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Hydrophobic WO₃/SiO₂ catalyst for the nitration of aromatics in liquid phase

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Highlights

- 20% WO₃/SiO₂ catalyst successfully modified using Dynasylan 9896
- No change in the acidity of the catalyst after modification
- Increase in the hydrophobicity of 20% WO₃/SiO₂ catalyst after modification
- *o*-Xylene conversion increased from 68% to 80% with modified catalyst
- Efficient catalyst recycle for benzene nitration without additional solvent

Abstract

 WO_3/SiO_2 solid acid catalyst synthesized using sol gel method has shown promising activity (up to 65% conversion) for aromatic nitration in liquid phase using commercial nitric acid (70%) as nitrating agent without using any sulfuric acid. The water formed during the reaction as well as water from dilute nitric acid (70%) was removed azeotropically, however due to the hydrophilic

nature of the catalyst, some water gets strongly adsorbed on catalyst surface forming a barrier layer between catalyst and organics. This prevents effective adsorption of substrate on catalyst surface for its subsequent reaction. To improve the activity further, the hydrophilic/hydrophobic nature of the catalyst was altered by post modification by grafting with commercial short chain organosilane (Dynasylan 9896). The modified 20% WO₃/SiO₂ catalyst when used for *o*-xylene nitration in liquid phase, showed significant increase in the conversion from 65% to 80% under identical reaction conditions. Catalyst characterization revealed decrease in the surface area of 20% WO₃/SiO₂ from 328 m²/g to 229 m²/g after grafting with Dynasylan 9896. The fine dispersion of WO₃ particles (2-5 nm) on silica support was not affected due to modification. NMR and FT-IR study revealed the decrease in surface hydroxyl groups imparting hydrophobicity to the catalyst. Interestingly the total acidic sites of the catalyst remained almost unaltered (0.54 mmol NH₃/g) even after modification. Even though, the acidity and other characteristics of the catalyst did not change appreciably, there was a considerable increase in the *o*-xylene conversion which can be ascribed to the hydrophobic nature of the catalyst.

Key words: Heterogeneous catalysis, Grafting, Hydrophobic, Sol-gel synthesis, Aromatic nitration.

1. Introduction

The nitration of aromatics using conventional nitrating mixture (nitric acid and sulphuric acid in 1:2 mole ratios) is the most common reaction in the production of bulk chemicals, dyes, pesticides, explosives etc [1]. However the major environmental hazard associated with this process is generation of dilute sulphuric acid in large volume which needs to be recycled using very expensive concentration process or needs to be treated before disposing in the environment [2]. Thus overall the conventional nitration is probably the most hazardous industrial process and an alternate environmentally benign process to overcome the above mentioned drawback is highly desired.

Over the years many efforts have been taken to make the nitration process more green by using alternate methods like developing various solid acid catalysts [3-6] for the nitration processes, use of solid supported reagents like nitrating mixtures, microwave assisted reactions

[7,8] or mechanochemical nitrations [9], use of ionic liquids, use of alternate solid nitrating agents [10] or nitration using liquid NO₂ [11] (high pressure autoclave reactions) as nitrating agent [12]. Solid acids have several advantages such as non corrosiveness, easy separation and regeneration during the reaction. Some of the solid acids used for nitration reactions are heteropolyacids [13], zeolites [14,15], clay supported metal nitrates [16,17], silica supported metal oxides [18,19], sulphated metal oxides [20,21] etc. Prakash et al. [8] have prepared complex of nitrating mixture with PVP (Poly(4-vinylpyridine)) and used it for nitration of various aromatics using 2.5 equivalent of nitrating mixture/PVP complex. After the reaction the PVP was recycled for making the complex again and using it for nitration. The system has shown high efficiency for aromatic nitration (upto 98% yield), with 2.5 equivalent of nitrating mixture.

