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Post synthesis alumination of KIT-6 materials with Ia3d symmetry and their catalytic efficiency towards multicomponent synthesis of 1*H*-pyrazolo[1,2-]phthalazine-5,10-dione carbonitriles and carboxylates

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ABSTRACT

Alumination of Si-KIT-6 materials with ordered three-dimensional (3D) structure were prepared by postsynthesis method with various Si/Al ratios. The catalysts were characterized by X-ray diffraction analysis (XRD), N₂ porosimetry and FT-IR spectra. The presence of framework and extra framework aluminium was predicted by Aluminium MAS NMR. The strength of the acid sites of the catalysts was studied by NH₃-TPD acidity measurements. The morphology of mesoporous materials was studied by SEM and TEM observation. The metal content of the samples was investigated by ICP-OES. The prepared solid acid catalysts were applied for the multi-component synthesis of 1*H*-pyrazolo[1,2-]phthalazine-5,10diones from the reaction of phthalhydrazide, malononitrile/ethylcyano acetate and aromatic aldehyde in ethanol under liquid phase conditions. Activities of the catalysts follow the order: Al-KIT-6(33) > Al-KIT-6 (56) > Al-KIT-6(81) > Al-KIT-6(110) > Nafion-H > Amberlyst-15 \gg HM (12) > H β (8) > HY (4). The effects of reaction conditions and different catalysts have been studied. Various advantages associated with these protocols include effective catalysis, simple work-up procedure, short reaction times, high product yields, easy recovery and reusability of the catalysts.

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1. Introduction

Heterogeneous catalysis is emerging technology and they have attracted considerable attention in organic synthesis due to their unique catalytic properties. Acid catalysis by mesostructured materials has attracted due to the large regular pore structure that make them suitable for liquid-phase acid catalysis by enabling rapid diffusion of reactants and products through the pores, thus minimizing consecutive reactions [1–3]. The mesoporous silicate materials consist of chemically inert silicate framework and in order to induce a specific catalytic activity, researchers have tried to incorporate a variety of metals into the mesostructure by either direct synthesis/ion-exchange or impregnation. The demand for large pore acid catalysts has prompted greater efforts in both the academicians and industrialists to synthesise mesoporous molecular sieves and such acidic forms of porous materials are important in organic synthesis for a number of catalytic reactions [4-6]. Among the mesoporous materials having uniform channels, large pore size, high specific surface area and high thermal stability, KIT-6 exhibits a three-dimensional cubic Ia3d

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symmetric structure with interpenetrating bicontinuous network of channels [7]. Three-dimensional pore structure of KIT-6 and its resistance against pore blockage of this phase could serve as an excellent candidate for catalytic applications. Ryoo et al. recently reported the synthesis routes by low acid concentrations using triblock copolymers as structure-directing agents and BuOH as a co-agent allowing the formation of great variety of mesostructures [8]. Direct synthesis of Al-KIT-6 is difficult because, under strongly acidic conditions during the synthesis, free aluminium species exist in cationic form and thus cannot enter the framework of silica. Post-synthetic routes are preferred for incorporating aluminium into mesoporous silica matrix and the resulting materials found to possess structural ordering with better catalytic activity. There are numerous applications of transistion metal supported KIT-6 [9-12], KIT-1 [13-15], SBA-15 [16-18] and MCM-41 [19-23] those favors organic reactions like esterification, condensation, isomerisation, acetalization, cyclo-dehyration reactions, hydrodesulfurization and oxidation reactions. Also, certain multi component reactions (MCRs) involving C-C bond formation, coupling reactions, Knoevenagel condensation reactions, Prins cyclization, cyclo-addition and dehydrative etherifications preceded well over a variety of silica modified catalysts [24-27].

Heterocyclic compounds containing phthalazine moiety are important in medicinal field due to their pharmacological and biological activities [28,29]. Pyrazolo[1,2-*b*]phthalazine-dione

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derivatives were reported as anti-inflammatory, analgesic, antihypoxic, and antipyretic agents [30]. Novel biologically important derivatives have been synthesized through MCRs which involve minimal work trail with quantitative yields of the respective products [31,32]. In recent times, we have demonstrated heterogenous acid catalysis over a variety of MCRs [33,34]. Recently, 1*H*-pyrazolo[1,2-*b*]phthalazine-5,10-dione derivatives have been synthesised by using pTSA [35] and ultrasound assistance [36]. Considering the above reports, herein we report the synthesis of 3D cubic mesoporous aluminosilicates (Al-KIT-6) and their activity as heterogenous solid acid catalysts towards the three component reaction of phthalhydrazide, malononitrile/ethylcyano acetate and aromatic aldehyde in ethanol under liquid phase conditions. The reaction was monitored under various solvents and aluminosilicates guides the multi-component reaction involving cyclo-condensation pathway to afford the products associated with easy separation and the recyclability of the catalysts.

