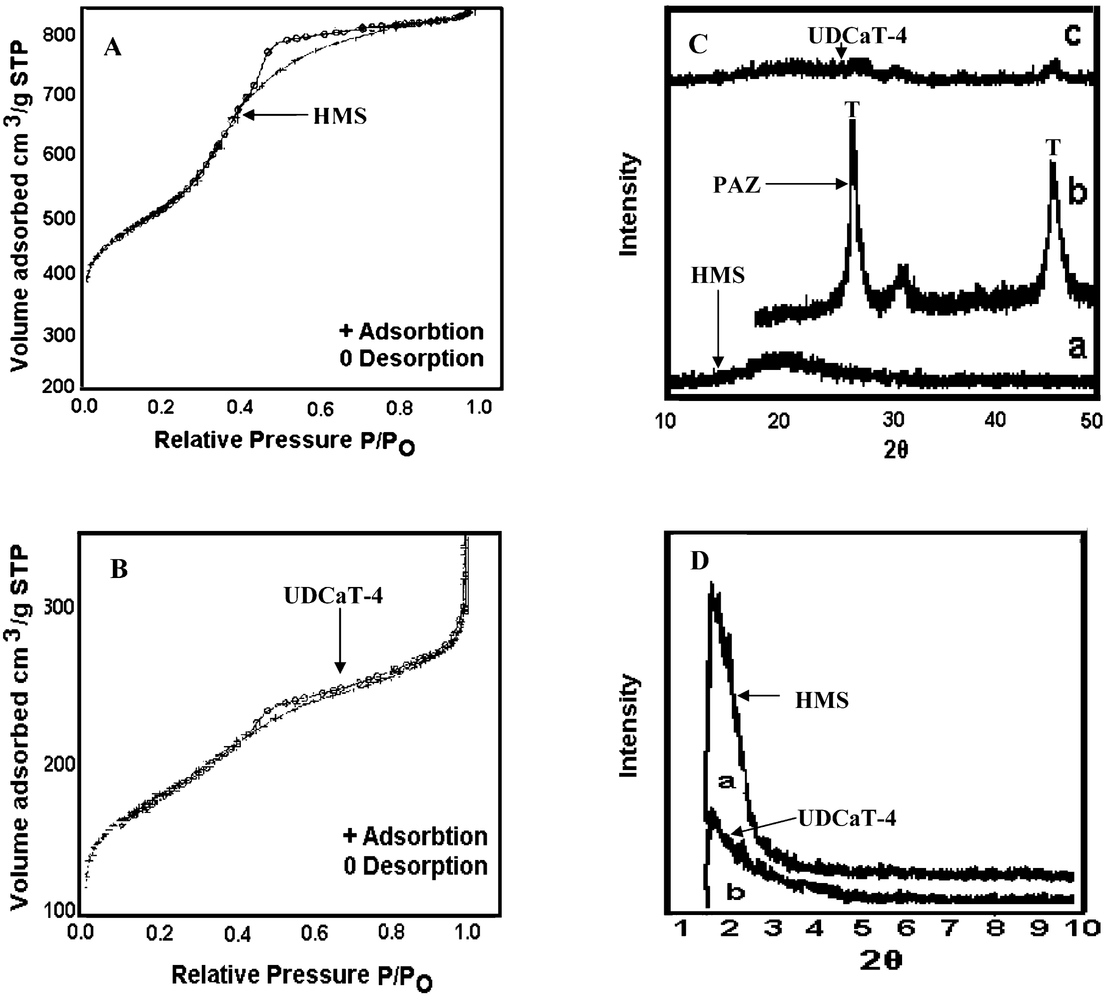

Figure 1. N_2 adsorption isotherms **A** of HMS; **B** of UDCaT-4. **C**: XRD pattern of **a**: HMS; **b**: PAZ; **c**: UDCaT-4 (T = Tetragonal phase) and **D**: XRD pattern of **a**: HMS; **b**: UDCaT-4.

Table 1. Textural characteristics, acidity and activity of HMS, PAZ and UDCaT-4.

Parameters	Catalysts		
	HMS	PAZ	UDCaT-4
Acidity by NH_3-TPD (mmol g^{-1})	0	0.09	0.56
BET surface area ($m^2\,g^{-1}$)	833	81	233
Langmuir surface area($m^2\,g^{-1}$)	865	90	364
Barrett–Joyner–Halenda (BJH) Average pore diameter Å	36	20	30
Pore volume ($cm^3\,g^{-1}$)	0.78	0.11	0.21
TON[a]	0	20	123
Selectivity*[a]	0	98	98
TON[b]	0	88	650
Selectivity*[b]	0	99	99

[a] Alkylation of mesitylene (for one pass).

