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A novel route synthesis of alkanes from glycerol in two step process using Pd/SBA-15 catalyst

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Glycerol is produced as a valuable by-product in transesterification of fatty acids but it cannot be used directly as a fuel additive. In this study, we have developed a systematic conversion with glycerol, which proceeds via synthesizing the key intermediate, 1,2,3-tribromopropane and Suzuki coupling reaction is utilized to introduce alkyl group. A series of Pd/SBA-15 catalyst with different wt% of Pd ranging from 10, 15 and 20 % was prepared by one step sol-gel method. The structure and composition of the catalysts were characterized with X-ray diffraction analysis (XRD), N_2 adsorption-desorption isotherm, transmission electron microscope (TEM) and inductively coupled plasma optical emission spectrometry (ICP-OES). Metallic state of dispersed palladium in SBA-15 is confirmed with X-ray photoelectron spectroscopy (XPS). Pd/SBA-15 with a Pd loading of 20 wt% expose good catalytic activity at 90 ^{o}C with methylboronic acid, allowing a complete conversion of 1,2,3-tribromopropane and a 64 % selectivity of 3-methylpentane. The optimized catalysts were also carried out in coupling reaction between various alkylhalides and methylboronic acid, which gave the desired product with excellent selectivity. The catalyst can be successfully recycled for five times. After the first cycle we observed a drop in activity with 20% Pd/SBA-15 which was due to leaching of palladium but in later cycles there was no significant decrease in activity.

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1. Introduction

Biodiesel production from vegetable oils is increasing rapidly, hence glycerol is formed as a major by-product in this process.[1] Around 4.53 kg of crude glycerol is produced as a by-product in every 45.3 kg of biodiesel synthesis.[2,3] It is a triol containing three hydroxyl group, which is a very important chemical compound for various applications. One mole of glycerol is produced per mole of triglyceride feed[4] in the transesterification of vegetable oil. Cost of glycerol is expected to diminish significantly from the actual cost as the biodiesel production increases.[5] Value added products such as hydrogen, syngas or liquid chemicals may be produced from glycerol if the financial supports for biodiesel production are improved. Biodiesel production increases which results in accumulation of glycerol in the market and also the prices of glycerol may fall to 50 %.[6] Conversion of glycerol to value added chemicals by heterogeneous catalyst is not new, acrolein and other oxygenated chemicals are produced from glycerol in an autoclave reactor using Pd/Fe_2O_3 and Ru-Cu/bentonitecatalysts.[7,8] Yuming Li *et al* used Pd/SBA-15 in glycerol hydrogenolysis to obtain 1,2-propanediol,[9] additives to fuel were synthesized by actualization of glycerol with butanol over zeolites.[10] Aqueous-phase reforming of glycerol in the presence of hydrogen over Pt/H-ZSM-5 catalyst has been carried out for propane formation.[11] Catalytic conversion of glycerol to liquid alkanes with Fischer-Tropsch synthesis in a two-bed reactor system using Pt-Re/C and Ru/TiO_2catalysts was reported by James A.Dumesic and co-workers.[12] Conversion of glycerol to hydrocarbons has been proven feasible in limited number of literatures and also further research has to be carried out for the enhancement in this area was concluded by Nor AishahSaidina Amin*et al*.[13]

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Over the past decade palladium catalyst has attracted much deliberation for c-c bond formation.[14-16] Suzuki coupling has been implemented using palladium complexes with various ligands under homogeneous condition, but this will bring the problem of separating the catalyst from the reaction mixture, recycling of catalyst and also product contamination.[17,18] Hence it is necessary to develop a heterogeneous catalysts to overcome the problem faced in homogeneous palladium catalysts. Palladium nanoparticles are anchored on various supports such as mesoporous silica, alumina, zeolites, organic polymer and dendrimers but heterogeneous systems are easy to handle, recover and are “green” processes.[19] Anna and co-workers synthesized palladium nanoparticles supported on alumina-based oxides by sol-gel method but the surface area of the support was fewer and the recycle of the catalyst were not reported. Palladium nanoparticles supported on functionalized polymers for the Suzuki reaction was carried out by many research groups and they acquired high efficiency of homogeneous catalysts but they observed little obstacles such as reusability and leaching of metal from the support.[20,21] Palladium nanoparticles encapsulated inside the dendrimers was carried out in Suzuki reaction by El-Sayed and co-workers, they obtained a good yield with desired products but the strong encapsulation of palladium nanoparticles resulted in the loss of catalytic activity[22] and also to the formation of palladium black. Mesoporous catalysts is used as a solid support because of its wide accessibility, excellent stability, porosity and inert environment for the immobilization of transition-metal nanoparticles[23] and the catalyst can be recycled by filtration. Numerous methods are there to anchor palladium nanoparticles in mesoporous silica such as ion exchange, wetness impregnation, chemical vapour infiltration, in-situ reduction and so on. Gao and co-workers have reported a simple one-step method to synthesize palladium nanoparticles in SBA-15 by sol-gel

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method, prepared catalyst which has a pore size in the range of 5-10 nm, a large specific area and a highly ordered pore structure.[24]

So many researches have been carried out for the production of liquid alkanes from glycerol as mentioned above, but all of these processes have some drawbacks such as high energy consumption to break the carbon-carbon bonds. To the best of our knowledge, no literature has been reported on the production of liquid alkane from glycerol at lower temperature. However, in the present work, we propose an alternative approach to augment the carbon chains by converting glycerol to alkane and also to explore the activation of Pd/SBA-15 catalysts in Suzuki coupling reaction with 1,2,3-tribromopropane intermediate and methylboronic acid for the synthesis of 3-methylpentane.

2. Experimental

2.1Reagents and Materials

Pd/SBA-15 was synthesized using tetraethylorthosilicate (TEOS, Sigma Aldrich, 99%) as a silica source and poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol) triblock copolymer (EO_{70} PO_{20} EO_{70}, Pluronic P123, M_{av}= 5800, Sigma Aldrich) as a structure directing agent, Palladium (II) Chloride ($PdCl_2$, Sigma Aldrich, 99%) as a palladium precursor. Methylboronic acid (97%), phosphorous tribromide (99%), cyclohexanol (99%), 4-methyl-2-pentanol (98%), glycerol (99%), cyclopentanol (99%), 2-Pentanol (98%) and potassium tert-butoxide (99%) were purchased from Sigma-Aldrich Company. K_3PO_4 and Na_2CO_3 were purchased from Thomas Baker, India. Solvents like 1,4-dioxane, DMF and DMSO were purchased from Merck Millipore.

2.2 Characterization techniques

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X-ray diffraction (XRD) patterns were measured using Bruker D8 diffractometer with Cu K_α radiation to identify the phase purity of the catalyst and the Bragg's angle (2θ) scanning from 0.5˚ to 5˚ for low angle and 10˚ to 90˚ for wide angle XRD. The surface area, pore volume and pore diameter were measured from N_2 adsorption-desorption isotherms (Micromeritics ASAP-2020) carried out in liquid N_2 temperature. Before taking the measurement, the surface of the sample was cleaned by evacuation to low pressure of the order of 10^{-3} torr and temperature of about 200 °C for 3 h. The pore size distributions were calculated from the nitrogen adsorption-desorption isotherm, using the Barret-Joyner-Hallenda (BJH) algorithm (ASAP-2020 built-in software from Micromeritics). Transmission electron microscope (TEM) was performed on Philips CM12. The oxidation state of metal present in the samples was determined by using X-ray photoelectron spectroscopy (Omicron Nanotechnology). The metal content of palladium in terms of palladium percentage was determined by ICP-OES Perkin Elmer Optima 5300DV instrument, the catalysts were assimilated with 0.5 ml HF and then make up to 25 ml of distilled water with wavelength of 340.458 nm for Pd was used. GCMS analysis was conducted on Perkin Elmer, Clarus 500 equipped with FID detector. ^1H and ^{13}C NMR was recorded on Bruker 400 MHz and 100 MHz spectrometer respectively.

