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Solventless triarylmethane synthesis via hydroxyalkylation of anisole with benzaldehyde by modified heteropoly acid on mesocellular foam silica (MCF)



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<i>Keywords:</i> Hydroxyalkylation Mesocellular foam silica (MCF) Heteropoly acid Anisole Cs _{2.5} H _{0.5} PW ₁₂ O ₄₀ Benzaldehyde	Triarylmethane (TRAM) compounds have wide applications such as leuco dyes for sensing tumors and other biological activities. Hydroxyalkylation of arenes with benzaldehyde results in formation of triarylmethane compounds. In the present study, 20 (wt.%) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs-DTP) supported on mesocellular foam (MCF) silica was prepared, characterized and tested for its activity in hydroxyalkylation reaction of anisole with benzaldehyde. Its activity was compared with commercial catalysts like Amberlyst-15, montmorillonite clay K-10, $H_3PW_{12}O_{40}$ and unsupported $Cs_{2.5}H_{0.5}PW_{12}O_{40}$. The prepared catalyst showed the best activity compared to others with advantage of separation of catalyst and reusability. Reaction parameters were studied in detail and kinetic study was carried out for the said reaction. 20 (wt. %) Cs-DTP/MCF was found to be the best, robust and reusable catalyst. Reaction mechanism and kinetics were also studied. The results are new

1. Introduction

Solventless reactions and use of heterogeneous catalysts are amongst the twelve important principles of green chemistry. Both principles improve the commercial feasibility of organic reactions. Friedel-Crafts alkylation and acylation are ubiquitous in a spectrum of industries and used, for instance, to make pharmaceuticals, fine chemicals and specialities [1,2]; however, a majority of these processes involves the use of AlCl₃, ZnCl₂ and H₂SO₄ types of homogeneous catalysts which are corrosive in nature and environmentally harmful [3,4]. Such processes involve tedious work up procedure to separate products from the reaction mass and beset with retention of deleterious impurities in the product. Heterogeneous catalysts are preferred to circumvent the demerits of homogeneous catalysts and thus newer costeffective, active and selective catalysts are needed.

Triarylmethanes (TRAM) are an important class of compounds. Different derivatives of TRAM have wide biological activities such as antimicrobial [5], antifungal [6] and antitubercular agents [7]. Amino derivatives of TRAM form a class of dyes which are used as leuco dyes for detection of tumors [8]. Various synthetic strategies have been pursued for synthesis of TRAM network which involves reaction of chloroform or triethylorthoformate with arenes [9], Pd catalyzed reaction of aryl halide with (aza aryl) methanes [10] and Friedel-Crafts hydroxylalkylation of arens with aromatic aldehydes using Lewis acid catalysts like AlCl₃ and BF₃-H₂O [11,12], and other metal based Lewis acid like AuCl₃/AgOTf [13], [Ir(COD)Cl]₂-SnCl₄ [14], FeCl₃/Ac₂O [15], and ZnBr₂/SiO₂ [16] have been reported. Molecular iodine [17] and *o*-benzenedisulfonimide [18] are also used for hydroxyalkylation. All of the foregoing processes involve use of non-reusable catalysts, harmful and voluminous solvents, and require longer reaction times.

Recently, Wang et al. [19] reported use of BAIL (Brønsted acid ionic liquids) to carry out hydroxyalkylation of electron rich arenes with aromatic aldehyde. Ionic liquid acts as a solvent as well as catalyst in these reactions and hence used in more quantity to achieve better conversion. However, reaction of moderately activated arenes like phenol and anisole with aldehydes requires longer time. Similarly, deep eutectic solvents have been also reported in synthesis of TRAM derivatives [20]. Hayden et al. [21] reported nafion–H catalysed continuous synthesis of TRAM using conventional as well as microwave heating.