*[a] Selectivity towards 1-isopropyl-2, 4, 6-trimethylbenzene.

[b] Alkylation of toluene with benzyl chloride

*[b] Mixture of benzylated toluene. TON (turn-over number) = moles of product/moles of zirconia in the catalyst.

tural integrity of the HMS is retained even after converting it into UDCaT-4. Bulk PAZ shows the pure tetragonal phase of zirconia in the ordinary region ($2\theta = 30^\circ$ and 50°); however, a completely different diffraction pattern is obtained for UDCaT-4 in the ordinary region above $2\theta = 20^\circ$ (Figure 1 C). UDCaT-4 shows reflection of zirconia at $2\theta = 30^\circ$ and $2\theta = 50^\circ$ having very low and broad intensities. These diffraction peaks can be attributed to the presence of a tetragonal crystalline zirconia rather than a monoclinic zirconia phase in the pores of HMS, showing that introduction of small amount of aluminum and sulfate ion must have stabilized the tetragonal phase of the zirconia, which is an ideal phase for the exhibiting superacidity for sulfated zirconia.[14] FTIR analysis further supports the inference about the introduction of sulfate ion on UDCaT-4.

XRD, BET surface area and pore size analysis provide an explanation for the entrapment of PAZ in mesoporous of HMS. During the synthesis of UDCaT-4, growth of crystalline zirconia and alumina is very unlikely because XRD as well as BET surface area indicate that the characteristic, hexagonal structure of the HMS and its mesoporosity are not perturbed after conversion to UDCaT-4, thus indicating framework stability. Growth inside the HMS framework would have resulted in extensive damage to the framework and broadening of the pore size distribution, which is not observed. Furthermore, past literature reports suggest that the intensity of the Bragg X-ray peak of a mesoporous material at low angle is significantly dependent on the scattering material present inside the pores. Anderson et al.[19] found that the removal of surfactant by calcination was accompanied by a very large increase (by a factor of almost five) in the intensity of the most intense Bragg X-ray peak in comparison to the uncalcined material. These results are in accordance with those of Marler et al.[20] and their results provide experimental evidence for a decrease in X-ray Bragg intensities upon filling the pores of calcined boron-substituted MCM-41 silica with various organic liquids. Pore filling by 1,2-dibromoethane, bromoform and diiodomethane almost completely eliminated the (100) Bragg reflection. Recalcination of the material to remove the organic adsorbent restored the (100) reflection to nearly its original intensity. Glinka et al.[21] have carried out neutron diffraction contrast studies on MCM-41 and observed that Bragg diffraction disappeared when the pores were filled with D_2O/H_2O mixtures that have the same cross-section scattering as SiO_2. Edler and White[22] reported large changes in Bragg intensities when MCM-41 silicas were dried for long periods. Furthermore, introduction of scattering material into the pores of HMS leads to an increased phase cancellation between scattering from the wall and the pore regions and therefore to reduced scattering intensities for the Bragg reflections at low angle ($2\theta = 1-7^\circ$). The degree of cancellation is mainly determined by the scattering contrast between the framework walls and the pores.[23] All previous literature suggests that the Bragg intensity of the mesoporous material below low angles is remarkably dependent on the scattering material present inside. Figure 1D shows the reduction of the typical reflections of UDCaT-4 in comparison to HMS. This implies that nanoparticles of PAZ ($\gg 10$ nm) must be formed inside the pores of the HMS and some of them are trapped in the pore junctions. Impregnation of aqueous salts of zirconia and alumina precursors by the incipient wetness technique into HMS and subsequent hydrolysis of these salts by ammonia gas results in the precipitation of $Zr(OH)_4$ and $Al(OH)_3$ in the mesopores of HMS. As a result, once precipitated, it is very difficult for $Zr(OH)_4$ and $Al(OH)_3$ to come out from the pores of HMS during washing of the catalyst and drying. Furthermore, after treatment with ammonium persulfate and during the calcination at 650 °C condensation of the hydroxy groups of $Zr(OH)_4$ occurs leading to a crystalline zirconia without a change of the sulfate species in the pores of HMS. The FTIR spectra provide an explanation for these findings as given latter. Hence, XRD show broad and low intensities of the crystalline phase of zirconia in the ordinary region $2\theta = 30°$ and $2\theta = 50°$. Furthermore, the pore volume of UDCaT-4 is much less than that of HMS indicating that a large amount of crystalline zirconia and alumina must be present inside the pores of HMS.