2.3 General procedure for synthesis of Pd/SBA-15

Pd/SBA-15 was prepared as reported in the literature.[24,25] 1.5 g of P123 was added to 11.5 ml of deionized water and stirred for 2 h at room temperature. 24 g of 2 M HCl was added drop wise and different weight percentage of $PdCl_2$ (10, 15, 20 wt%) was added at 40 ˚C under stirring for 4 h, then 3.5 g of TEOS was added at once. The mixture was once again stirred for 24 hat 40 ˚C, and it was transferred into Teflon lined autoclave and aged at 100 ˚C for 48 h. The obtained solid was filtered off, rinsed with deionized water and then dried at 100 ˚C for 12 h. The

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pulverized sample was calcined at 550 ˚C for 6 h. The compositions of the three samples were labeled as 10% Pd/SBA-15, 15% Pd/SBA-15 and 20% Pd/SBA-15. Then, the labeled samples were reduced under H_2 atmosphere at 100 ˚C for 1 h.

2.4 General procedure for alkylbromide reaction

Alcohol (2 g, 1.0 equiv.) was added to a 50 ml round bottomed flask and cooled to 0 ^{o}C, after being stirred for 10 min. Phosphorous tribromide (see Table 1 for amount and equiv.) was added drop wise over a period of 1 h. The reaction mixture was slowly warmed at room temperature, the mixture was further heated at 60 ^{o}C with stirring for 1 h and the crude was purified by preparative reverse-phase HPLC using Atlantis dC18 column coupled with evaporative light scattering detector (ELSD). The product was confirmed with GCMS, ^{1}H NMR and ^{13}C NMR spectroscopy.

1,2,3-tribromopropane (Table 1, entry 1). Selectivity (61 %), pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 3.86 (4H, d, CH_2), 3.98-4.04 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 34.76, 45.71.

2-bromo-4-methylpentane (Table 1, entry 2). Selectivity (70 %), pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.04 (6H, d, CH_3), 1.14-1.23 (3H, m), 2.23 (3H, d, CH_3), 4.05-4.27 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 25.78, 28.26, 35.73, 48.31, 55.73.

Bromocyclohexane (Table 1, entry 3). Selectivity (75 %), pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.13-1.58 (6H, m, CH_2), 1.74-2.24 (4H, m, CH_2), 3.79-3.85 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 24.01, 25.55, 37.90, 53.50.

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Bromocyclopentane (Table 1, entry 4). Selectivity (74 %), pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 1.54-1.74 (4H, m, CH_2), 1.81-2.17 (4H, m, CH_2), 3.75-3.83 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 25.16, 36.44, 55.21.

2-bromopentane (Table 1, entry 5). Selectivity (70 %), pale yellow liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.95-1.22 (3H, m, CH_3), 1.22-1.50 (4H, m, CH_2), 1.63-1.84 (3H, m, CH_3), 3.62-3.71 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 14.03, 26.81, 43.10, 51.20.

2.5 General procedure for Suzuki coupling reaction

The 20 ml sealed tube reactor was charged with alkylhalide (1 g, 1.0 equiv.), 1,4-dioxane (10 ml), KOt-Bu (3 equiv.) and methylboronic acid (see Table 2 for amount and equiv.), degassed for few minutes. 20% Pd/SBA-15 (0.025 mol% Pd) was added and again degassed for few minutes. The resulting mixture was heated at 90 ˚C with stirring for 3 h, the mixture was cooled down to room temperature, and the catalyst was removed by filtration. Ethyl acetate (4x10 ml) and water were added to the reaction mixture and stirred well for few minutes. The organic layer was dried over Na_2SO_4 and the product was isolated after distillation and confirmed with GCMS, ^{1}H NMR and ^{13}C NMR spectroscopy.

3-methylpentane (Table2, entry 1). Selectivity (64 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.61-0.87 (9H, m, CH_3), 0.99 (4H, m, CH_2), 1.06-1.09 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 11.26, 20.82, 28.99, 36.30 (Supplementary information; Fig. S1).

2,4-dimethylpentane (Table 2, entry 2). Selectivity (86 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.86 (12H, d, CH_3), 1.13-1.19 (2H, m, CH_2), 1.24-1.50 (2H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 25.35, 27.13, 50.24 (Supplementary information; Fig. S2).

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Methylcyclohexane (Table 2, entry 3). Selectivity (93 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.85 (3H, d, CH_3), 1.07-1.69 (10H, m, CH_2); ^{13}C NMR (100 MHz, $CDCl_3$): 23.31, 26.45, 27.11, 32.74, 35.44 (Supplementary information; Fig. S3).

Methylcyclopentane (Table 2, entry 4). Selectivity (85 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.96 (3H, d, CH_3), 1.52-1.81 (8H, m, CH_2), 1.68-1.80 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 20.13, 25.02, 35.33 (Supplementary information; Fig. S4).

2-methylpentane (Table 2, entry 5). Selectivity (84 %), colorless liquid. ^{1}H NMR (400 MHz, $CDCl_3$): 0.57-0.61 (9H, t, CH_3), 0.82-0.89 (4H, m, CH_2), 0.97-0.99 (1H, m, CH); ^{13}C NMR (100 MHz, $CDCl_3$): 15.01, 20.74, 23.82, 27.75, 42.70 (Supplementary information; Fig. S5).

3. Results and discussion

3.1 Characterization of Pd/SBA-15

Nitrogen adsorption-desorption isotherm of SBA-15 and Pd/ SBA-15 are shown in Fig. 1. The textural parameters of the samples are summarized in Table 3. Isotherm of all the catalysts depict an ordered mesoporous nature, type IV isotherm with sharp hysteresis loops observed at relative pressure $p/p_o = 0.6$ to 0.8 corresponds to capillary condensation of N_2 and also which indicate well defined cylindrical narrow pore size distribution inserted in Fig. 1. BET surface area, BJH pore size and pore volumes of bare SBA-15 are 658 m^2/g, 5.2 nm and 0.71 cm^3/g respectively. Palladium was introduced in SBA-15. The gradual decrease in surface area, pore size and pore volume are observed which suggests that the palladium nanoparticles are dispersed and incorporated into the pore channels of SBA-15[26] and also the metal is anchored successfully without disintegrating the structure. The palladium percentage in SBA-15 derived from ICP-OES is tabulated in Table 3, and the results show that palladium loading decreases from 7.13 wt% to

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16.85 wt% for 10% Pd/SBA-15 and 20% Pd/SBA-15 which is less than the expected palladium loading i.e. 10, 15 and 20 wt%. These results suggest that Pd precursor does not deposit completely into the silica matrix.

The crystalline nature and ordered hexagonal mesostructures of parent SBA-15 and Pd/SBA-15 were determined by XRD, exhibit the three well resolved diffraction peaks in Fig. 2. One intense peak in the range of 0.9-0.95° and two weak peaks in the range of 1.5-1.6° corresponds to (100), (110) and (200) planes respectively. These peaks are the characteristic patterns of SBA-15, in good correlation with the reported prototype of plain SBA-15.[27] Therefore, the retention of ordered hexagonal mesostructure of SBA-15 was maintained. Palladium loading increases, there is a gradual decrease in the intensity of d_{100}, d_{110} and d_{200} peaks, this indicating the incorporation and blocking of pores channels in SBA-15 with palladium crystallites. In addition, diffraction peaks shifted to a higher 2θ values which might be due to constriction of framework, similar to the results previously reported in the literature.[28] The wide angle XRD patterns of SBA-15 and Pd/SBA-15 showed a typical broad diffraction peak at about 22.64° corresponds to amorphous silica was shown in Fig. 3. The four diffraction peaks at 2θ= 40.08°, 46.62°, 68.08° and 82.14° correspond to the diffraction of (111), (200), (220) and (311) planes that are assigned to face-centered cubic patterns of crystalline palladium and also it reveals that the palladium species remains as metallic state.[29] The average crystalline size distribution of 10%, 15% and 20% of Pd/SBA-15 can be calculated based on Debye-Scherer equation and the crystalline size of the samples which are found to be approximately 7.4, 9.4 and 11.9 nm respectively.