Our group has extensively used mesoporous silica supported metal oxide (MoO₃ and WO₃) based solid acid catalysts with very high acidity and hence very high efficiency for various acid catalyzed organic transformations including nitration [10,15,19,22,23]. WO₃/SiO₂ catalyst has also been reported by other research groups for various acid catalysed reactions as well as oxidation reactions [24-27]. MoO₃/SiO₂ catalyst with 20 mol% loading of MoO₃ has shown very high activity for vapor phase nitration of benzene without sulphuric acid [23]. Whereas WO₃/SiO₂ catalyst prepared by similar method (sol-gel) was also quite active for nitration of various aromatics in liquid phase with commercial (70%) HNO₃ as nitrating agent [19]. Nitration of oxylene in liquid phase using WO₃/SiO₂ catalyst (without H₂SO₄) showed almost 60-65% conversion with 60/40 % selectivity for 4/3-nitro o-xylene respectively with <1% oxidation products. However, the -OH groups present on silica surface impart hydrophilic nature to the catalyst leading to strong adsorption of water from the reaction system on the catalyst surface. During the course of the reaction, the catalyst gets wet and sticks to the wall of the reaction flask lowering the reaction rate. Hence we attempted to modify the hydrophilic nature of WO₃/SiO₂ catalyst for preventing strong adsorption of water on the catalyst surface so that the catalyst does not stick to the reactor wall and the catalyst can remain suspended in the reaction mixture for efficient catalytic reaction.

It is well known that the precipitated silica is hydrophilic owing to the presence of surface silanol (Si-OH) groups and the hydrophilic nature of silica is modified by surface functionalization i.e. by grafting of alkyl groups on the precipitated silica [28] to make it hydrophobic. Conventionally various organosilanes are used for modification of the silica surface to modify

various surface properties of silica based materials like acidity, basicity and in some cases hydrophobicity [29-31]. Mainly two methods are popular for surface functionalization, (i) direct co-condensation of alkylating agent and (ii) post-synthesis grafting of alkylating agent [30-32]. In later method the organosilane species are covalently linked to surface silanol groups to achieve surface functionalization. Post modification/functionalization of solid acid catalysts has been carried out before [33] by grafting organosilanes to improve the acidity of the catalyst.

Rassy et al. have tuned the hydrophilic and hydrophobic properties of the silica aerogels by adjusting the proportion of methyltrimethoxy silane and studied the properties in details by FTIR and NMR analysis [34]. Bagwe et al. have modified silica nanoparticles using 3-(trihydroxysilyl)propyl methylphosphonate (THPMP), (3-Aminopropyl)triethoxysilane (APTS) and octadecyltriethoxysilane for reducing agglomeration and non specific binding in biological systems [35]. Hydrophobicity and pH stability of Fe₂O₃ magnetic nanoparticles was improved by coating with silica and further grafting with (3-Aminopropyl)triethoxysilane (APTS) and octyltriethoxysilane (OTES). Addition of APTS introduced basicity to the material thus making it better catalytic material for esterification reaction whereas hydrophobicity was tuned by adjusting the amount of OTES additionally grafted on the surface [29]. (3-Aminopropyl) triethoxysilane (APTS) has been widely used for modification of the silica based catalysts like SBA-15 to introduce basicity and carry out base catalysed organic transformations like Knoevenagel condensation, Henry reaction and Claisen-Schmidt condensation [32]. The above examples illustrate the modification of silica surface by organosilane to improve the material characteristics in terms of hydrophobicity/hydrophilicity or introduction of functionality (acidity/basicity) essential for organic transformations.

Previously we have carried out nitration of aromatics in liquid phase using 20 wt% WO₃/SiO₂ catalyst [19]. 20 wt% WO₃/SiO₂ catalyst showed highly hydrophilic nature due to surface silanol groups which had adverse effect on catalytic activity. In the present work we have post grafted the 20 wt% WO₃/SiO₂ catalyst with commercial organosilane, Dynasylan-9896 to improve the hydrophobic nature of the catalyst. The ethoxy groups of Dynasylan 9896 reacts with surface Si-OH to form covalent Si-O-Si bond upon hydrolysis. This grafted catalyst has been evaluated for the nitration of various aromatics in liquid phase and the results are discussed below.

2. Experimental Section

2.1 Materials

Ammonium metatungstate (AMT), 25% aq. ammonium hydroxide solution, ethyl silicate-40 (ES-40), *iso*-propyl alcohol (IPA), *o*-xylene, *p*-xylene, *m*-xylene, toluene, benzene, HNO₃, sodium bicarbonate, 1,2-dichloroethane (EDC) were obtained from Merck chemicals, India LOBA and Thomas Baker. All the chemicals were used as received without additional purification. Dynasylan 9896 was received from Evonik India as free sample.