Infrared Spectroscopy: PAZ and UDCaT-4 were synthesized by immersing $Zr(OH)_4/Al(OH)_3$ and $Zr(OH)_4/Al(OH)_3$ on HMS, respectively, in a 0.5 M aqueous solution of ammonium persulfate while allowing adequate adsorption of ammonium persulfate onto surface of the respective hydroxide forms. It was expected that during the thermal treatment of PAZ and UDCaT-4, the aqueous solution of ammonium persulfate would decompose and sulfate ion should be retained on the surface of the both PAZ and UDCaT-4 after calcination. The FTIR spectra depict the presence of the characteristic covalent S=O band in the region of 1000 – 1200 cm^{-1} on the surface of the both PAZ and UDCaT-4 (Figure 2A). This bond is often held responsible for the exhibition of superacidity in sulfate-promoted zirconia[14,24] and the same phenomenon was observed in the case of the PAZ and UDCaT-4. The band at 1631 – 1642 cm^{-1} is attributed to an –OH bending frequency of water molecules present in both the catalysts.[25] An additional broad band at 3400 cm^{-1} corresponds to the stretching vibration δ_{OH} of the hydroxy group.[25] FTIR analysis further corroborated the assumption drawn from XRD analysis on the stabilization of the tetragonal phase of the zirconia in the pores of HMS.

NH_3-TPD: The TPD profiles of PAZ and UDCaT-4 are based on the desorption temperature maxima which could be divided into three regions corresponding to (i) intermediate or medium (100 – 200 °C), (ii) strong (200 – 400 °C), and (iii) very strong acid strengths (> 400 °C). PAZ exhibits three peaks, at 180 °C, 450 °C and 550 °C. The first and second peaks suggest that PAZ possesses a large number of acid sites with intermediate and strong acid strength (Figure 2B). The peak at 550 °C corresponding to very strong acid strengths implies superacidic centers for zirconia-based catalysts.[26] On the contrary, UDCaT-4 exhibits only one peak at 225 °C which corresponds to strong acid sites. It should be noted here that catalytically active centers are generated in UDCaT-4 by embedding 20% of PAZ into otherwise inactive HMS. Thus, due to the low content of PAZ in UDCaT-4,(that is, 20% w/w PAZ in UDCaT-4 as compared to 100% PAZ), UDCaT-4 does not exhibit strong acid strength peaks at 450 °C and 550 °C. Although UDCaT-4 possesses medium and strong acid strength, the total acid sites of UDCaT-4 (0.56 mmol g^{-1}) are greater than those of PAZ (0.09 mmol g^{-1}) and hence UDCaT-4 shows more activity per unit mass in comparison with PAZ (Table 1).

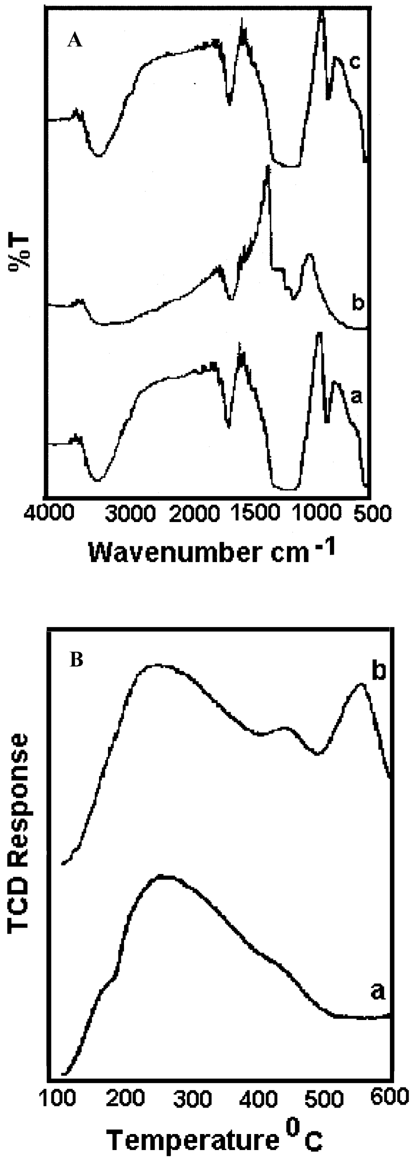

Figure 2. A: FTIR of **a** HMS; **b** PAZ; **c** UDCaT-4 and **B:** NH_3-TPD of **a** UDCaT-4 and **b** PAZ.

Catalytic Activity and Stability of UDCaT-4: The activity of UDCaT-4 was compared with microporous PAZ for liquid-phase benzylation of toluene with benzyl chloride and vapour-phase alkylation of mesitylene with isopropyl alcohol (Table 1). Due to high surface area and ordered mesoporosity of UDCaT-4 as compared to microporous PAZ, the turn over number of UDCaT-4 was found to be greater than PAZ for both reactions.

The reusability of the catalyst was tested thrice in the case of the benzylation of toluene. After each reaction, the catalyst was separated by filtration and washed with toluene and dried at 120 °C for 1 h. It was observed that UDCaT-4 shows the same activity after the third use.

