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Alkylation of *O*-xylene and Styrene Catalyzed by Cross-linked

Poly Acidic Ionic Liquids Catalyst with Novel

Mesoporous-macroporous Structure

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GRAPHICAL ABSTRACT
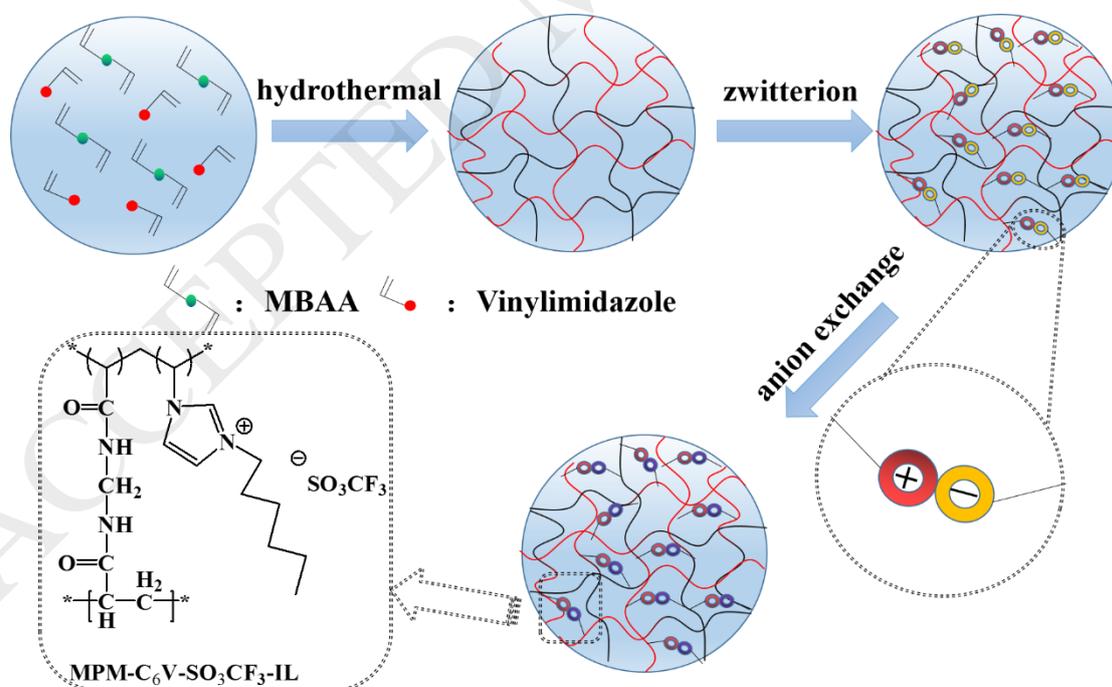
HIGHLIGHTS

- Cross-linked poly acidic ionic liquids have been synthesized in different solvents.
- Utilization in the alkylation of *o*-xylene and styrene for the first time.
- Obtained catalyst with mesoporous and macroporous network structure.

Abstract

Cross-linked poly acidic ionic liquids (MPM-C$_6$V-SO$_3$CF$_3$-IL) with mesoporous and macroporous network structure have been synthesized in different solvents. The novel solid acid catalyst with special network structure has a large surface area (103.83 m^2/g), large pore volume (0.72 cm^3/g) and abundant mesopores and macropores, which help to improve the contact between active site and reactants. Catalytic performance of catalyst was investigated through alkylation of *o*-xylene and styrene. Different reaction parameters specifically solvent on obtained catalyst and production of PXE were systematically investigated. Under optimal reaction conditions (reaction time was 3 h, reaction temperature was 120 °C, catalyst amount was 0.17 g (0.5 wt%), and *o*-xylene/styrene mass ratio was 7.5:1), a high conversion of styrene (100 %) and 1,2-diphenylethane (PXE) yield of 99.67 % was obtained, which is superior to commercial acid in liquid and even previous acids synthesized by our own group. Moreover, catalyst could keep relatively high thermostability under reaction and are easy to be separated and recycled from the solution, which are critical for heterogeneous solid catalysts. Thus, this novel catalyst can be potentially applied in other acidic reactions.