Keggin anion based heteropoly acids (HPA) and their salts are proven effective catalysts to carry out a variety of organic reactions like alkylation, acylation, esterification, oligomerisation, etherification and many more [22]. Udayakumar et al. [23] have reported the use of dodecatungstophosphoric acid (DTP) and DTP supported on MCM-41 in TRAM synthesis in a solvent.. Hamidian et al. [24] used different types of HPA in ultrasonic condition with a solvent. Substantial solubility of heteropoly acids in common polar organic solvents and water is a major

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drawback. Hence any reaction in which the byproduct is water or alcohol type moieties, the catalyst gets dissolved in the reaction mass and hence it is difficult to separate from it. Alkali metal salts of HPA convert homogeneous HPA into heterogeneous catalyst. Amongst group I alkali metals, Cs salt of DTP particularly, Cs2.5H0.5PW12O40 was found better acid catalyst than DTP [25,26]. However, the problem encountered with Cs2.5H0.5PW12O40 (Cs-DTP) salt catalyst is separation from reaction mass because of ultrafine particle size [27]. Hence a technique was used to impregnate Cs-DTP catalyst on high surface area supports in our laboratory. Reports have shown successful impreganation of Cs_{2.5}H_{0.5}PW₁₂O₄₀ on mesoporous silicas like HMS [28], MCM-41 [29] and SBA-15 [30]. Nano-particles of Cs2.5H0.5PW12O40 generated into the porous matrix of acidic montmorillonite clav K-10 have been proved to be versatile catalysts for several industrially important reactions [31-36]. Mesocellular foam (MCF) is a modified version of SBA-15 with 3D ultracage spherical particles and higher pore volume than SBA-15 itself. This ultracage 3D spherical particles make MCF a good choice as a support for enzymes [37], metal oxide [38] and heteroply acid [39,40] catalysts as well.

In the present work, incipient wetness technique was adopted to prepare 20% (wt.%) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ supported on MCF which was characterized by different analytical techniques. As per our knowledge, there is no literature on the reported catalyst to be used in solventless hydroxyalkylation of anisole with benzaldehyde with a detailed kinetic study.

2. Experimental

2.1. Catalyst synthesis

The catalysts used in this study were prepared by methods developed by our laboratory.

2.1.1. Mesocellular foam silica (MCF) support and 20 (wt.%) $Cs_{2.5} H_{0.5} PW_{12} O_{40}/MCF$

MCF support and 20 (wt.%) $Cs_{2.5}H_{0.5}PW_{12}O_{40}/MCF$ (abbreviated as Cs-DTP/MCF) were prepared by the detailed procedure mentioned in our previous report [40].

2.1.2. Bulk Cs_{2.5}H_{0.5}PW₁₂O₄₀ (Cs-DTP)

Bulk Cs-DTP catalyst was prepared according to the procedure reported in literature [41]. 0.2808 g $(1.671 \times 10^{-3} \text{ mol})$ of CsCl was dissolved in 10 ml of 50% aq. methanol and added drop wise to 2 g $(6.688 \times 10^{-4} \text{ mol})$ of dodecatungstophosphoric acid (DTP) in 10 ml of methanol. With progress in addition of CsCl solution, a white precipitate of Cs_{2.5}H_{0.5}PW₁₂O₄₀ catalyst was formed. After complete addition, resulting mixture was stirred further for 1 h. Solvent was removed by heating in rotary evaporator. The dried catalyst was calcined at 300 °C for 3 h. This catalyst will be called bulk Cs-DTP henceforth.