2.2 Catalyst Preparation

The 20% WO₃/SiO₂ catalyst was synthesized using reported method [17]. The typical synthesis procedure is described below:

a) Sol-gel synthesis of 20% WO₃/SiO₂(A)

Ammonium metatungstate (10.62 g) was dissolved in 20 mL distilled water and added drop wise with constant stirring to ethyl silicate-40 (100 g) solution in dry IPA (70 mL). Further dil. NH₄OH (2.5%) solution (6 mL) was added to the above solution and stirred till white gel was obtained. The gel thus formed was dried in air and subsequently calcined in a muffle furnace at 500 °C for 5 h.

b) Post grafting of 20% WO₃/SiO₂ using Dynasylan 9896 (B)

5.0 g calcined 20% WO₃/SiO₂ was dispersed in 25 mL dry toluene to which 0.265 g Dynasylan 9896 (6.6 wt% with respect to SiO₂) was added and the resultant mixture was heated at 80 °C with constant mixing on rotary evaporator for 8 h. Then toluene was evaporated under vacuum and the obtained powder was dried at 100 °C in oven for 5 h. This catalyst was named as B.

5.0 g calcined 20% WO₃/SiO₂ was dispersed in 25 mL dry toluene to which 0.08 g Dynasylan 9896 (2 wt% with respect to SiO₂) was added and the resultant mixture was heated at 80 °C with constant mixing on rotary evaporator for 8 h. Then toluene was evaporated under vacuum and the obtained powder was dried at 100 °C in oven for 5 h. This catalyst was named as B'.

5.0 g calcined 20% WO₃/SiO₂ was dispersed in 25 mL dry toluene to which 0.4 g Dynasylan 9896 (10 wt% with respect to SiO₂) was added and the resultant mixture was heated at 80 °C with constant mixing on rotary evaporator for 8 h. Then toluene was evaporated under

vacuum and the obtained powder was dried at 100 °C in oven for 5 h. This catalyst was named as B".

2.3 Characterization of the catalysts

X-ray diffraction analysis was carried out using PAN analytical XPert Pro Dual Goniometer diffractometer with X'celerator solid state detector with CuK α (1.542 Å) radiation and a Ni filter.

The BET surface area was estimated using N_2 sorption at -196 °C using NOVA 1200 (Quantachrome) equipment. Initially the material was evacuated at 300 °C under vacuum. The specific surface area, BET, was determined according to the BET equation.

The Fourier transform infrared (FT-IR) analysis was carried out on a Thermo Nicolet Nexus 670 IR model. The spectrum was recorded in the range of 4000-400 cm⁻¹ at a resolution of 4 cm^{-1} and averaged over 128 scans.

The ²⁹Si and ¹³C Cross Polarization Magic Angle Spinning (CPMAS) NMR experiments were carried out on a Bruker AVANCE 300 wide bore spectrometer equipped with a superconducting magnet with a field of 7.1 tesla. The RF-powers were 50 kHz and 60 kHz while contact times were 6 ms and 3 ms for the ²⁹Si and ¹³C CPMAS experiments. All the chemical shifts are referenced to TMS.

Micromeritics Autochem 2910 instrument was used for determining acidity by NH₃-TPD experiments Approximately 100 mg sample in a quartz reactor was pretreated in a He flow at 500 °C for 1 h (ramp rate of 10 °C min⁻¹). Later it was cooled to 100 °C and then exposed at 100 °C to ammonia gas (5% NH₃–95% He) with a flow of 50 mLmin⁻¹. the sample was further evacuated for 3 h at 100 °C. The desorbed ammonia was measured in the temperature range of 100 to 700 °C (heating rate 5 °C min⁻¹) with He as a carrier gas (flow rate 60mLmin⁻¹).

FEI quanta 200 3D dual beam (ESEM) was used to record scanning electron microscopic (SEM) images with thermionic emission tungsten filament in the 3 nm range at 30 kV. HRTEM images were obtained using Tecnai G2-30 FEI instrument with an accelerating voltage of 300 kV. For sample preparation, the powder was dispersed in *iso*-propanol using ultrasonic bath. Two drops of sonicated *iso*-propanol solution were deposited on a carbon coated copper grid.

XPS measurements were carried out using Thermo Kalpha+ spectrometer using micro focused and monochromated Al Kα radiation with energy 1486.6 eV. The pass energy for spectral

acquisition was kept at 50 eV for individual core-levels. The electron flood gun was utilized for providing charge compensation during data acquisition. The peak fitting of the individual core levels were done using XPSpeak 41 software with a Shirley type background.