2. Experimental

2.1. Materials

Tetraethylorthosilicate, aluminiumisopropoxide and triblock copolymer (Pluronic P123, EO₂₀PO₇₀EO₂₀; Aldrich: Mol. Wt. 5800) were purchased from Aldrich (98% pure). Hydrochloric acid (35%) and *n*-butanol, as co-solvent, used in the synthesis were AR grade chemicals. Phthalhydrazide was purchased from Aldrich (99% pure) and malononitrile, ethylcyanoacetate, various aromatic aldehydes were purchased from SRL Biochem (India) Ltd. (98% pure) and were used without further purification.

2.2. Synthesis of Al-KIT-6 materials

Si-KIT-6 materials were synthesized hydrothermally with the gel composition of 1 TEOS:0.017 P123:1.83 HCl (35%):1.3 n-BuOH:195 H₂O. Pluronic P123 (4 g) was added to 144 g water and 7.9 g 35% HCl in a polypropylene bottle and stirred at 35 °C. A homogenous solution was obtained after 4h and then *n*-butanol (4g) was then added and the stirring was continued for 1h. 8.6g of TEOS was added at once and the mixture was stirred for 24 h at 35 °C and then the mixture was aged at 100 °C for 24 h under static hydrothermal condition. The solid material was filtered hot without washing and then dried at 100 °C for 12 h in air. The dried sample was powdered and calcined at 550 °C for 8 h in air atmosphere to remove the template. Alumination of siliceous KIT-6 was done by post synthetic route according to the procedure reported for SBA-15 in the literature [37]. The method involves the addition of appropriate amounts of aluminium isopropoxide (for Si/Al: 25, 50, 75 and 100) to 1 g of Si-KIT-6 in hexane (50 ml). The solution was stirred for 12 h, filtered and dried at 100 °C. In order to remove the extra-framework aluminium, the dried materials were washed with 1 M HCl and calcined at 550 °C for 5 h in air. The samples are designated as Al-KIT-6 (33), Al-KIT-6 (56), Al-KIT-6 (81) and Al-KIT-6 (110) with various Si/Al ratios after acid treatment as obtained from ICP-OES results.

2.3. Catalytic experiments

A mixture of pthalhydrazide (1 mmol), malononitrile or ethylcyanoacetate (1 mmol), aromatic aldehyde (1.1 mmol), 300 mg of catalyst and solvent (5 ml) was taken in a magnetically stirred glass vessel fitted with a reflux condenser and was kept in a constant temperature oil bath and refluxed at 60 °C for appropriate time (4 h). The completion of the reaction was monitored by TLC using ethyl acetate and *n*-hexane as eluent. After completion of the reaction, the catalyst was removed and the filtrate was re-crystallized with methanol to get pure product. All the products were characterized by ¹H NMR, ¹³C NMR and IR spectra and have been identified by comparison of the spectral data with those reported. All yields refer to isolated products. NMR spectra were recorded on a Bruker 500 MHz and IR spectra were run on a Perkin-Elmer spectrometer.