2.2. Catalyst characterization techniques

Bruker D8 advances X-Ray diffractometer was used for determination of XRD patterns of prepared catalysts using Cu K α radiation ($\lambda = 0.1540562$ nm). Samples were step scanned from 5 to 80° in 0.045 steps with a stepping time of 0.5 s. Surface area, pore volume and pore size distribution were done by liquid nitrogen adsorption-desorption at 77 K on Micromeritics ASAP 2010. The analysis was carried out after preheating of sample at 300 °C for 4. Infrared spectra of the samples pressed in KBr pellets were obtained at a resolution of 2 cm⁻¹ between 4000 and 400 cm⁻¹. Spectra were collected with a Perkin-Elmer instrument and in each case the sample was referenced against a blank KBr pellet. The SEM images and elemental composition of MCF and 20% (wt%) CS-DTP on MCF were obtained on FEI quanta 200 instrument operated at 20 kV with a working distance of 2–10 mm. Dried samples were mounted on specimen studs and scanned at various magnifications using SEM. Acidity of catalyst samples determined by recording ammonia desorption thermograms on AutoChem II 2920 TPD/TPR instrument (Micromeritics, USA) by using 10% v/v NH₃ in He. Approximately 0.1 g of catalyst was loaded in the sample holder, heated to 573 K in helium, and subsequently cooled to 298 K. After being dosed with 10 % v/v ammonia in helium at a flow rate of 30 ml \min^{-1} for 30 min; the system was purged with helium for 1 h at the same temperature. The physisorbed ammonia was removed by passing helium gas at room temperature for 30 min. After cooling to 298 K, the temperature was raised to 1023 K at 20 K/min, and the outlet gases were analyzed by a thermal conductivity detector. TGA/DSC analysis was carried out on NETZSCH instrument (model STA 449 F3 Jupiter). Approximately, 5–10 mg sample quantity was used. TGA analysis was done under flow of nitrogen gas. Nitrogen flow of 50 ml/min was maintained during heating as well as cooling. Results were obtained with downward exotherm mode. Since catalyst is well characterized and discussed in our previous work [40] only a few results are discussed in the present study.

2.3. Reaction procedure and analysis

Experiments were conducted in a thermostatic oil bath containing a flat bottom glass reactor of 50 ml capacity provided with baffles and six bladed turbine impeller. In a typical experiment, 0.07 mol anisole, 0.014 mol benzaldehyde and 0.6 ml n-undecane as internal standard were charged in the reactor. Total volume of the reaction mixture was 9.6 ml Catalyst (0.048 g) was added (which corresponds to 0.005 g/ml of liquid volume) to the reaction mass which was maintained at 130 °C. In the case of 20 (wt.%) Cs-DTP/MCF, the weight corresponds to 20% active catalyst. The speed of agitation was maintained at 1000 rpm. At 403 K, a zero minute sample was withdrawn immediately after addition of catalyst and agitation started. Samples were then withdrawn periodically and analyzed b gas chromatography (Chemito 8610 GC) equipped with FID and 5% SE-30 packed column. Conversions were calculated on the basis of limiting reactant benzaldehyde (Supporting Information (SI), Figure S1 and S2). Confirmations of products were done by GC-MS (Figure S3). The major product, p,p'-isomer was isolated by column chromatography and its NMR analysis was done (Figure S4, S5)

3. Results and esults and discussion

3.1. Catalyst characterization

The catalysts were systematically characterized by different techniques and are described in detail in our previous report [40]. Only a few points related to surface area, acidity measurements and TGA/DSC analysis are discussed here.

3.1.1. Surface area

Cs-DTP is insoluble in water and solvents making it heterogeneous [41]. The adsorption of active Cs-DTP catalyst on surface of MCF support results in decrease in surface are and pore volume. The detailed comparison of surface area of MCF and 20% Cs-DTP/MCF is already discussed in our previous publication [40]. Here only nitrogen adsorption-desorption isotherm results are summarized in Table 1. MCF has large pore volume and high surface area. Decrease in the value of surface area and pore volume of MCF after impregnating Cs-DTP indicates proper distribution of active catalyst on silica surface.

3.1.2. Acidity measurement

Acidity of catalysts was measured by ammonia-TPD method (SI, Figure S6). MCF silica does not show any typical acidic behaviuor because of its neutral nature. Bulk $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ showed weak acidity peak at around 115 °C and strong acidity at higher temperature range. 20% (wt.%) $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ - MCF showed better acidity at lower as

Table 1

N2 adsorption-desorption textural analysis.