2.4 Catalytic activity

Liquid phase nitration of aromatics

The catalytic nitration reaction in liquid phase was carried out in a 100 mL flask containing three necks for fitting reverse Dean-Stark apparatus, reflux condenser and dropping funnel. To the solution of substrate in 1,2-dichloroethane solvent was added catalyst (20% by weight of the substrate) and heated to desired temperature. Commercial HNO₃ was added to the reaction mixture over a period of 30 min with simultaneous azeotropic removal of water formed during the reaction. As the density of 1,2-dichloroethane is higher than water, reverse Dean-Stark apparatus was used. At the end of the reaction, the catalyst was separated by filtration in hot condition. The products were extracted in 1,2-dichloroethane, and further washed with 5% NaHCO₃ solution, and water and dried using anhydrous sodium sulfate. The progress of the reaction was monitored by GC (Hewlett Packard 6890 GC equipped with HP-5 column of 50 m length, 0.25 mm internal diameter and 1 mm film thickness with flame ionization detector (FID). Conversion was calculated = [moles of reactant reacted]/[Initial moles of reactant used] \times 100 and the selectivity of products was calculated by [total moles of the product formed]/[total moles of substrate converted] \times 100. The individual yields were calculated and normalized with respect to the GC response factors. The product identification was carried out by injecting authentic samples in GC. The carbon and the material balance for most of the experiments was found to be >96%.

Catalyst recycle study

The catalyst was recycled for benzene nitration for which, a round bottom flask (3-necked, 500 mL capacity) was fitted with reflux condenser, Dean-Stark apparatus and magnetic stirrer. The reaction mixture containing benzene (70 g, 0.9 mol) and 10 g catalyst was heated at 90 °C using oil bath. At 90 °C, 70% nitric acid (61.2 g, 0.68 mol) was added to the reaction mixture over a period of 30 min. Benzene formed azeotrope with water which was removed using Dean-Stark apparatus. The aqueous phase was titrated after completion of the reaction, to estimate the nitric acid distilled out along with the azeotropic mixture. The reaction mixture was decanted and fresh charge of benzene (70 g, 0.9 mol) was added to the same catalyst charge followed by nitric acid

addition (61.2 g, 0.68 mol) and azeotropic removal of water as in first cycle. Similarly three recycles were carried out.

3. Results and discussion

Hydrophilic nature of the catalyst A poses problems due to the surface silanol groups during liquid phase nitration reactions. To overcome this problem of hydrophilic surface, commercially available Dynasylan 9896 was used for post-modification for improving hydrophobic character of the surface. Dynasylan 9896 is commercial product of Evonik Industries which is an oligomeric silane with short chain alkyl functional groups along with ethoxy groups. It is used for surface modification mainly for increasing hydrophobicity and dispersion in filler, pigment coating, and polymers. The surface modification by Dynasylan 9896 is achieved by hydrolysis with surface -OH groups which liberate ethanol forming covalent bond. However there are no reports on application of Dynasylan 9896 for catalyst modification. Hence in the present work Dynasylan 9896 was used to improve hydrophobicity of catalyst A with the aim of improving nitration activity.

3.1 Characterization

All the physicochemical characterizations of the catalyst A and B are given in Table 1. **Table 1:** Surface area and acidity of catalyst A and B and quantification of grafting on catalyst B by FTIR analysis

	Catalyst A	Catalyst B
Surface area, m ² /g	356	302
Pore volume, cc/g	0.37	0.33
Pore radius, Å	22.2	20.5
NH ₃ desorbed, mmol/g	0.56	0.54
Peak area for Si-OH stretching @ 3350 cm ⁻¹ (x)	33.7	35.1
Peak area for O-Si-O bending @ 467 cm ⁻¹ (y)	10.1	19.3
Ratio x/y	3.3	1.8

a) XRD analysis

The XRD patterns of the catalyst A and B are presented along with WO₃ in Fig. 1. The sharp peaks at 23.2°, 23.6°, 24.2°, 26.6°, 28.8° and 33.5° in the XRD pattern could be assigned to (002), (020), (220) and (202) planes of monoclinic WO₃ (JCPDS No. 43-1035). The broad underlying peak centered at $2\theta = 24^{\circ}$ is attributed to amorphous silica support In case of catalyst B, it was observed that monoclinic phase of WO₃ is unaltered. However there was significant decrease in the intensity of WO₃ peaks observed after modification which may be attributed to the formation of surface silane layer due to grafting of short chain alkyl silane on the surface.