TEM images of bare SBA-15 and 20% Pd/SBA-15 samples are illustrated in Fig. 4a, b and c respectively. A very narrow distribution of palladium particles was observed on the

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support and the highly ordered mesoporous structure was preserved in 20% Pd/SBA-15, which was consistent with the results of XRD and N_2 adsorption-desorption isotherm. The average pore diameter of SBA-15 precursor is about 6.5 nm. The crystalline palladium was not found on the external surface in Fig. 4c. These findings show that the palladium nanoparticles are dispersed uniformly inside the pore channels of SBA-15 with an average particle size of about 5 nm.

A typical XPS elemental survey scan of 20% Pd/SBA-15 is depicted in Fig. 5. Palladium was detected as a minor peak around 335 eV and the other peaks corresponding to silicon and oxygen were observed as an intense peak. The peaks around 104, 155 and 535 eV are assigned to Si2p, Si2s and O1s respectively.[31] XPS spectrum of 20% Pd/SBA-15 is shown in Fig. 6. The peaks at 335 eV and 340 eV were attributed to Pd $3d_{5/2}$ and Pd $3d_{3/2}$ respectively. Binding energy values of Pd $3d_{5/2}$ and Pd $3d_{3/2}$ ascribed to metallic Pd, suggest that the prepared 20% Pd/SBA-15 catalyst exhibits good catalytic activity in C-C bond formation. This result is in accordance with XRD observation.[32,33]

3.2 Impact of various parameters in Suzuki coupling reaction

Suzuki coupling reaction of 1,2,3-tribromopropane with methylboronic acid was chosen as a model reaction to find out the catalytic activity of (10, 15 and 20 wt%) Pd/SBA-15. Conversion obtained over different catalyst are presented in Fig. 7a and the order of activity is 20% Pd/SBA-15> 15% Pd/SBA-15> 10% Pd/SBA-15. It is noted that the selectivity increases with high Pd loading, reaches maximum at 3 h and also attain complete conversion of 1,2,3-tribromopropane with a TON of 2560 was achieved. For comparison, 10% Pd/SBA-15 and 15% Pd/SBA-15 were also tested under similar experimental condition but only 34-70 % of 1,2,3-tribromopropane is consumed with low TON of 760 and 1640 respectively. In contrast with the

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results of previous studies 20% Pd/SBA-15 catalyst provides high TON,[24,34] it is suggest that even though the palladium content is high in 20% Pd/SBA-15 the metal is dispersed uniformly over the support and possess higher activity.[35] Besides, the activity of catalysts with different palladium loading was further examined for the Suzuki coupling reaction of various alkyl bromides and methylboronic acid. The details are summarized in Table 2.

We have attempted a series of experiments with different temperature, bases and solvents in Suzuki coupling reaction between 1,2,3-tribromopropane and methylboronic acid (3.5 equiv.) using 20% Pd/SBA-15 catalyst. TON value calculated for different experimental run is presented in Table 4. To study the influence of temperature to achieve a reasonable reaction rate, the reaction was carried out at room temperature and 60 ^{o}C (Fig. 7b). 1,2,3-tribromopropane conversion is initially low but increases rapidly beyond 60 ^{o}C and complete conversion is attained at 90 ^{o}C. At lower temperature, presence of other compounds like 1-bromo-2-methylbutane (BMB) and 1,2-dibromobutane (DBB) are high but decrease significantly at 90 ^{o}C. The major product of the reaction is 3-methylpentane (MP) at the end of 3 h, however reasonable amount of BMB and DBB is also present in the reaction mixture suggesting the reaction might be proceed in the sequence 1,2,3-tribromopropane ⟶ 1,2-dibromobutane (DBB) ⟶ 1-bromo-2-methylbutane (BMB) ⟶ 3-methylpentane (MP).

The reaction was investigated with different solvents like 1,4-dioxane, DMF and DMSO, the choice of solvents made a significant impact on c-c bond formation.[36, 37] Among the solvents examined 1,4-dioxane was the most efficient with complete conversion of 1,2,3-tribromopropane for the formation of alkyl-alkyl Suzuki coupling reaction, DMSO and DMF exhibit 39-79 % conversion of 1,2,3-tribromopropane and also gave the desired product in slightly less selectivity (Fig. 7c).

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The main role of base in Suzuki reaction is to increase the reactivity of boronic acid towards the Pd-halide complex.[38] To study the effect of bases, the reaction was explored with different bases such as Na_2CO_3, K_3PO_4 and KOt-Bu. As shown in Fig. 7d, KOt-Bu gave complete conversion of 1,2,3-tribromopropane while examining the other two bases, the conversion being 7-50 % for Na_2CO_3 and K_3PO_4 respectively; however, previous studies in alkyl-alkyl Suzuki coupling reaction showed that KOt-Bu favor the reactivity of alkylhalide and alkylboronic acid.[39]

The recyclability and stability of the 20% Pd/SBA-15 catalyst was investigated with 1,2,3-tribromopropane and methylboronic acid, the catalyst gave 64 % selectivity for the fresh catalyst. Recyclability was checked by recovering the catalyst after the reaction by filtration, washed with water and acetone, dried at 100 °C for 12 h. The selectivity was diminished to 60 % in the first cycle which was due to the loss of palladium in to the reaction medium. The recovered 20% Pd/SBA-15 catalyst was analyzed by ICP-OES for Pd content and the results confirmed that 15.20 wt% of Pd is present and the catalyst was reused up to 5 cycles. In later cycles, there is no significant loss of palladium is noticed thus signifying the stability of the catalyst up on recycle (Fig. 8).

Hot filtration test[40] was performed to check the heterogeneity of 20% Pd/SBA-15 catalyst in 1,2,3-tribromopropane and methylboronic acid (Fig. 9). For this purpose, the catalyst was removed by filtration from the reaction mixture after 30 minutes in a hot condition and the mixture was left to react for 5 h. At 30 minutes of run the selectivity of the product is 5 % and furthers the selectivity decreasing when compared with 20% Pd/SBA-15 catalytic run. But after 5 h the product selectivity is raised only up to8 %, this might be due to Pd leaching which is confirmed from ICP-OES. Whereas with the catalytic run the selectivity of the product is found

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to increase. These verdicts indicate that the reaction is proceeding truly with heterogeneous catalyst.

4. Conclusions

The current work reports the successful synthesis of 3-methylpentane from glycerol at lower temperature. In the first step 1,2,3-tribromopropane is prepared from glycerol with PBr_3at 60 ^{o}C followed by Suzuki reaction to install alkyl group. We have also synthesized three different wt% of Pd/SBA-15 by sol-gel method, and the activity of the catalyst is investigated individually in the second step for Suzuki coupling reaction with 1,2,3-tribromopropane and methylboronic acid. The resulting 20% Pd/SBA-15 acts as a highly efficient, low palladium leaching catalyst and also provides 64 % product selectivity at 90 ˚C for 3 h. The reusability of the catalyst carried out for 20% Pd/SBA-15 exhibits a better recycling effect and stability for fifth cycle. In this process, we have developed a new methodology for the production of liquid alkanes; it has major advantages over the other reported literatures such as low temperature employed in the reaction. In this work, we prominently utilize the by-product of glycerol and also it provides an alternative route for the production of fuel additives in a "green" manner.