Catalyst	$S_{BET}^{[a]}(m^2/g)$	Pore volume ^[b] (cm ³ / g)	Pore size ^[c] (nm)
MCF	606.7	1.90	9.1
20% (w%/w%) Cs- DTP/MCF	534.7	1.32	7.7

[a] BET surface area [b] BJH desorption pore volume [c] BJH desorption avg. pore size.

Table 2

Ammonia-TPD results of catalysts.

Catalyst	NH_3 desorption temp. (°C)	NH3 desorbed (mmol/g)	Total NH3 desorbed (mmol/g)
MCF Bulk Cs-DTP 20 (wt.%) Cs- DTP/MCF	130.4 115.2, 643.1 102.8, 535.4	0.097 0.14, 0.16 0.23, 0.25	0.097 0.3 0.48

well as higher temperature range. The quantitative results are depicted in Table 2. The higher acidity of supported catalyst confirms proper distribution of acidic sites on support and is responsible for maintaining the catalytic activity in reaction.

3.1.3. SEM/EDXS and TEM

Surface morphology of catalysts was studied by using SEM and TEM techniques (Figure S7 in SI). Bulk Cs-DTP particles are smaller in size which can be observed in SEM image (a1) and as black dots in TEM image (a₂). This ultrafine size of Cs-DTP particles makes it inseparable from the reaction mass. Mesoporous MCF silica particles help in maintaining its activity as well as proper separation from the reaction mass and makes it a perfect heterogeneous catalyst. MCF particles are spherical in nature $(2-10 \,\mu\text{m})$ as shown in SEM image (b_1) . TEM image of MCF (b₂) shows strut like structure with uniform sized spherical cells. This strut like structure is a characteristic feature of MCF silica [42]. With impregnation of Cs-DTP on MCF, the strut is slightly affected as seen in TEM image (c2) of 20 (wt.%) Cs-DTP. The active catalyst species is observed as black dark spots. Being ultrafine size particles, Cs-DTP is seen as agglomerates in TEM image (c₂). SEM image (c₁) of 20 (wt.%) Cs-DTP on MCF does not show much distortion in the spherical shape of MCF particles. All these observations suggest that the 3D ultracage like spherical shape of MCF support after impregnation of the active acidic catalyst is maintained.

Energy dispersive X-ray (EDAX) spectroscopy results of 20 (wt.%) Cs-DTP-MCF catalyst for elemental compositions are shown in Table 3. Theoretical and observed values of each element are tabulated. Each element detected as a peak in EDX spectrum and its corresponding weight and atomic percentages were observed (Figure S3 in SI). Since EDX technique detects elements on surface of catalyst and hence percentage of oxygen (O) was found more than its expected value. Oxygen has high content in catalyst. However, content of caesium (Cs) and tungsten (W) was found similar to the expected one. Percentage of P found was slightly higher than theoretical value. Difference was

Table 3

Comparison of	elemental	composition.
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Elements	Theoretical weight % in 20 (wt. %) Cs-DTP-MCF	Observed weight % in 20(wt.%) Cs-DTP/MCF by EDXS
0	46.6	60.42
Si	37.4	23.85
Р	0.2	0.54
Cs	2.1	1.99
W	13.7	13.21



Fig. 1. (a). TGA/DSC comparison of DTP and Cs-DTP catalysts. (b). TGA comparison of MCF and 20 (wt.%) Cs-DTP/MCF. (c). DSC comparison of MCF and 20 (wt.%) Cs-DTP/MCF. (d). DSC comparison of bulk Cs-DTP and 20 (wt.%) Cs-DTP/MCF.



Fig. 2. Catalyst screening for conversion of benzaldehyde and selectivity to p, p' isomer. Reaction conditions: anisole (0.07 mol); benzaldehyde (0.014 mol), n-undecane (0.6 ml), total reaction volume (9.6 ml), catalyst (0.005 g/ml), temperature (403 K), speed of agitation (1000 rpm).

observed in the value of O and Si.