Fig. 1: XRD pattern of catalyst B (a), catalyst A (b) and WO₃ (c)

b) FTIR analysis

FTIR spectrum of catalyst B (Fig. 2i) showed the prominent bands in the range of 1300-1000 cm⁻¹ assignable to the various Si-O-Si vibrations (asymmetric, symmetric stretching and bending) [36]. The IR bands at 954 and 811 cm⁻¹ could be attributed to the W=O_t and W-O-W stretching vibrations, respectively [37]. The Si-O-Si bending vibration was observed at 468 cm⁻¹. When the spectrum of catalyst B (Fig. 2ii (c)) was compared with catalyst A (Fig. 2ii (b)) and Dynasylan 9896 (Fig. 2ii (a)) in the spectral range of 3600-2400 cm⁻¹, the bands in the region of

2800-3100 cm⁻¹ were attributed to the C-H stretching vibrations of $-CH_2$ and $-CH_3$ groups of Dynasylan 9896 grafted on SiO₂.



Fig. 2: (i) FTIR spectrum of catalyst B in the range of 4000-400 cm⁻¹ (ii) FTIR spectra in the range of 2400-3600 cm⁻¹ of Dynasylan 9896 (a), catalyst A (b) and catalyst B (c)

The exact quantification for Dynasylan 9896 grafting on surface -OH groups was not possible by FTIR of modified catalyst as KBr palate technique was used for FTIR analysis. However for approximate quantification of grafting on catalyst A surface, the peak area of Si-O-Si bending vibration at 467 cm⁻¹ was used as internal standard assuming peak area of Si-O-Si would remain almost constant even after modification and this peak is not interfering with any other peaks of tungsten oxo species and organic fraction of Dynasylan 9896. The ratio of peak

areas for Si-OH stretching vibration at 3350 cm⁻¹ (x) and Si-O-Si bending vibration at 467 cm⁻¹ (y) was calculated (Table 1) for catalyst A and B. The ratio x/y for catalyst A was 3.3 which decreased to 1.8 after modification suggesting decrease in surface Si-OH groups due to grafting of alkyl silane chain on Si-OH.

c) Surface area measurements

The surface area data of catalyst A and B is shown in Table 1. A very high surface area of 356 m^2/g was obtained for catalyst A due to the sol-gel method and ethyl silicate-40 as the silica precursor. However as expected the decrease in the surface area to 302 m^2/g was observed after modification of the catalyst surface with Dynasylan 9896. The hysteresis behavior of the catalyst (Fig. S1) before and after modification clearly showed decrease in the total volume of N₂ adsorbed. The total pore volume decreased from 0.37 to 0.33 cc/g, with decrease in pore size from 22.2 to 20.5 Å indicating the change in surface nature of the catalyst due to short chain alkyl groups of organosilane. When Dynasylan 9896 was added to the original catalyst, it gets hydrolysed with surface silanol groups (Si-OH) and gets attached to the silica surface, decreasing the surface area due to alkyl chain of Dynasylan 9896 blocking some of the pores of the solid catalyst leading to decrease in pore volume as well as pore size.

d) ^{13}C & ^{29}Si NMR studies

The grafting of organosilane on surface of catalyst A was confirmed by CPMAS ¹³C and ²⁹Si NMR analysis. The comparison of the ¹³C NMR spectrum of Dynasylan 9896 with that of catalyst B is shown in Fig. 3. Dynasylan 9896 showed multiple peaks in the range of 16-18 ppm corresponding to different carbon atoms of alkane group viz. –CHx (where x = 1/2/3 and peak around 58 ppm for carbon of alkoxysilane group (-Si-OCHx; x = 2-3). The catalyst B showed a broad peak at 15.9 ppm corresponding to alkane –CHx (where x = 1/2/3) groups whereas peak at ~58 ppm corresponding to alkoxysilane disappeared confirming hydrolysis of alkoxysilane group. No ¹³C NMR signal was observed for catalyst A due to absence of any organic moiety. ¹H NMR analysis of catalyst B was not successful and it showed very broad peak which could not be compared with very sharp ¹H NMR signal of liquid Dynasylan 9896.