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DOI: 10.1039/C5RA10744J

References

1. M. Ayoub and A.Z. Abdullah, Renew. Sust. Energy Rev., 2012, **16**, 2671.

2. Ma Fangrui and M.A. Hanna, Bioresour. Technol., 1999, **70**, 1.

3. A. Corma, G.W. Huber, L. Sauvanaud and P. O'Connor, J. Catal., 2008, **257**, 163.

4. G.W. Huber, S. Iborra, and A. Corma, Chem. Rev., 2006, **106**, 4044.

5. M. Mc Coy, Chem. Eng. News, 2005, **83**, 19.

6. K. Pathak, K. M. Reddy, N.N. Bakhshi and A.K. Dalai, ApplCatal. A 2010, **372**, 224.

7. M. Musolino, L. Scarpino, F. Mauriello and R. Pietropaolo, Green Chem., 2009, **11**, 1511.

8. T. Jiang, Y. Zhou, S. Liang, H. Liu and B. Han, Green Chem., 2009, **11**, 1000.

9. Y. Li, H. Liu, L Ma and D He, RSC Adv., 2014, **4**, 5503.

10. H. Serafim, I.M. Fonseca, A.M. Ramos, J. Vital and J.E. Castanheiro, Chem. Eng. J., 2011, **178**, 291.

11. K. Murata, I. Takahara and M. Inaba, React. Kinet.Catal.Lett., 2008, **93**, 59.

12. D. A. Simonetti, J. Rass-Hansen, E.L. Kunkes, R.R. Soares and J.A. Dumesic, Green Chem., 2007, **9**, 1029.

13. Z.Y. Zakaria, N.A. Saidina Amin and J. Linnekoski, Biomass Bioenergy, 2013, **55**, 370.

14. I.P. Beletskaya and A.V. Cheprakov, Coord. Chem. Rev., 2004, **248**, 2337.

15. W.A. Herrmann, V.P.W. Bohm, C.P. Reisinger and J. Organomet.Chem., 1999, **576**, 23.

View Article Online
DOI: 10.1039/C5RA10744J

16. M. Albrecht and G.V. Koten, Angew. Chem. Int. Ed., 2001, **40**, 3750.

17. K.M. Clapham, A.S. Batsanov, M.R. Bryce and B. Tarbit, Org. Biomol. Chem., 2009, **7**, 2155.

18. K.B. Lee, S.M. Lee, and J. Cheon, Adv. Mater., 2001, **13**, 517,

19. H. Yang, X. Han, Zhancheng Ma, R. Wang, J. Liu and X. Ji, Green Chem., 2010, **12**, 441.

20. A. Fihri, M. Bouhrara, B. Nekoueishahraki, J.M. Basset and V. Polshettiwar, Chem. Soc. Rev., 2011, **40**, 5181

21. A. Gniewek, J.J. Ziolkowski, Anna M. Trzeciak, M. Zawadzki, H. Grabowska and J. Wrzyszcz, J. Catal., 2008, **254**, 121.

22. Y. Li and M.A. El-Sayed, J. Phys. Chem., B 2001, **105**, 8938.

23. D.E. De Vos, M. Dams, B.F. Sels, and P.A. Jacobs, Chem. Rev., 2002, **102,** 3615.

24. P. Han, X. Wang, X. Qui, X. Ji and L. Gao, J. Mol. Catal. A: Chem., 2007, **272**, 136.

25. D. Zhao, Q. Huo, J. Feng, B.F. Chmelka, and G.D. Stucky, J. Am. Chem. Soc., 1998, **120**, 6024.

26. P. Wang and X. Zheng, Powder Technol., 2011, **210**, 115.

27. J. Jarupatrakorn and T.D. Tilley, J. Am. Chem. Soc., 2002, **124**, 8380.

28. F. Zhang, Y. Yan, H. Yang, Y. Meng, C. Yu, B. Tu and D. Zhao, J. Phys. Chem., B 2005, **109**, 8723.

29. H. Wang and C.J. Liu, Appl. Catal. B 2011, **106**, 672.

View Article Online
DOI: 10.1039/C5RA10744J

30. J. Zhi, D. Song, Z. Li, X. Lei and A. Hu, Chem. Commun., 2011, **47**, 10707.

31. K. Belkacemi and S. Hamoudi, Ind. Eng. Chem. Res., 2010, **49**, 6878.

32. T.L. Barr, J. Phys. Chem., 1978, **82**, 1801.

33. Y. Li and B.W.L. Jang, Appl. Catal. A 2011, **392**, 173.

34. K. Karami and N.H. Naeini, Appl. Organometal. Chem., 2015, **29**, 33.

35. J.W. Sun, Y.S. Fu, G.Y. He, X.Q. Sun and X. Wang, Catal.Sci. Technol., 2014, **4**, 1742.

36. E. Alza, L. Laraia, B.M. Ibbeson, S. Collins, W.R. J. D. Galloway, J.E. Stokes, A.R. Venkitaraman and D.R. Spring,Chem. Sci., 2015, **6**, 390.

37. B. Saito and G.C. Fu, J. Am. Chem. Soc., 2007, **129**, 9602.

38. C.F.R.A.C. Lima, A.S.M.C. Rodrigues, V.L.M. Silva, A.M.S. Silva, and L.M.N.B.F. Santos, Chem. Cat. Chem., 2014, **6**, 1291.

39. Z. Lu and G.C. Fu, Angew. Chem. Int. Ed., 2010, **49**, 6676.

40. V. Udayakumar and A. Pandurangan, J. Porous. Mater., 2014, **21**, 921.

41. J.H. Kirchhoff, M.R. Netherton, I.D. Hills and G.C. Fu, J. Am. Chem. Soc., 2002, **124**, 13662.

42. J.Terao, Y. Naitoh, H. Kuniyasu and N. Kambe, Chem. Lett., 2003, **32**, 890.

43. J. Zhou and G. C. Fu, J. Am. Chem., Soc., 2004, **126**, 1340.

View Article Online
DOI: 10.1039/C5RA10744J

44. Y. Yagi, H. Kimura, K. Arimitsu, M. Ono, K. Maeda, H. Kusuhara, T. Kajimoto, Y. Sugiyama and H. Saji, Org. Biomol. Chem., 2015, **13**, 1113.

45. J. Sun, Y. Fu, G. He, X. Sun and X. Wang, Appl. Catal. B 2015, **165**, 661.

46. M. Eckhardt and G.C. Fu, J. Am. Chem. Soc., 2003, **125**, 13642.

47. A. Bahl, W. Grahn, S. Stadler, F. Feiner, G. Bourhill, C. Brauchle, A. Reisner and P.G. Jones, Angew. Chem. Int. Ed., 1995, **34**, 1485.

48. M. R. Netherton and G. C. Fu, Angew. Chem. Int. Ed., 2002, **114**, 4066.

49. M. R. Netherton, C. Dai, K. Neuschutz and G. C. Fu, J. Am. Chem. Soc., 2001, **123**, 10099.

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DOI: 10.1039/C5RA10744J

Table captions

1. Alkyl bromide reaction of various alcohols with phosphorous tribromide[a]

2. Suzuki coupling reaction of various alkyl bromide with methylboronic acid catalyzed by Pd/SBA-15[a]

3. BET analysis of SBA-15-Palladium catalyst and its metal content.

4. Turn over number value for different experimental run.

Figure captions

1. Nitrogen adsorption-desorption isotherms and pore size distribution of Palladium loaded SBA-15 catalysts.

2. Low angle X-ray diffraction patterns of calcined Palladium loaded SBA-15 catalysts.
(a) SBA-15; (b) 10% Pd/SBA-15; (c) 15% Pd/SBA-15; (d) 20% Pd/SBA-15

3. Wide angle X-ray diffraction patterns of calcined Palladium loaded SBA-15 catalysts.
(a) 20% Pd/SBA-15; (b) 15% Pd/SBA-15; (c) 10% Pd/SBA-15; (d) SBA-15

4. TEM images of SBA-15 (a) and 20 % Pd/SBA-15 (b and c).

5. Elemental survey scan XPS spectrum of 20 % Pd/SBA-15.

6. XPS spectrum of 20 % Pd/SBA-15.

7. Influence of various parameters in Suzuki coupling reaction of 1,2,3-tribromopropane with methylboronic acid catalyzed by 20 wt% Pd/SBA15.