2.4. Measurements

The crystalline phase identification and phase purity determination of the calcined samples of Al-KIT-6 were recorded by XRD (PAN Analytical, diffractometer) using nickel filtered Cu Kα radiation (λ = 1.5406 Å). The metal content in the catalysts was measured by inductively-coupled plasma optical emission spectroscopy (ICP-OES Optima 5300 DV - PerkinElmer). ASAP-2010 volumetric adsorption analyzer manufactured by the Micromeritics Corporation (Norcross, GA) was used to determine the specific surface area of the catalysts at liquid nitrogen temperature. Before the measurement, each sample was degassed at 623 K at 10^{-5} Torr overnight in an out gassing station of the adsorption apparatus. The full adsorption-desorption isotherm was obtained using BET method at various relative pressures; the pore size distribution were calculated from the nitrogen adsorption-desorption isotherms using the BJH algorithm (ASAP-2010 built-in software from Micromeritics). Mid-infrared spectra were recorded on a Nicolet (Avatar 360) instrument using a KBr pellet technique. ²⁷Al MAS NMR spectra were recorded at 104 MHz on a Bruker DRX-400 spectrometer equipped with a magic angle spin probe at room temperature. NH₃-TPD measurements were carried out in a flow reactor (Micromeritics Instrument Corporation Chemisoft TPx V1.02 Unit 1-2750). Samples were activated at 700 °C for 1 h in a flow of helium; subsequently, ammonia was introduced by a He stream containing 10 vol.% of ammonia at 100 °C. The physically adsorbed NH₃ was removed by purging with a helium flow at 100 °C until the baseline was flat. Then the reactor temperature was ramped at a rate of 10°C/min. SEM micrographs and EDS spectra of the active catalysts was obtained from HITACHI (E-1010) ION SPUTTER instrument. TEM was performed using a IEOL 3010 electron microscope operated at 300 kV. This has a filament made up of LaB_6 and the instrument works under a vacuum in the range 10^{-5} to 10⁻⁶ Pa.

3. Results and discussion

3.1. Characterization of Al-KIT-6

3.1.1. XRD

Low-angle XRD patterns confirm the formation of the mesophase of the synthesized aluminosilicates. Fig. 1(A) represents the low angle XRD pattern of the calcined Si-KIT-6 parent material and Fig. 2 represents the XRD pattern of calcined Al-KIT-6 materials, which shows a sharp intense peak at $2\theta = 1.01$ corresponding to (211) plane and a hump for (220) plane. The XRD pattern clearly indicates that the material is well ordered mesostructure and belongs to bicontinuous cubic space group Ia3d symmetry [37]. The unit cell parameter a_0 of calcined sample was calculated from $a_0 = 6^{1/2} d_{(211)}$, in good agreement with the literature and suggests that mesoporous silica KIT-6 is with body centered cubic symmetry of the space group Ia3d, with sharp peak due to the (211) reflection and these data are presented in Table 1. The d spacing and a_0 values of the fresh aluminosilicates suggests that there is a marginal difference with varying aluminium content as the insertion of a heteroatom leading to thickening of the pore wall through transition metal promoted cross-linking of the amorphous silica walls [38].



Fig. 1. (A)X-ray diffraction pattern of Si-KIT-6 [low angle (2θ)] and inset (B) nitrogen adsorption-desorption isotherms of Si-KIT-6.

3.1.2. N₂ sorption analysis

Nitrogen adsorption-desorption isotherms and the corresponding pore size distributions for the mesoporous KIT-6 materials are shown in inset of Figs. 1, 3 and 4, respectively. The BET surface area, pore volume, and average pore size of selected samples are listed in Table 1. The isotherms are of type IV with a sharp capillary condensation step at intermediate p/p_0 at 0.6–0.7 and a hysteresis loop characteristic for materials with narrow pore size distribution. A marginal difference in N₂ sorption isotherms was observed for Al-KIT-6 with Si/Al ratio 33, 56, 81 and 110. This difference supports the presence of metal in the mesopores. Those have a pore radius around 3.0-3.1 nm (maximum large pore diameter around 6.2 nm) and a total pore volume from $0.6 \text{ to } 0.7 \text{ cm}^3/\text{g}$. The sharp capillary condensation step indicating a regular pore size distribution at the mesopore level exists in all catalysts. Although the inclusion of aluminium into KIT-6 was expected to decrease the specific surface area and the cumulative pore volume, a relatively high surface area was observed ranging from 653 to $714 \text{ m}^2/\text{g}$. The surface area of the materials increased with decreasing aluminium

Table 1

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Fig. 2. X-ray diffraction pattern of Al-KIT-6 [low angle (2θ)]: (a) Al-KIT-6 (33), (b) Al-KIT-6 (56), (c) Al-KIT-6 (81), (d) Al-KIT-6 (110) and (e) Al-KIT-6 (33) after fourth cycle for the synthesis of Entry (a).

content. Wall thickness was derived using $P_{\rm W} = (a_0/2) - P_{\rm d}$ (where $P_{\rm d}$ is pore diameter and a_0 the unit cell parameter) is presented in Table 1 for comparison.