Fig. 3: ¹³C NMR spectrum of Dynasylan 9896 (a) and catalyst B (b)

The modification of surface silanol groups was analyzed by ²⁹Si NMR analysis (Fig. 4). Typically quaternary (Q4), tertiary (Q3) and secondary (Q2) –Si groups were observed at 110, 98 and 88 ppm respectively. Catalyst A (Fig. 4a) showed presence of Q4, Q3 and Q2 -Si groups at 109, 99.8 and 90.3 ppm respectively. There was increase in quaternary (Q4) -Si with corresponding decrease in tertiary (Q3) -Si groups on the surface of catalyst B (Fig. 4b, Table 2). This is attributed to Si-O-Si bond formation between surface –Si-OH (Q3) groups and Dynasylan 9896 during condensation reaction. This is further evidence for the successful surface modification of catalyst A.



Fig. 4: ²⁹Si NMR spectrum of catalyst A (a) and catalyst B (b), original (i) and deconvulated (ii)

Sample	% composition			Total
	Q^4	Q^3	Q^2	
Catalyst A	58.6	35.2	6.2	100
Catalyst B	74	21.6	4.4	100

Table 2: Analysis of surface Si-OH groups of catalyst A and B by ²⁹Si NMR

e) NH₃ TPD

The total acidity of the catalyst B was determined using ammonia-TPD experiments (Fig. 5). The total acidity of catalyst A did not change significantly after modification with Dynasylan 9896. The ammonia desorption curve of 20% WO₃/SiO₂ (Fig. 5 a) confirmed the availability of maximum number of medium and weak acid sites (150 - 350 °C) with total acidity of 0.56 mmol/g which decreased marginally to 0.54 mmol/g (Fig. 5 b) after modification with similar distribution of weak and moderate acid sites. Thus even after grafting the silica surface with Dynasylan 9896, the surface acid sites i.e. tungsten oxo species did not get affected.



Fig. 5: NH₃-TPD of catalyst A (a) and catalyst B (b)

f) XPS analysis

The XPS analysis WO₃, catalyst A and B was carried out and the results revealed presence on +6 oxidation state of W in all the catalysts (Fig. 6). The BE value of W $4f_{7/2}$ was found to be 35.4, 35.4 and 35.3 eV for WO₃, catalyst A and B respectively, whereas W $4f_{5/2}$ value was found to be 37.5, 37.4 and 37.4 respectively. The BE values are in accordance with the literature for W⁺⁶ [38]. Compared to WO₃ there is no change in the BE values observed for catalyst A and B indicating no change in the environment of W in WO₃/SiO₂.



Fig. 6: W(4f) core level spectra of WO₃ (a), catalyst A (b) and catalyst B (c).

g) SEM analysis

The SEM analysis of 20% WO_3/SiO_2 and catalyst B did not show any specific morphology (Fig. S2). However, the SEM image of catalyst B showed more spongy or floppy nature which may be attributed to the repulsion between particles due to alkyl chain. The particle size for catalyst B was smaller than catalyst A. The EDAX analysis of catalyst A showed increase in the surface Si content after modification due to addition of alkyl silane. Due to surface modification with Dynasylan 9896 there is increase in Si concentration on the surface which increased the Si/W ratio to 1.73 from 0.86 for catalyst A (Table 3).

Table 3: Elemental analysis of catalyst A and B

Sample	We	ight % by el	ement	Tatal	Si/W
	O K	Si K	WL	Total	ratio
Catalyst A	24.8	34.7	40.5	100	0.86
Catalyst B	41.5	37.1	21.4	100	1.73

h) TEM analysis

TEM analysis (Fig. 7) of the catalyst A and B showed no change in particle size and dispersion of WO₃ particles. The modified catalyst showed dispersion of nano particles (2-5 nm) of tungsten oxide on silica surface.