3.1.4. Thermo-gravimetric (TGA)/differential scanning calorimetry (DSC) analysis

TGA/DSC analysis was carried out to confirm thermal stability of prepared catalysts. Fig. 1 (a) represents TGA and DSC comparison of DTP and Cs-DTP catalysts. In the case of DTP, three stages of weight loss are observed. Choi et al. [43] studied thermal stability of DTP and bulk Cs-DTP in detail. During initial heating, at less than 300 °C, physically adsorbed water and water of crystallization is lost (first two stages of weight loss) because of which weight loss was observed [44]. These two weight losses in the case of DTP are endothermic processes which are shown by upward peak in Fig. 2(a) whereas at 600 °C, DTP decomposes in to corresponding metal oxide as per following reaction [44]. This decomposition is an exothermic process (downward peak).

$$H_3 P W_{12} O_{40} \rightarrow \frac{1}{2} P_2 O_5 + 12 W O_3 + \frac{3}{2} H_2 O_5$$

Bulk Cs-DTP shows only one endothermic peak near 373 K which corresponds to removal of physisorbed water molecule. Later on, weight decrease is almost nearly constant which proves that the addition of Cs imparts thermal stability to Keggin structure of DTP. Fig. 1(b) and (c) represents TGA and DSC comparison of MCF and 20% (wt.%) Cs-DTP/MCF. Both TGA and DSC trends of MCF support and Cs-DTP supported on MCF are comparable becasue there are no major changes observed. Furthermore, the DSC trends of bulk Cs-DTP and supported Cs-DTP are also comparable (Fig. 1(d)). These comparisons prove that the thermal stability of bulk Cs-DTP is maintained after supporting it on MCF.

3.2. Optimization of reaction parameters

3.2.1. Catalyst screening

Hydroxyalkylation of anisole with benzaldehyde was carried out in solventless condition (Scheme 1). Different catalysts were screened for hydroxyalkylation (Fig. 2). Commercial catalysts Amberlyst-15 and montmorillonite clay- K10 gave 24% and 8% conversion of benzaldehyde respectively. Althogh Amberlyst-15 is highly active Brønsted acidic catalyst still the conversion was found very low which may be

due to low surface area of Amberlyst-15 and less available catalytic sites. Dodecatungstophosphoric acid (DTP) gave the highest conversion of benzaldehyde (\sim 87%) with \sim 88% selectivity of *p*,*p*'- triarylmethane isomer.

DTP contains 3 replaceable acidic protons which impart high catalytic activity but on the contrary, DTP shows solubility in polar solvents as well as leaches in reaction which was observed in this reaction as well. DTP acts as a homogeneous catalyst because during the course of reaction water is formed as co-product and DTP has solubility in water and hence it behaves as homogeneous catalyst. DTP was not selected for further studies because of its homogeneous nature in the reaction system. Unsupported and supported Cs-DTP catalysts were compared on equal loading of active catalyst used in the reaction. Bulk Cs-DTP and 20 (wt.%) Cs-DTP/MCF gave almost similar conversions, namely, 65% and 64.5% respectively. Selectivity to p,p'- triarylmethane isomer was also found similar in both the cases (85% with bulk Cs-DTP and 85.2% with 20 (wt.%) Cs-DTP/MCF. Since almost equal conversions and selectivity to desired product are obtained with both the catalysts, it would mean that all active Cs-DTP particles are well supported on MCF and available for reaction. Cs-DTP particles are occluded in MCF porous matrix and hence there is no intra-particle diffusion and no leaching of the active catalyst whereas unsupported Cs-DTP catalyst has very small particle size (SI, Fig. S2 SEM and TEM) and thus is difficult to separate it from the reaction mixture. Hence further reaction parameters were optimized with 20% (wt.%) Cs-DTP/MCF catalyst.