3.1.3. ²⁷Al MAS NMR

²⁷Al MAS NMR spectra of the Al-KIT-6 (33) materials are shown Fig. 5. In general, the resonance at 0 ppm is assigned to octahedral aluminium corresponding to extra-framework aluminium species and resonance at 50 ppm is assigned to framework aluminium species in tetrahedral coordination [39]. The spectrum of the sample shows two resonance peaks around 0 and 50 ppm and most of the aluminium are in tetrahedral environment. The single sharp resonance at 54 ppm corresponding to framework aluminium species is maxima for the spectrum of all Al-KIT-6 materials. ICP-OES values of the materials with Si/Al ratios: 25, 50, 75 and 100 before the acid treatment was found with Si/Al ratios: 28, 52, 79 and 106. It was evident with the ICP-OES results of the acid treated Al-KIT-6 materials (final product) that were found with Si/Al ratios: 33, 56, 81 and 110. This indicates that de-alumination occurred during the acid treatment and the removal of extra-framework

Catalysts	Si/Al ^c (final product)	XRD		S_{BET}^{b} (m ² /g)	P _d ^b (nm)	P _v ^b (cm ³ /g)	Pw ^b (nm)	Acidity (mmol/g) ^e	
		d spacing ^a (Å)	a _o a (nm)						
Si-KIT-6	-	92.51	22.57	765	6.2	0.73	5.0	-	
Al-KIT-6 (25)	33	83.52	20.42	653	6.0	0.65	4.2	0.32	
Al-KIT-6 (50)	56	84.28	20.64	671	6.1	0.67	4.2	0.27	
Al-KIT-6 (75)	81	86.66	21.20	684	6.1	0.68	4.5	0.19	
Al-KIT-6 (100)	110	91.37	22.30	714	6.2	0.71	4.9	0.11	
Al-KIT-6 (33) ^d	37	84.15	20.58	580	6.0	0.61	4.3	-	
Nafion-H	-	-	-	0.02	-	-	-	0.8	
Amberlyst-15	-	-	-	64	-	-	-	0.75	
HM (12)	-	-	-	481	-	-	-	1.14	
Ηβ(8)	-	-	-	502	-	-	-	0.92	
HY (4)	-	-	-	367	-	-	-	0.58	

 S_{BET} , specific surface area; P_d , pore diameter; P_w , pore wall thickness $[a_0/2 - P_d \text{ (where } a_0 = \sqrt{6}d)]$.

^a Values obtained from XRD studies.

^b Values obtained from N₂-adsorption results.

^c Measured by ICP-OES technique.

^d Fourth cycle for the synthesis of Entry (a).

^e Values obtained from NH₃-TPD results.



Fig. 3. Nitrogen adsorption-desorption isotherms of the catalysts: (a) Al-KIT-6 (33), (b) Al-KIT-6 (56), (c) Al-KIT-6 (81), (d) Al-KIT-6 (110) and (e) Al-KIT-6 (33) after fourth cycle for the synthesis of Entry (a).

aluminium and other impurities is obvious with the respective difference in Si/Al ratios [40].

3.1.4. NH₃-TPD

The temperature-programmed desorption of ammonia (NH₃-TPD) was performed to determine the nature of surface acidity of the catalysts with various Si/Al ratios as shown in Fig. 6. The spectra shows a well defined high temperature desorption peaks as the strength of acid sites is related to the corresponding desorption temperature. Generally, the acid sites are classified into weak (200 °C), medium (200–350 °C), and strong (350 °C) acid sites [41]. In the given TPD profiles, the area under the peak for Al-KIT-6 (33) gave 0.32 mmol/g total acidity which is high enough when compared to Al-KIT-6 (110), i.e. 0.11 mmol/g. Also the acid site density is 0.49 μ mol/m² for Al-KIT-6 (33) and 0.4 μ mol/m², 0.27 μ mol/m², 0.15 μ mol/m² for Si/Al: 56, 81 and 110 respectively. The area of the TPD peaks implies that the samples have maximum amounts of weak-medium acid sites and the measured acidity of the solids is presented in Table 1.



Fig. 4. Pore size distribution of the catalysts: (a) Al-KIT-6 (33), (b) Al-KIT-6 (56), (c) Al-KIT-6 (81), (d) Al-KIT-6 (110) and (e) Al-KIT-6 (33) after fourth cycle for the synthesis of Entry (a).