Fig. 7: TEM micrographs of catalyst B (a & b) & catalyst A (c & d)

3.2. Nitration of o-xylene

The catalyst A and catalyst B were used for the *o*-xylene nitration in liquid phase (1 equivalent HNO₃ at 90 °C for 8 h) as shown in Scheme 1. Commercial nitric acid (70%) was used as nitrating agent and water from the reaction system was removed azeotropically using 1,2-dichloroethane (EDC) as solvent (Table 4). The catalyst A showed 68% conversion with 45 and 54% selectivity for 3-nitro *o*-xylene (3-NOx) and 4-nitro *o*-xylene (4-NOx) respectively with 1%

oxidized products. During the nitration experiment using catalyst A, the catalyst settles at the bottom of the flask after addition of aqueous HNO_3 . Due to accumulation of water on the catalyst surface, it sticks to the reaction vessel. The careful observation indicated the formation of water layer between catalyst and organics because of which the catalyst was not suspended freely in the reaction medium forming lumps. The hydrophobic catalyst B (6.6%) remained suspended in the reaction mixture without sticking to the walls of the reaction flask. The hydrophobic catalyst B showed increase in conversion up to 80% without altering the selectivity for 3-NOx and 4-NOx when the same reaction conditions were used. This improved catalytic activity may be attributed to the increased hydrophobicity of the catalyst B. The water from HNO₃ and formed as byproduct in the reaction do not get strongly absorbed on the catalyst surface due to enhanced hydrophobicity and the catalyst remains suspended throughout the reaction increasing the conversion. When the reaction was carried out using catalyst B with 2 (B') and 10% (B") Dynasylan 9896, lower o-xylene conversion (70 and 65 respectively) was obtained, indicating 6.6 % loading to be optimum. The 2% Dynasylan 9896 loading in case of catalyst B' may be too less to impart significant hydrophobicity due to which only marginal increase in o-xylene conversion (70% compared to 68% for unmodified catalyst) was observed. The hydrophobicity increased with further increase in Dynasylan 9896 loading to 6.6% (Catalyst B) with significant increase in nitration conversion to 80%. However further increase in Dynasylan 9896 loading to 10% (catalyst B") has led to decrease in o-xylene conversion to 65%. The higher loading of alkoxy organosilane may lead to hydrolysis and self condensation among the alkoxy organosilane molecules forming separate aggregates of organosilane along with condensation with surface silanol groups of silica. These aggregates may mask some of the surface active sites leading to decrease in nitration activity. The progress of the o-xylene nitration reaction was monitored with time (Fig. 8) and the results showed 15% conversion after 1 h which gradually increased to 74% after 5 h. However the rate of reactions decreased after 5 h and in next 3 h only additional 6 % conversion was obtained (80 % conversion after 8 h). The selectivity for 3-NOx and 4-NOx remained same throughout the reaction.



Fig. 8: *o*-Xylene conversion with time using catalyst A and B *Reaction conditions: o*-xylene (0.2 mol): 70% HNO₃ (0.2 mol) 1:1, catalyst 20 wt% of *o*-xylene, EDC (1,2-dichloroethane): 120 mL, Temp. 90 °C, reaction time 8 h.



Scheme 1: Nitration of *o*-xylene

Table 4:	Nitration	of o-x	vlene	using	catalyst	A and B
			2	<i>U</i>	2	

Entry	Catalyst	Conversion,		Selectivity, %			
Enuy	Catalyst	%	3-NOx	4-NOx	[#] OP	NOx ratio	
1	Catalyst A	68	45	54	1.0	1.2	
2	Catalyst B	80	46	53	1.0	1.2	
3.	Catalyst B'	70	45	54	1.0	1.2	
4.	Catalyst B"	65	45	54	1.0	1.2	

Reaction conditions: o-xylene (0.2 mol): 70% HNO₃ (0.2 mol) 1:1, catalyst 20 wt% of *o*-xylene, EDC (1,2-dichloroethane): 120 mL, Temp. 90 °C, reaction time 8 h, [#]Oxidized products