Keywords: Poly acidic ionic liquids; catalyst; mesoporous–macroporous structure; alkylation; cross-linked polymer

1. **Introduction**

As an industrially important Friedel–Crafts (FC) reaction, the alkylation of *o*-xylene with styrene has been extensively studied and reviewed for many years. Nowadays, Phenylxylylethane (PXE) has been widely used in various areas, *e.g.*, the pressure-sensitive record materials, a heating medium, an electric-insulating oil and so on. PXE is generally produced through–homogeneous Brønsted, Lewis or compound acid catalysts, such as H_2SO_4, HF, $AlCl_3$ and $FeCl_3$ [1, 2]. However, the aforementioned traditional acids are generally high cost and corrosion, low active performance, selectivity and recyclability. Therefore, the environmental friendly heterogeneous solid catalysts are highly desirable to optimize catalytic technology. Sun et. al. demonstrated that binary mixtures [BMIM]Br-$AlCl_3$ can be used as catalyst for the alkylation of o-xylene and styrene，with good separation and regeneration, but it generated a large portion of byproduct BPXE during the reaction [3]. Zhao et. al. investigated alkylations of 2-methylnaphthalene with long-chain alkenes catalyzed by ethyl-containing amine chloroaluminate ionic liquids modified with HCl [4]. Cao et. al. explored the alkylation mechanism of *o*-xylene with styrene, using DFT method in $AlCl_3$-ionic liquid catalytic system. The reactive energy catalyzed by superelectrophilic $AlCl^{2+}$ (12.6 kcal/mol) was distinctly lower than $AlCl_3$ (43.0 kcal/mol), which was considered as the ratedetermining step in long-chain styrene with *o*-xylene [5]. These explorations concentrated on the catalysis of $AlCl_3$-ionic liquid, which $AlCl_3$ molar ratio was a key factor for deciding catalysis activity in above.

Up to date, solid acid materials has been widely utilized in various reactions such like esterification [6], Beckmann rearrangements [7], Friedel-Crafts reaction [8],

transesterification [9]. Numerous solid acids can be prepared facilely, including, zeolites, heteropolyacids (HPAs), metal oxides, sulfonated carbon materials and ion-exchanged resins [10]. Among which, HPAs, exemplified with Keggin structured phosphotungstic acid (H_3PW), have exhibited excellent performance in different kinds of acid-catalyzed reactions due to their superior acidity, versatile composition and structure [11]. Moreover, the strategy of combing zeolite and H_3PW has been demonstrated as an efficient method to synthesize high active catalyst [12]. The replacement of homogeneous liquid catalysts by heterogeneous solid catalysts has received wide attention in the synthesis of green or sustainable chemistry [13-15]. In particular, ionic liquids (ILs) supported on porous materials and polystyrene-based polymers are efficient catalysts with excellent recyclability for the production of fine chemicals [9, 16]. Specifically, these kinds of catalysts with exposed active sites, synthesized by the introduction of cross-linking agent, show a relatively higher catalytic activity than normal heterogeneous IL catalysts.

As an immerging group of smart ionic liquids, poly (ionic liquids) (PILs) or ionic liquid (IL) polymers not only present attractive mechanical characteristics of polymers, but also retain the superior physicochemical properties of ionic liquids [17]. Such as, the unique physicochemical properties of negligible vapor pressure, fine physical and chemical stability, specifically, low volatility, non-flammability, high thermal stability, high ionic conductivity and wide electrochemical potential window [18-20]. Li and co-workers had synthesized sulfonic group tethered mesoporous poly (ionic liquid) Poly(DVB-VMPS) for catalyzing deoximation reactions with improved activity and enhanced stability [21]. Yan *et. al.* had prepared a lot of excellent functional materials

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based poly(ionic liquid)s, which shown superior performances in electronic devices [22, 23]. Poly (Ionic Liquid) as an brilliant new class of polymers exhibited applications in numerous areas such as: fuel desulfurization [24], biodiesel production [25], deoximation catalyst [21], gas separation membranes [26], flexible electrolytes [27], and dye sensitized solar cells [28]. Moreover，the polymerized acidic ionic liquid is a relatively unexplored sub-group in the polymeric ionic liquids arena and these acidic polymers can combine ionic liquid, acidic and polymer characteristics into a single material [29]. Lots of research groups have made great efforts to synthesize polymerized acidic ionic liquid during past three to four years, polymeric compounds with acidic ionic liquid pendant groups had been successfully synthesized. Additionally, the acidic IL functionalized polymeric materials with imidazolium-SO_3H, and pyridinium-SO_3H as pendant groups have been used as catalysts for the biodiesel synthesis from waste oil [30]. Ananda *et. al*. had firstly reported the novel strategy to synthesize a polymeric acidic ionic liquid with imidazolium ionic liquid moieties and p-phenylene-sulfonic acid units in the main polymer chain named poly (bis-imidazolium-p-phenylenesulfonic acid), catalyzed in the preparation of 1-amidoalkyl-2-naphthols [31].