3.2.2. Effect of speed of agitation

Effect of agitation speed was studied between 800 and 1200 rpm (SI, Figure S5) keeping other reaction parameters unchanged as in section 3.2.1. At 800 rpm, benzaldehyde conversion was 54.7% whereas at 1000 and 1200 rpm, the final conversions were found practically the same during the course of reaction (~64%) thereby suggesting the mass transfer resistance was eliminated. Hence further parameter optimizations were carried out at 1000 rpm.

3.2.3. Effect of catalyst loading

The catalyst loading studies were carried out between 0.005 and 0.015 g/ml. At low catalyst loading of 0.005 g/ml, the final conversion was \sim 65% in 180 min. Further increase in catalyst loading to 0.01 g/mL, conversion of benzaldehyde reached to 82% and 100% conversion was achieved with catalyst loading of 0.015 g/ml in 180 min (Fig. 3). From these results, it can be concluded that increased catalyst loading helps in providing more acidic sites and increase the rate of reaction.

To understand the exact effect of catalyst loading, initial reaction rates were plotted against catalyst loading (Fig. 4). Initial reaction rate increased linearly with catalyst loading which proves that the increase in catalyst loading increases the number of catalytic active sites proportionately which in turn increases the rate of reaction. Also there is no mass transfer resistance and intra-particle diffusion resistance. Theoretical calculations for external mass of transfer resistance and intra-particle diffusion resistance (Weisz-Prater modulus < < 1) were also performed to validate these results according our earlier work [45,46].

3.2.4. Effect of mole ratio

Mole ratio studies were carried out between 3:1 and 5:1 (anisole:benzaldehyde). Catalyst loading were kept constant (i.e. 0.015 g/mL) in all experiments. With low mole ratio of 3:1, conversion was ~84% in 180 min (Fig. 5). With increase in mol ratio to 4:1 and 5:1, the conversion was found 100% in both the cases. The selectivity of products was found nearly the same in all cases (~84% for *p*,*p*'- isomer). Hence for temperature studies, 4:1 mol ratio was selected.

3.2.5. Effect of temperature

Effect of temperature is very important to provide further proof of intrinsic kinetic rate equation. Hence under all optimized reaction



o,o'- product (minor)

Scheme 1. Hydroxyalkylation of anisole with benzaldehyde.



Fig. 3. Effect of catalyst loading on conversion of benzaldehyde. Reaction conditions: anisole (0.07 mol); benzaldehyde (0.014 mol), *n*-undecane (0.6 ml), total reaction volume (9.6 ml), temperature (403 K), speed of agitation (1000 rpm).



Fig. 4. Initial reaction rate vs. catalyst loading.



Fig. 5. Effect of mole ratio on conversion of benzaldehyde. Reaction conditions: anisole: benzaldehyde (mole ratio 3:1, 4:1 and 5:1), n-undecane (0.6 mL), catalyst loading (0.015 g/mL), temperature (403 K), speed of agitation (1000 rpm).

parameters, reaction was tested at different temperatures. At 373 K, the final conversion was 78% (Fig. 6). With further 10 K rise in temperature, final conversion reached to ~97%. Complete conversion of benzaldehyde was observed in case of 393 K and 403 K. Selectivity of products was almost nearly same in all cases (~ 84% for p,p' isomer). Hence optimum temperature for the said reaction was selected as 393 K.

3.2.6. Catalyst stability and reusability study

To confirm heterogeneous nature of catalyst, a leaching test was carried out. Reaction was carried out at 4:1 mol ratio of anisole: benzaldehyde, catalyst loading 0.015 g/ml and speed of agitation 1000 rpm and temperature 403 K. The experiment was conducted first 30 min and a sample withdrawn for analysis. The conversion was found as 34.2%. Thereafter the reactor was removed from oil bath and the reaction mass filtered to remove catalyst. It was placed again in the bath. The liquid reaction mass without the catalyst was further stirred at 403 K at 1000 rpm, and sampling was done at 60, 120 and 180 min and analysed. There was no major increase in the conversion even after 180 min



Fig. 6. Effect of temperature on conversion of benzaldehyde. Reaction conditions: anisole (0.07 mol), benzaldehyde (0.0175 mol), *n*-undecane (0.6 ml), total reaction volume (9.9 ml), catalyst loading (0.015 g/mL), speed of agitation (1000 rpm).