Fig. 5. 27 Al MAS NMR spectra of catalysts (a) Al-KIT-6 (33), (b) Al-KIT-6 (56), (c) Al-KIT-6 (81) and (d) Al-KIT-6 (110).

3.1.5. Energy dispersive X-ray spectral analysis

The energy dispersive spectra of Al-KIT-6 (33) is illustrated in Fig. 7 which represents the presence of Si, O and Al for their respective K α signals confirming their presence of aluminium in the KIT-6 material for fresh catalyst. Si/Al ratio calculated from EDX data was 31 and this value was close to the value (33) obtained by ICP-OES.

3.1.6. TEM analysis

The structure and symmetry of the materials were determined by transmission electron microscopy. The HRTEM images of the fresh Al-KIT-6 (33) and reused catalyst shows that the material



Fig. 6. NH_3 -TPD spectra of (a) Al-KIT-6 (33), (b) Al-KIT-6 (56), (c) Al-KIT-6 (81), (d) Al-KIT-6 (110) and (e) Si-KIT-6.



Fig. 7. EDX spectrum of Fresh Al-KIT-6 (33).

consists of the presence of large domains of pure bicontinuous meso structure (3-D silica-aluminium network) which highlights the interconnectivity in the pore structure of the Ia3d cubic phase (Fig. 8(a-d)).

3.2. Catalytic studies

3.2.1. Synthesis of 1H-pyrazolo[1.2-lphthalazine-5.10-diones from phthalhydrazide, malononitrile/ethylcyanoacetate, aromatic aldehvdes

Initially the synthesis of 1H-pyrazolo[1,2-]phthalazine-5,10-diones was performed by taking a mixture of stoichiometric amount of pthalhydrazide, benzaldehyde malononitrile/ethylcyanoacetate along with 300 mg and of catalyst in ethanol and refluxed at 60°C for 4h. The reaction involves dehydration and cyclization to yield 1H-pyrazolo[1,2-]phthalazine-5,10-diones. the respective



1H-pyrazolo[1,2-]phthalazine-5,10-

Phthalhydrazide R = CN or COOEt

Different substituted

diones were prepared changing the aromatic aldehyde

substituents. The para-substituted aldehydes gave good results in

short time compared to the ortho-substituents as there is more

steric hindrance for the ortho substituted aldehvdes o-(OCH₃, -Cl.

-Br, $-NO_2$) on the product formation than the *para*-substituted

p-(OCH₃, -CH₃, -Cl, -Br, -NO₂) aldehydes with the use of

Al-KIT-6 catalysts. The presence of electron-donating or electron-

withdrawing groups in the aromatic ring of the aldehydes had no

Primary elucidation of the structures for all the isolated prod-

ucts was done by FT-IR spectra. For Entry [a] - Table 2: a band

at 3361 cm⁻¹ for NH stretching, a band at 3025 cm⁻¹ for alkyl

CH stretching, a band at 2215 cm^{-1} for nitrile (CN stretching),

1656 cm⁻¹ for C=O stretching (Fig. 9). The structure of the product

substitution effect on the yield to afford respective products.

3.2.2. Structural determination of isolated products

1H-Pyrazolo[1,2-]phthalazine-5,10-diones

catalysts is important for the reaction which is evident from the fact that there was no reaction without the use of any catalyst or with Si-KIT-6. The lower activity of Al-KIT-6 (110) compared to other Al-KIT-6 catalysts is due to the low aluminium content with low acid amount even though the surface area is high. On the other hand, amberlyst-15 and nafion catalysts offered low yield which shows that the mesoporosity of silica is indispensable. The yield of the product was less over zeolites because of the microporosity and high acidity that could hinder the formation of the required products. The acid sites of Al-KIT-6 catalysts induce the reaction by proton transfer to afford the products through the condensation of the aldehyde and active methylene nitriles (malononitrile/ethylcyano acetate) followed by the cyclization with phthalhydrazide. The mechanism (as in Fig. 11) involves the formation of carbo-cation by the proton donation by the catalyst to aldehyde with the removal of water molecule, and in subsequent steps, proton goes to catalyst and again proton transfer

was further confirmed by ¹HNMR spectra; ¹H NMR (500 MHz, DMSO-*d*₆): d = 6.11 (1 H, s, CH), 7.49-7.7 (5 H, m, ArH), 7.82-7.8 (4 H, m, ArH), 8.09 (2 H, s, NH_2) ppm as shown in Fig. 10.