8. Recyclability of 20% Pd/SBA-15 in 1,2,3-tribromopropane with methylboronic acid
(Reaction conditions: Temperature - 90 ^{o}C; 20 % Pd/SBA-15 (0.025 mol); KOt-Bu (3 equivalent); reaction time - 3 h; solvent- 1,4-dioxane)

9. Hot filtration test.

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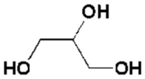
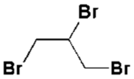
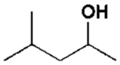
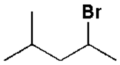
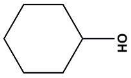
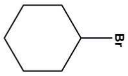
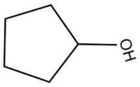
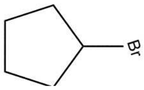
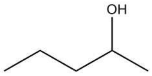
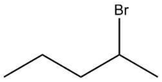
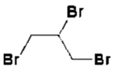
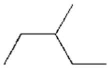
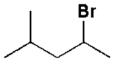
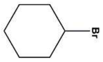
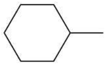
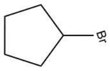
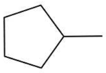
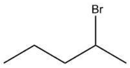
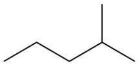
Table 1

Entry	Compound	PBr_3 (molar equiv)	Product	Time (h)	Product selectivity (%)[b]
1		0.5		1	61
2		0.12		1	70
3		0.12		1	75
4		0.12		1	74
5		0.12		1	70

[a] Reaction conditions: For entry 1, Glycerol (2 g, 1.0 equiv.), phosphorous tribromide (2.13 g, 0.5 euiv.), Temperature = 0-60 °C, Time = 1 h. For entries 2-3, Substrate (2 g, 1.0 equiv.), phosphorous tribromide (0.73 g, 0.12 euiv.), Temperature = 0-60 °C; Time = 1 h.
[b] Determined by GCMS.

Table 2

Entry	Compound	Product	10% Pd/SBA-15 (0.012 mol% Pd)		15% Pd/SBA-15 (0.018 mol% Pd)		20% Pd/SBA-15 (0.025 mol% Pd)	
			Product Selectivity (%)^b	TON^c	Product Selectivity (%)^b	TON^c	Product Selectivity (%)^b	TON^c
1			19	1583	41	2277	64	2560
2			23	1916	53	2944	86	3440
3			25	2083	56	3111	93	3720
4			22	1833	51	2833	85	3400
5			20	1666	49	2722	84	3360

Reaction conditions: For entry 1, 1,2,3-tribromopropane (1 g, 1.0 equiv.), methylboronic acid (0.94 g, 3.5 equiv.), KOt-Bu (3 equivalent), 1,4-dioxane (10 ml) Temperature - 90 °C, Time- 3 h. For entries 2-5, Substrate (1 g, 1.0 equiv.), methylboronic acid (0.5 g, 1.5 equiv.), KOt-Bu (3 equivalent), 1,4-dioxane (10 ml) Temperature - 90 °C, Time- 3 h.

[b] Determined by GCMS.

[c] TON= mmol of products/mmol of Pd.

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Table 3

Entry	**Catalysts**	**BET surface area (m^2/g)**	**Pore size BJH_{Ads} (nm)**	**Pore volume BJH_{Ads} (cc/g)**	**Pd loading[a] (wt %)**
1	SBA-15	658	5.3	0.71	-
2	10 % Pd/SBA-15	614	5.0	0.69	7.13
3	15 % Pd/SBA-15	572	4.9	0.65	11.92
4	20 % Pd/SBA-15	513	4.8	0.61	16.85

[a] Determined by ICP-OES measurements.

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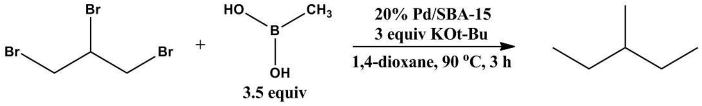
Table 4



"Optimized" conditions

Entry	Deviation from "optimized" conditions	Pd (mol%)	Product selectivity (%) [a]	TON[b]	Ref.
1	None	0.025	64	2560	[37,39,41]
2	room temperature	0.025	10	400	[41,42]
3	60 °C	0.025	36	1440	[43]
4	D.MS.O	0.025	21	840	[44,45]
5	D.M.F	0.025	42	1680	[45,46]
6	Na_2CO_3	0.025	4	160	[47,48]
7	K_3PO_4	0.025	19	760	[49]

[a] Determined by GCMS.
[b] TON= mmol of products/mmol of Pd.