Fig. 7. Catalyst stability study.

(35.9%). Thus, within experimental results it is concluded that the catalyst is stable and heterogeneous (Fig. 7).

The robustness of catalyst in terms of activity and selectivity was studied by the reusability test. The reaction was carried out under optimal conditions of mole ratio of anisole: benzaldehyde, (4:1), speed of agitation (1000 rpm), catalyst loading (0.015 g/ml) and temperature (393 K) for 180 min. After the reaction was over, the catalyst was filtered and separated from reaction mass. The separated catalyst was taken in cyclohexane and refluxed for 3 h to remove any adsorbed or trapped reactants and products from its surface and pore space. It was filtered, dried and weighed. There was some loss during filtration (\sim 4-5%) due to attrition of catalyst which was made up in the next experiment with fresh one keeping the same reaction conditions. There was a marginal loss in activity (Fig. 8) thereby proving heterogeneous nature of catalyst and its reusability.

The third reused catalyst was characterised and compared with the freshly prepared. FTIR comparison (Fig. 9) showed no specific change in IR bands in finger print region (400-1400 cm⁻¹).

However, a slight variation was found in surface area and acidity of reused catalyst which could be due to some occlusion of product in some junctions of porous network which could be removed by solvent at reflux. Comparison of fresh and reused catalyst is shown in Table 4.



Fig. 8. Reusability of catalyst. Reaction conditions: anisole (0.07 mol), benzaldehyde (0.0175 mol), *n*-undecane (0.6 ml), total reaction volume (9.9 ml), catalyst loading (0.015 g/ml), temperature (403 K), speed of agitation



Fig. 9. FTIR comparison of fresh 20 (wt.%) Cs-DTP/MCF and reused catalyst after reaction.

Table 4	ł
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(1000 rpm).

Comparison	of fresh	and re	eused	catalyst.	
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Catalyst	Surface area (m ² /g)	Total acidity (mmol/g)
Fresh Catalyst	534.7	0.48
After 3 rd reuse	518.4	0.37

3.2.7. Substrate study as extension of catalyst application

Different arenes as well as aldehydes were tested under the similar reaction conditions in order to understand the effect of each of them. Table 5 shows effect on conversion and selectivity based on different substrates.

During substrate study, phenol (entry 1) being activated arene gave 100% conversion when reacted with benzaldehyde but with addition of methyl group at *para* position it reduced the conversion to 89% (entry 2). This observation indicates that presence of methyl group does not activate an arene up to a considerable extent. The difference in reactivity of phenol and *p*-cresol was also observed by Wang et al [19] while using ionic liquid as a catalyst. Veratrole (entry 3) with two methoxy groups at ortho position to each other gave 100% conversion which supports the activating effect of methoxy group. When anisole

Table 5

Extension of catalyst	: 20 (wt.%)	CsDTP-MCF	to other	arenes	and	aldehydes.
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Entry	Arenes	Aldehydes	Products (% GC Selectivity)		% (GC) Conversion
1	OH	H + O	HO	ОН	100
2	OH	H + C	(99.8) (99.8) ОН (99.6)	(0.2) Он но	89
3	̰ − o	H + C	(73.4)		100
4)°-	H OH	(99.4) (83)		30
5	\sim			(17)	52
			(87)	(13)	

Reaction conditions: Arene: aldehyde, 4:1, catalyst 0.015 g/mL, temperature 403 K, n-undecane 0.6 ml, time 3 h. Conversion and selectivity calculated by GC results.

reacted with different aldehydes, namely, salicylaldehyde (entry 4) and p- methoxy benzaldehyde (entry 5) low conversions were obtained, namely, 30% and 52%. These observations conclude that aromatic aldehydes with electron donating groups reduce conversion. Similar results are obtained by Wang et al. [19] while using BAIL (Brønsted acid ionic liquids).