3.2.3. Effect of different solvents on product yield

Synthesis of 1*H*-pyrazolo[1,2-]phthalazine-5,10-diones was carried out with different solvents such as ethanol, methanol, acetonitrile and ethyl acetate. The order of various solvents over product yield is as follows: ethanol > acetonitrile > methanol > water >> ethyl acetate respectively as shown in Table 3. Ethanol was found to be good solvent for all the reactions and frequently pulls out the product through the pores of the catalyst as the reaction proceeds further with ease. The less polar solvents showed low product yield since the solvent would have not been capable of getting the products at the catalyst surface in that way the deactivation of the active surface of the catalyst occurs and there was no reaction using solvents like DMSO, DMF as the solvent plays a negative role by retarding the multi-component pathway. This might be due to the adsorption of solvent on the catalyst surface or the solvent-reactant interactions. The product yield was less when water was used as solvent and this is due to the solubility problems of the reactants.

3.2.4. Effect of catalyst and reusability

The reaction of phthalhydrazide, malononitrile/ethylcyanoacetate and aromatic aldehyde was performed over various catalysts to evaluate the catalytic activity individually. In the Entries [a–n], the product yields for various catalysts were compared under the same conditions. All the catalysts were compared to support the activity based on the product yield, recovery and reusability. The catalysts takes the order as presented in Table 4 ; Al-KIT-6 (33)>Al-KIT-6 (56)>Al-KIT-6 (81)>Al-KIT-6 (110)>Nafion-H>Amberlyst-15 \gg HM (12)>H β (8)>HY (4). All catalysts showed a good yield of products. Among the mesoporous alumino silicates, the activity was high with Al-KIT-6 (33) nearly 93% and the isolated yield using Al-KIT-6 (56), KIT-6 (81) and Al-KIT-6 (110) was 79%, 71% and 64%. This indicates that the conversion decreases with Si/Al ratios and respectively increases with acidity of the catalysts. Acidity and mesoporosity of the

Table 2

Synthesis of 1*H*-pyrazolo[1,2-]phthalazine-5,10-diones.







Reaction conditions: mole ratio=1:1:1.1 (phthalhydrazide:malononitrile/ethylcyanoacetate:benzaldehyde); solvent=ethanol; catalyst=Al-KIT-6 (33); wt. of the catalyst=300 mg; reaction temperature=60°C; reaction time=4 h.

takes place to give the carbo-cation. The addition of the formed cation to phthalhydrazide takes place with the release of proton which in turn cyclise to give pyrazolo phthalazine diones. For all the substituted pyrazolo[1,2-b]phthalazine-2-carbonitrile and pyrazolo[1,2-b]phthalazine-2-carboxylate derivatives, the mesoporous aluminosilicates benefits the reactions involving large organic molecules. The three-dimensional mesopores and high surface area of KIT-6 aluminosilicates with acid centres as a whole is highly accountable for the expected products in good yields. In addition they were diffusion resistant for the reactants to react completely.

The extent of leaching of the metal from the support is important when dealing with heterogeneous-type catalysts in liquid-phase reactions. After each experiment, the amount of aluminium was determined by ICP after removal of the solid catalyst by filtration. The extent of reusability was studied by choosing the model reaction of phthalhydrazide, benzaldehyde and malononitrile/ethyl cyanoacetate. The reusability of the Al-KIT-6 catalysts was tested by recovering the catalysts by filtration from the solution and washed with acetone and dried to get the material. The isolated yield of Entry [a], 3-amino-5,10-dihydro-5,10-dioxo-1-phenyl-1*H*-pyrazolo[1,2-b]phthalazine-2-carbonitrile for four runs were 93–79% respectively. In the case of Entry [j] ethyl 3-amino-5,10-dihydro-5,10-dioxo-1-phenyl-1*H*-pyrazolo[1,2b]phthalazine-2-carboxylate, the yield percentage for fresh and up to four recycles were found to be 90–71%. The isolated yield



Fig. 8. TEM images of Al-KIT-6 (33): (a and b) fresh and (c and d) recycled catalyst after 4th cycle.



Fig. 9. [Table 2, Entry (a)]: IR (KBr); 3361 cm⁻¹, 3025 cm⁻¹, 2215 cm⁻¹, 1656 cm⁻¹.