These results clearly show the stability of the UDCaT-4 in the presence of corrosive acids like HCl. The stability of zirconia-based catalyst is questionable when water is generated as a co-product. When fresh sulfated zirconia is mixed with water, the pH of the suspension decreases quickly as a result of sulfate group hydrolysis which is confirmed by the identification of sulfate ions in the aqueous phase. A test for sulfate leaching was conducted for fresh and reused catalyst by pH measurement[27] and it was found that there was no leaching of sulfate ions from UDCaT-4. UDCaT-4 was found to retain its activity for isopropylation of mesitylene at 250 °C for more than 50 h with a zero drop in conversion and selectivity. This study further supports that there is no leaching of the sulfate ion from UDCaT-4 and that it is a stable catalyst. These activity studies further bolster the assumption drawn from the spectroscopic studies regarding the generation of more acidic centers in UDCaT-4 than in PAZ.

In conclusion, a novel mesoporous solid acid catalyst UDCaT-4 was synthesized with superior activity and stability and high surface area and ordered mesoporosity. This catalyst exhibits superior activity than bulk PAZ in the liquid-phase alkylation of toluene with benzyl chloride and vapour-phase alkylation of mesitylene with isopropanol. It is being tested in several other organic syntheses.

Experimental Section

Catalyst Preparation

HMS: The hexagonal mesoporous silica (HMS) was prepared using the following procedure. Dodecylamine (5 g) was dissolved in ethanol (41.8 g) and distilled water (29.6 g). Tetraethyl orthosilicate (20.8 g) was added under vigorous stirring. The addition of ethanol improved the solubility of the template. The reaction mixture was aged for 18 h at 30 °C. The clear liquid above the white colored precipitate was decanted and the precipitated HMS was dried on a glass plate. The template was removed by calcining the resulting material at 500 °C in the air for 3 h.[24]

Persulfated alumina and zirconia (PAZ): Persulfated modified alumina and zirconia (abbreviated as PAZ) was prepared according to the method described elsewhere. [16]

UDCaT-4: Zirconium oxychloride (2.39 g) and aluminum nitrate (0.11 g) were dissolved to give an aqueous solution which was added to of precalcined HMS (5 g) by the incipient wetness technique. After addition, the solid was dried in an oven at 110 °C for 3 h. The dried material was hydrolyzed by ammonia gas and washed with deionized water until a neutral filtrate was obtained and the absence of chlorine ion in the filtrate was detected by phenolphthalein and silver nitrate tests. It was then dried in an oven for 24 h at 110 °C. Persulfation was carried out by immersing the above solid material in a 0.5 M aqueous solution of ammonium persulfate for 30 min. The material was dried at 110 °C for 24 h and calcined at 650 ° for 3 to afford the catalyst called UDCaT-4; anal.: Zr 9.01, Al 0.16%, S 1.17% w/w.

Reaction Procedure and Analysis

Liquid-phase reactions were conducted in a glass reactor of 5 cm. i.d. and 10 cm height with four glass baffles and a four-bladed disc turbine impeller located at a height of 0.5 cm from the bottom of the vessel and mechanically agitated with an electric motor. In a typical alkylation reaction, 0.5 mol toluene was reacted with 0.05 mol benzyl chloride with a catalyst loading of 0.018 g/cm^3, 1000 rpm and 90 °C. The reaction mixture was allowed to reach the desired temperature, the initial/zero time sample collected and catalyst added thereafter. Samples were withdrawn periodically and analyzed on a Chemito GC equipped with a stainless steel column (dia. 1/8 in and length 4 m) packed with a liquid stationary phase of 10% OV-17 on Chromosorb WHP, and an FID detector.

Vapour-phase alkylation was conducted in a down-flow fixed-bed haste alloy HC-276 reactor with 25.4 mm ID and 300 mm length at atmospheric pressure, equipped with an upstream vaporizer and a downstream condenser. The liquid feed containing a 1:1 molar ratio of mesitylene and isopropyl alcohol was fed by a double piston (Well Chrom HPLC-pump K-120) pump to the vaporizer using N_2 as a carrier gas at a WHSV of 20 h^{-1} at 250 °C and the effluent was analyzed by GC (GC1000 Chemito) equipped with stainless steel column of 3.8 mm × 4 m packed with 10% SE-30 on chromosorb WHP and a FID detector.

In a typical run, 1 g catalyst was charged to the reactor and stacked in between glass beads and ceramic wool. The reactor was maintained under isothermal conditions during all runs.

Acknowledgements

GDY acknowledges Darbari Seth Professorship Endowment for financial assistance and CSIR under NMITLI programme (2001–03).

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