4. Reaction mechanism and kinetic model

4.1. Reaction mechanism

A probable reaction mechanism is shown in Scheme 2, where the first step is adsorption of reactants on the catalyst surface followed by surface reaction in the second step. Finally products are desorbed from the surface of catalyst in the third step and the cycle continues.

4.2. Kinetic modeling

A variety of models have been discussed [45,46] for solid-liquid catalytic reaction including adsorption, surface reaction and desorption. As explained earlier, in the absence of both external mass transfer and intra-particle resistances, the Langmuir-Hinshelwood-Hougen-Watson (LHHW) model was tested. According to LHHW mechanism, adsorption of A (anisole) and B (benzaldehyde) takes place on two adjacent vacant sites of surfaces (S) and surface reaction between

both the species occurs resulting in formation of p,p^{-1} isomer (C) and o,o^{-1} isomer (D). The complete derivation of the model is given in supplementary information (Eqs. (25) and (26)).

When $C_{A_0} > > C_{B_0}$ or M > > 1, the final equation is as follows:

$$\frac{-dC_B}{dt} = k_1 C_B w \tag{1}$$

In terms of fractional conversion, it becomes a pseudo-first order equation to get the following integrated form:

$$-\ln(1 - X_B) = k_1 wt \tag{2}$$

Hence a plot of $\ln(1-X_B)$ vs. time t would be a straight line with slope equal to k_1w from which the rate constant k_1 could be evaluated. Moreover, the linearity of this plot would confirm the pseudo first order behavior of the reaction.

It was found that equation fitted that data very well. Fig. 10 shows the validity of this theory at different temperatures.

From the slopes of lines in Fig. 10, the rate constants, k_1 at different temperatures were calculated.

$$k_1 (100 \,^{\circ}\text{C}) = 0.01 \,^{-1}$$

 $k_1 (110 \,^{\circ}\text{C}) = 0.0144 \,^{-1}$
 $k_1 (120 \,^{\circ}\text{C}) = 0.01666 \,^{-1}$
 $k_1 (130 \,^{\circ}\text{C}) = 0.0355 \,^{-1}$



Scheme 2. Mechanism of hydroxyalkylation of anisole.



Fig. 10. Pseudo first order kinetic plot at different temperatures.



From, Arrhenius plot (Fig. 11), apparent activation energy was calculated and found to be 11.74 kcal/mol.

In the absence of both external mass transfer resistance and intraparticle diffusion limitation, and adsorption and desorption resistance, intrinsic kinetics should control and hence effect of temperature will be pronounced on initial rate of reaction which is confirmed by activation energy values (> 8 kcal/mol) [28,45–47]. In the current work, Arrhenius plot was made to get the apparent energy of activation as 11.74 kcal/mol to prove that the reaction was intrinsically kinetically controlled.

5. Conclusion

Solventless hydroxyalkylation of anisole was studied in detail with several catalysts including commercial ones. 20 (wt.%) Cs-DTP supported on MCF silica was the best catalyst. The MCF supported Cs-DTP showed better catalytic activity than commercial catalysts like Amberlyst-15 and montmorillonite clay K-10 and equivalent activity to the bulk Cs-DTP catalyst with the advantage of easy recovery from the reaction mass. The catalyst is thermally stable and reusable. The optimum temperature was 120 °C and 100% conversion was obtained with 84% selectivity to the *p*, *p*' - triarylmethaane isomer. The LHHW mechanism was used to determine the mechanism and kinetics of the reaction. All species were found to be weakly adsorbed thereby leading to a pseudo-first rate equation. Overall reaction is intrinsically kinetically controlled and follows second order rate equation. The apparent activation energy was found to 11.74 kcal/mol. The process is green.

Conflict of interest statement

The authors declare no conflict of interest.

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Appendix A. Supplementary data

Supplementary material related to this article can be found, in the online version, at doi:https://doi.org/10.1016/j.mcat.2018.06.003.

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