Fig. 10. 1 H NMR (DMSOd₆, 500 MHz) spectrum of the compound [Table 3, Entry (a)].



Fig. 11. Plausible mechanism for the formation of 1H-pyrazolo[1,2-]phthalazine-5,10-diones over Al-KIT-6.

after each cycles are presented in Table 5 . From the observation, the catalyst Al-KIT-6 (33) showed minor difference in the yield of the reaction and the ICP analysis showed leaching of aluminium from 33 to 37 after the last cycle. Also it is clear that on recycling the catalysts, aluminium still exists without major leaching as to support that there is a strong interaction with SiO₂. The pore wall thickness was 4.3 nm and surface area decreased to 580 m²/g with a pore volume 0.61 cm³/g and pore diameter 6.0 nm. Also, for the

determination of the structure and symmetry of the final recycled catalyst Al-KIT-6 (33), XRD was employed which showed practical decrease in patterns as shown in Fig. 2 and the data are presented in Table 1.

Table 3

Effect of various solvents on the synthesis of 3-amino-5,10-dihydro-5,10-dioxo-1
phenyl-1 <i>H</i> -pyrazolo[1,2-b]phthalazine-2-carbonitrile over Al-KIT-6.

Sl. no.	Solvent	Isolated yield (%)
1	Ethanol	93
2	Acetonitrile	72
3	Methanol	59
4	Water	29
5	Ethyl acetate	15
6	DMSO	-
7	DMF	-

Reaction conditions: mole ratio =1:1:1.1 (phthalhydrazide/malononitrile/benzaldehyde); solvent=ethanol; catalyst=Al-KIT-6 (33); wt. of the catalyst=300 mg; reaction temperature = reflux; reaction time = 4 h.

Table 4

Effect of various catalysts on 3-amino-5,10-dihydro-5,10-dioxo-1-phenyl-1*H*-pyrazolo[1,2-b]phthalazine-2-carbonitrile over various catalysts.

Sl. no.	Catalysts	Isolated yield (%)
1	Al-KIT-6 (33)	93
2	Al-KIT-6 (56)	79
3	Al-KIT-6 (81)	71
4	Al-KIT-6 (110)	64
5	Nafion-H	56
6	Amberlyst-15	41
7	HM (12)	26
8	Ηβ (8)	19
9	HY (4)	12
10	Si-KIT-6	-
11	Without catalyst	-

Reaction conditions: mole ratio =1:1:1.1 (phthalhydrazide/malononitrile/benzaldehyde); solvent=ethanol; wt. of the catalyst=300 mg; reaction temperature= $60 \circ C$; reaction time=4 h.

Table 5

Reusability of Al-KIT-6 (33) catalyst for the synthesis of 3-amino-5,10dihydro-5,10-dioxo-1-phenyl-1*H*-pyrazolo[1,2-b]phthalazine-2-carbonitrile^a and ethyl 3-amino-5,10-dihydro-5,10-dioxo-1-phenyl-1*H*-pyrazolo[1,2-b]phthalazine-2-carboxylate.^b.

Isolated yield ^b (%)			

Reaction conditions: mole ratio = 1:1:1.1 (phthalhydrazide:malononitrile/ ethylcyanoacetate:benzaldehyde); solvent = ethanol; wt. of the catalyst = 300 mg; reaction temperature = $60 \degree C$; reaction time = 4 h.

4. Conclusion

Post-synthetic implantation of aluminium over Si-KIT-6 was successfully done under hydrothermal conditions. Acid leaching by 1 M HCl had certain impact to remove the alumina impurities and extra framework aluminium. The mesoporous aluminosilicates were found to be good recyclable solid acid catalysts for three component cyclo-condensation of phthalhydrazide, malononitrile/ethyl cyano acetate and aromatic aldehyde. This represents a convenient catalytic system leading to the synthesis of 1*H*-pyrazolo[1,2-]phthalazine-5,10-diones. The reaction proceeds smoothly over Al-KIT-6 catalysts in ethanol and solvent-free under reflux conditions on varying the aromatic aldehydes in the stoichiometric ratios. In the reactions presented above one can oversee the advantages of Al-KIT-6 mesoporous materials for acid catalyzed reactions due to the benefit of the large regular pores. The interconnectivity of the cage-like mesopores and the uniformity of the channel dimensions of the Al-KIT-6 materials are suitable catalysts for such organic transformations.

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