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Fig. 1

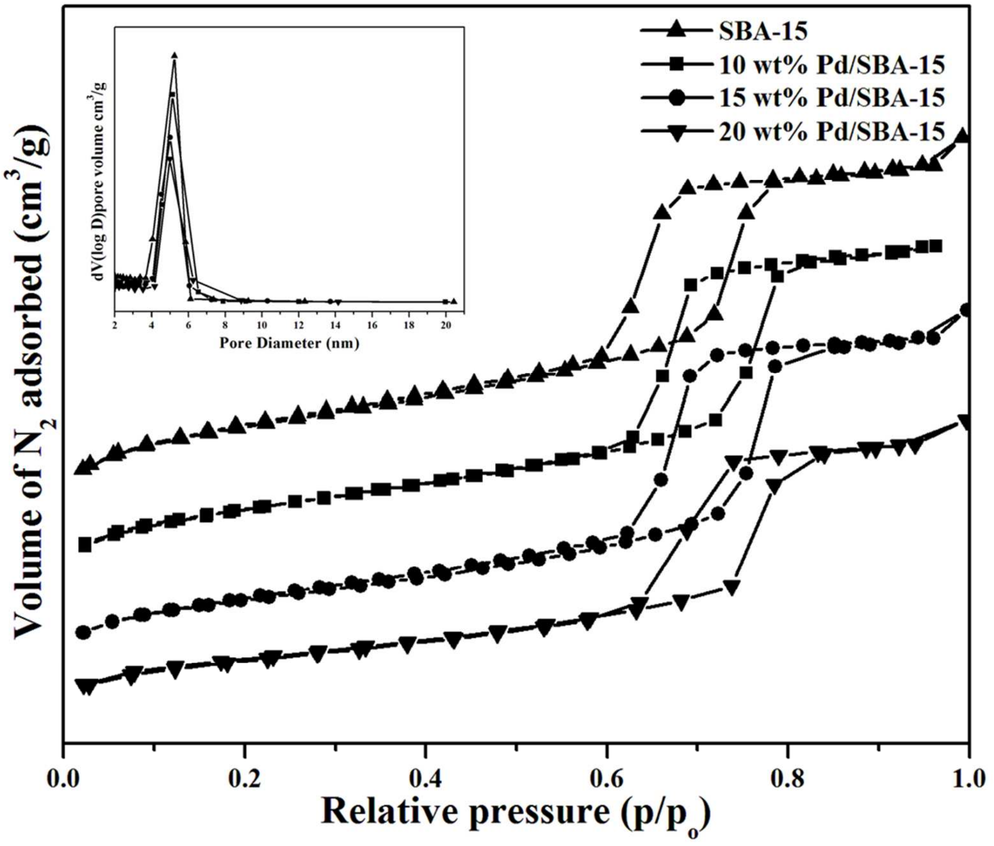

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Fig. 2

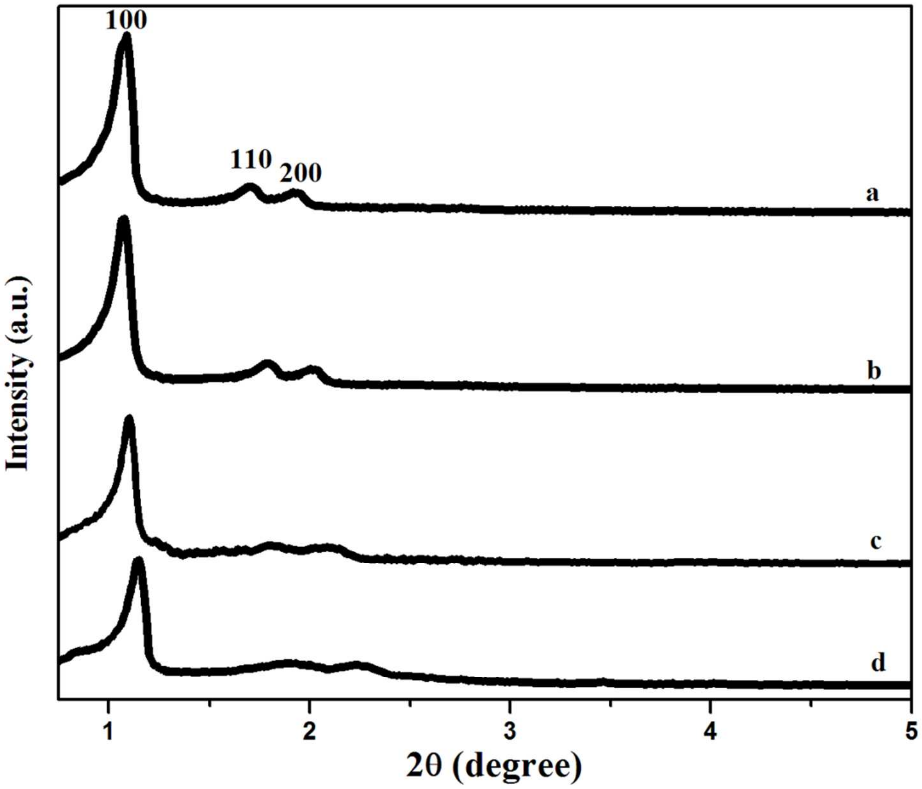

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Fig. 3

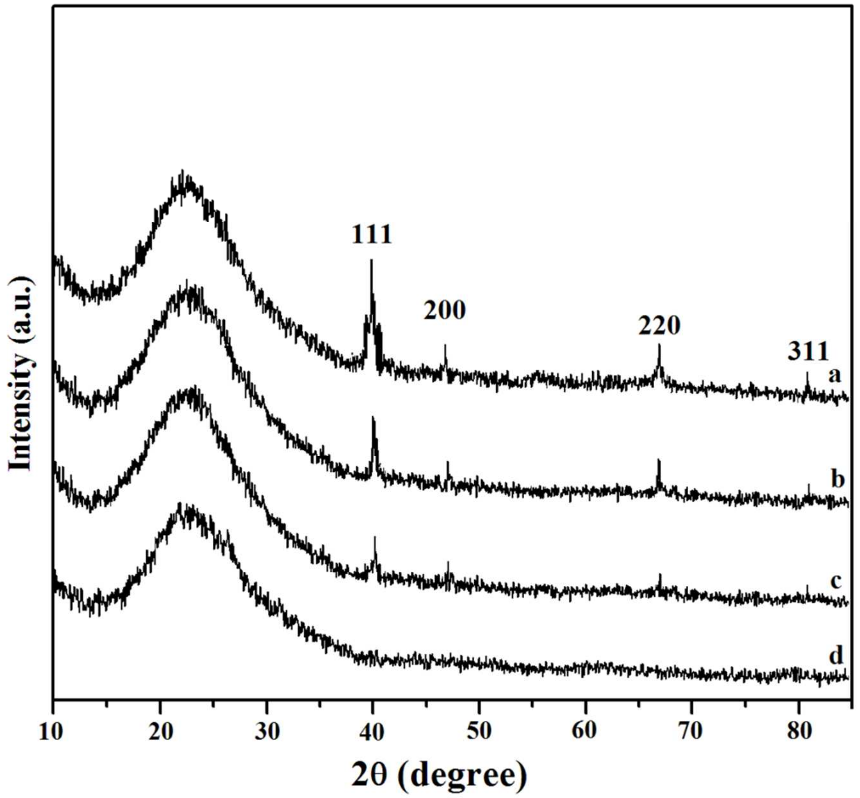