3.3 Nitration of various aromatic substrates

Wider applicability of the catalyst B was evaluated under optimized reaction conditions (solvent EDC, 90 °C, substrate: HNO₃ molar ratio; 1:1.33, 8 h) for nitration of range of important aromatics containing various functionalities and the results are compared with the catalyst A (Table 5). The o-xylene nitration with catalyst B showed 84% conversion (Table 5, entry 1) with 45% and 54% selectivity for 1,2-dimethyl-3-nitrobenzene and 1,2-dimethyl-4-nitrobenzene respectively. The o-xylene conversion was only 74% with catalyst A under identical conditions. Nitration of *p*-xylene gave 75% conversion (Table 5, entry 2) with catalyst B and only 63% conversion with catalyst A. The selectivity for 1,4-dimethyl-2-nitrobenzene was 96%. Nitration of *m*-xylene showed 90% conversion with 85% selectivity for 1,3-dimethyl-4-nitrobenzene whereas only 81% conversion was obtained with catalyst A with similar selectivity pattern. The toluene nitration gave 81% conversion (Table 5, entry 4) with 55% and 42% selectivity for 1-methyl-2nitrobenzeneand 1-methyl-4-nitrobenzene respectively with ~4% oxidized products. Benzene nitration was carried out without using any additional solvent (EDC) as benzene forms azeotrope with water at lower temperature and helps remove water from the reaction. Hence excess benzene was used for azeotropic removal of water keeping benzene to 70% HNO₃ molar ratio 5:1 (Table 5, entry 5). In this case the nitric acid conversion was calculated. About 50% nitric acid was consumed during the reaction. From the nitration results in Table 5, significant improvement in nitration activity for wide range of aromatics was observed for catalyst B compared to the catalyst A.

Entry Substrate		Catalyst	% % Selectiv				
Lintry	Linty Substrate	Cuturyst	Conversion	2- Nitro	3- Nitro	4- Nitro	OP#
C	o-Xylene	А	84	-	45	54	1
		В	74		45	54	1
2	<i>p</i> -Xylene	А	75	NO ₂	-	-	4.0

Table 5: Nitration of aromatics using catalyst A and B

				96			
		В	63	94	-	-	6.0
3	<i>m</i> -Xylene	А	90	15	-	NO2 85	
		В	81	16	-	84	-
4	Toluene	А	84	55	S	42	3.0
		В	81	52	-	44	4.0
5	Benzene*	A	50 [@]	10 [^]	-	-	_
	×	В	24 [@]	5^	-	-	-

Reaction conditions: Substrate (0.2 mol): 70% HNO₃ (0.266) mol ratio 1:1.33, catalyst: 20 wt% with respect to substrate, Temp. 90 °C, EDC (1,2-dichloroethane) as solvent (50 mL), reaction time 8 h [#]Oxidized products, *Benzene: 70% HNO₃ mole ratio 5:1 without solvent, 8 h, [@]HNO₃ conversion, ^Nitrobenzene (mono nitro product);

3.4 Catalyst recycle study

Benzene forms azeotrope with water at lower temperature (69.3 °C) compared to EDC (72 °C), hence liquid phase benzene nitration was carried out in excess benzene without additional solvent. Benzene: HNO₃ (70%) molar ratio of 1.33 was maintained with slow addition of nitric acid (Table 6). Some nitric acid distilled out along with the azeotropic mixture and the recovered nitric acid was estimated by titration. In the first run 69% nitric acid conversion was obtained whereas ~21% HNO₃ was recovered. The pH of the reaction mixture was acidic due to unreacted acid remaining thought the exact quantification of nitric acid remaining in the reaction mixture could not be estimated. After completion of the reaction, the catalyst was separated by simple decantation of the reaction mixture leaving behind the catalyst in the flask. Fresh charge of benzene

was added to the same catalyst charge and nitric acid was added dropwise at 90 °C with azeotropic removal of water. The catalyst was recycled efficiently for four cycles with ~70% nitric acid conversion. Thus the hydrophobic catalyst B could be recycled efficiently for solvent less benzene nitration. The recovered nitric acid can be used in the next run of nitration if used for dilution of fuming nitric acid and can be the additional advantage of this catalytic reaction.

%
%
, 0
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Table 6:	Catalyst	recycle	study	for	benzene	nitration	using	catalyst B	
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Reaction conditions: 10 g catalyst, 90 °C, 8 h.

[#] Calculated from GC results using calibration, ^{\$} Calculated by titration of the aqueous phase, [€] Calculated based on nitrobenzene formed

4. Conclusions

Hydrophilic solid acid catalyst A was successfully modified using Dynasylan 9896 to increase the hydrophobic nature of the surface. The catalyst B showed better hydrophobicity without altering the acidity of the catalyst. The functionalization of surface silanol groups by alkyl silane decreased the surface area marginally. Significant improvement in *o*-xylene nitration with increase in the conversion from 68 to 80% was observed without alteration in selectivity for 3- and 4-nitro *o*-xylene. The catalyst could be recycled efficiently for benzene nitration without using additional solvent as benzene forms azeotrope with water at lower temperature thus enabling easy removal of water from the reaction system.

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