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Fig. 4

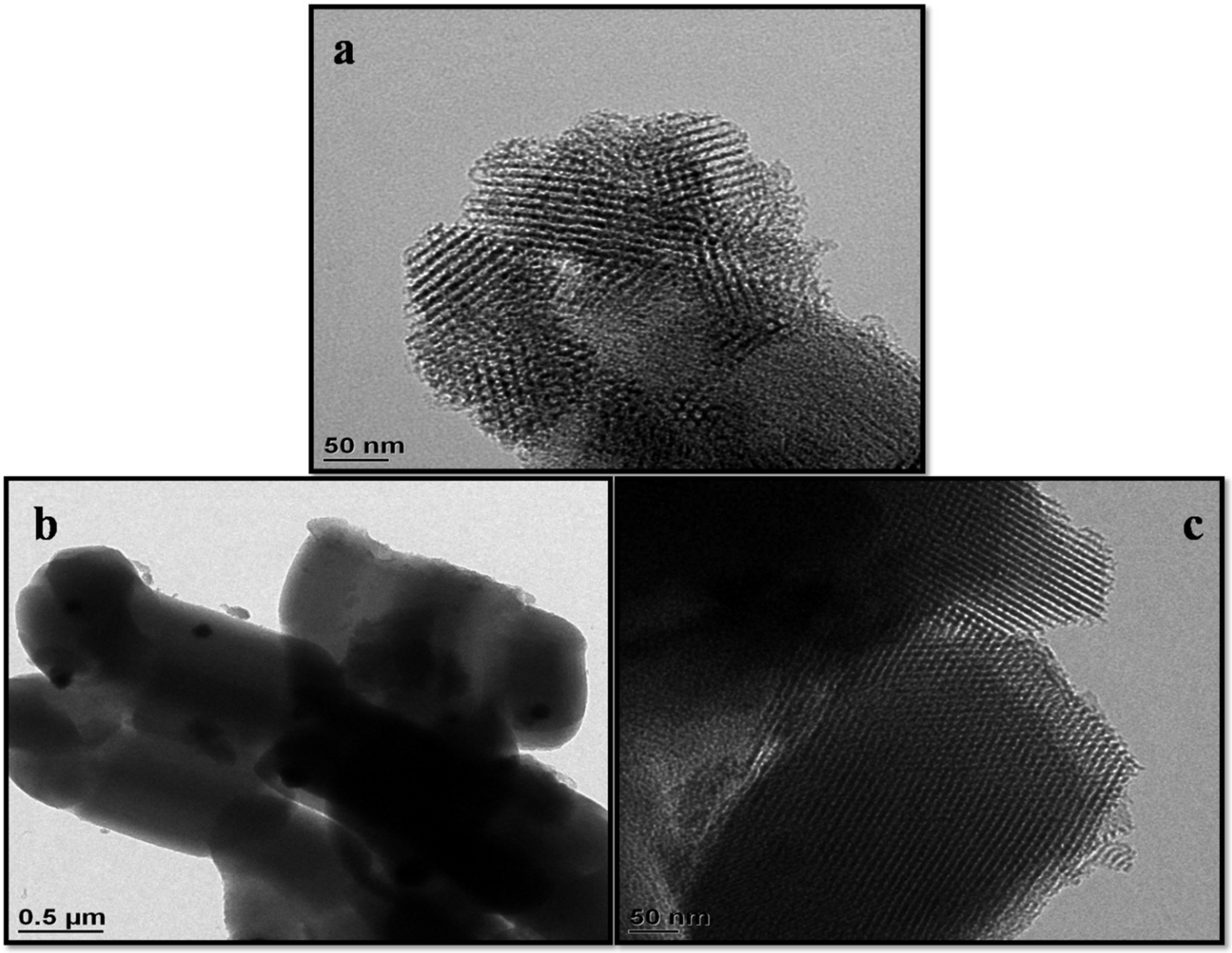

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Fig. 5

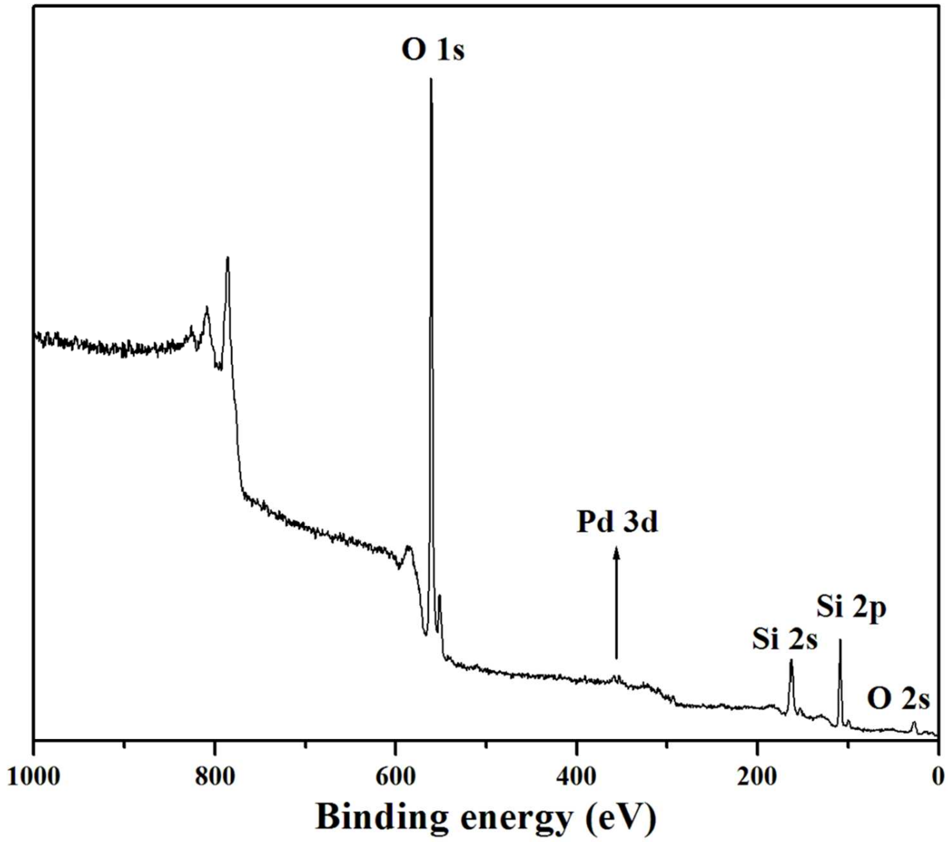

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Fig. 6

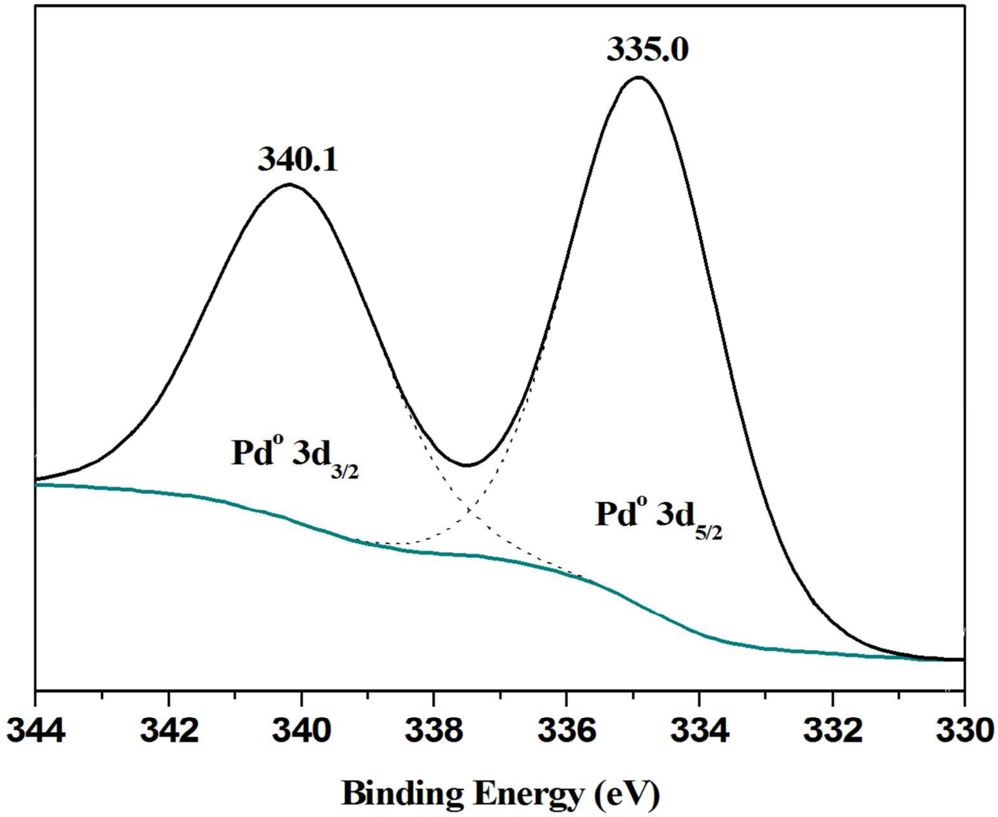

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Fig. 7

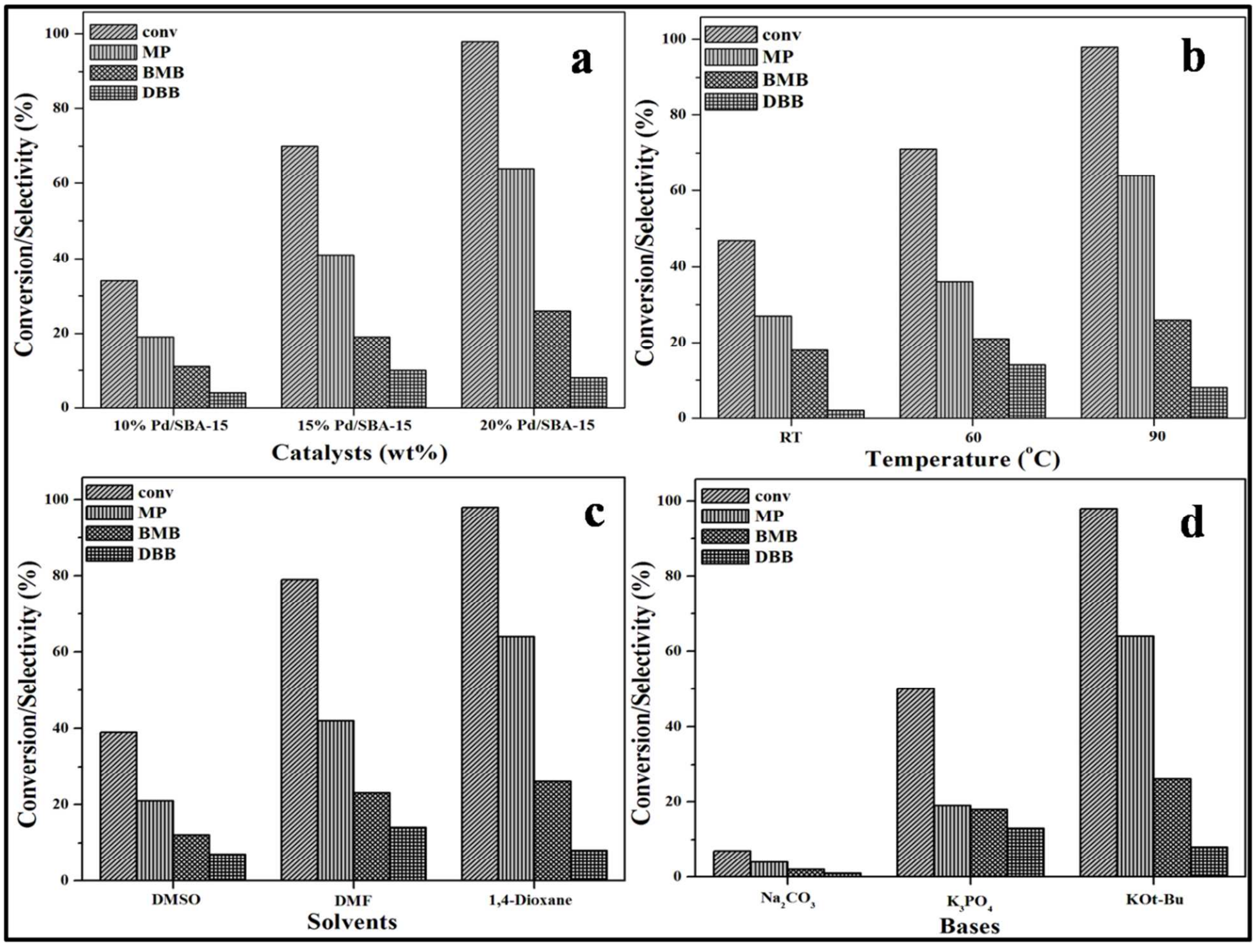

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Fig. 8

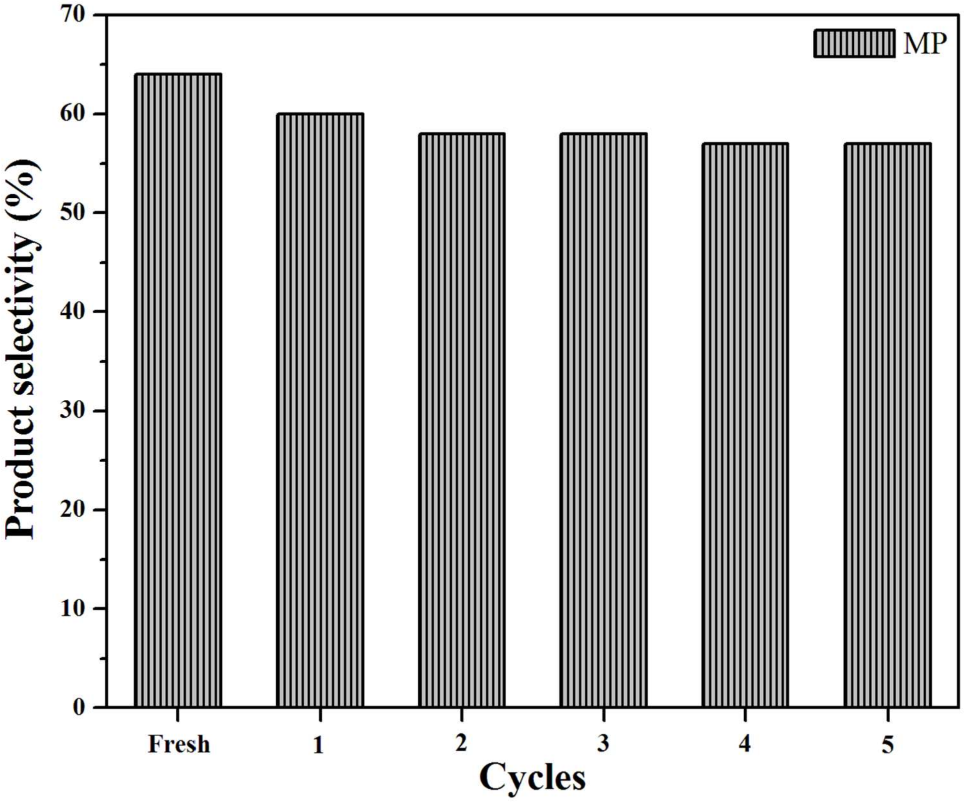

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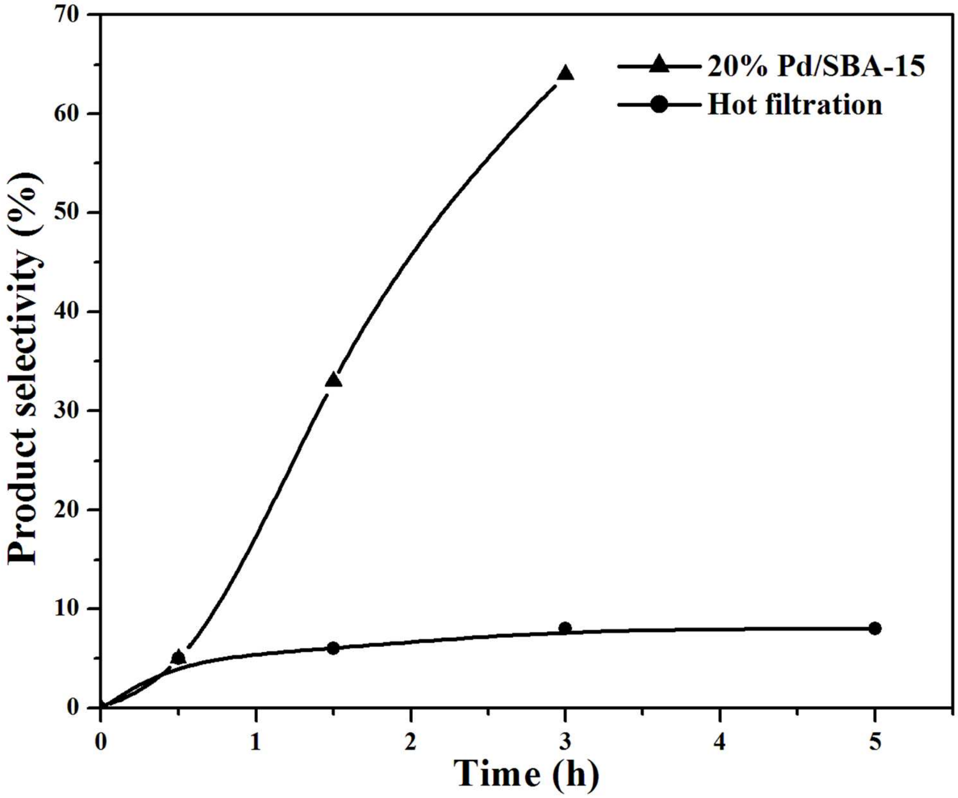
Fig. 9



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Graphical Abstract