Therefore, mesoporous and macroporous poly (ionic liquid)s are promising multifunctional materials with the features of multiporous materials, polymers and ionic liquids (ILs) [32]. In this work, cross-linked poly acidic ionic liquids with mesoporous and macroporous structure were successfully synthesized, via hydrothermal polymerization and anion exchange, sequentially. The catalyst could be separated and recycled easily and exhibited enhanced catalytic activities in alkylation

of *o*-xylene and styrene. Furthermore, a series of contrasting experiments were carried out to investigate the effect of solvents, addition of catalysts, reaction temperature. Among the obtained samples, compared with traditional solid acid, MPM-C₆V-SO₃CF₃-IL (DMF) occupies a large surface area (103.83 m^2/g), high pore volume (0.72cm^3/g) and abundant mesopores and macropores. Thus, the results achieved in this study may provide important insight into the field of alkylation, which has never been reported yet.

2. **Experimental**

2.1. Materials

All chemicals and solvents were commercially available and used as received. 1-Vinylimidazole (99 wt%) (V), N,N'-Methylenebis (acrylamide) (M), 2,2'-Azobis (2-methylpropionitrile) (AIBN) were purchased from Aladdin Industrial Corporation, N,N-Dimethylformamide (AR) (DMF), acetone (AR), anhydrous ether (AR), isopropanol (AR) (IPA) and Ethanol absolute (AR) were purchased from Sinopharm Chemical Reagent Co., Ltd. 1-Bromohexane(99 wt%), *o*-xylene, methylbenzene and styrene were supplied by Shanghai Lingfeng Chemical Reagent Co., Ltd., Tr fluoromethanesulfonic acid was acquired from Sun chemical Technology (Shanghai) Co., Ltd.

2.2. Preparation of mesoporous and macroporous polymer (MPM-V)

The mesoporous and macroporous polymer (MPM-V) was hydrothermally synthesized from copolymerization of M with V, according to the previous literature [33] with a slight

modification. In a typical procedure, the mixture composed of M (1.68 g) and V (0.68 g) was dissolved into 30 mL DMF (acetone or IPA) in a 100ml flask, followed by addition of AIBN (0.08 g). After vigorous stirring at room temperature for 3 h, the mixture was transferred into a 100 mL Teflon-lined stainless-steel autoclave and sealed to hydrothermally treat at 100 °C in an oven for 24 h. After evaporating DMF (acetone or IPA) at 40 °C in vacuum drying oven for 12 h, the monolithic solid was grounded into the powder, and finally, mesoporous and macroporous polymer (MPM-V) sample in yellowish powder morphology was obtained.

2.3. Preparation of cross-linked poly acidic ionic liquids (MPM-C_6V-SO_3CF_3-IL)

The ionic liquids functionalized on mesoporous and macroporous polymers were prepared by quaternary ammoniation $CH_3CH_2CH_2CH_2CH_2CH_2Br$ ($C_6H_{13}Br$), followed by anion-exchange treatments (HSO_3CF_3). As a typical synthesis of MPM-C_6V-SO_3CF_3-IL. 1.0 g of MPM-V was added to 25 mL of ethanol under stirring, followed by addition of 2.5 mL of $C_6H_{13}Br$ in the dark. After stirring for 12 h, the sample was filtered and washed with a large amount of ethanol to remove $C_6H_{13}Br$. After drying at 60 °C for 12 h, the MPM-C_6V sample was obtained, where C_6 stands for the $C_6H_{13}Br$ alkylation reagent. Furthermore, MPM-C_6V was treated with a solution containing 25 mL of toluene and 3mL HSO_3CF_3 for 24 h at room temperature, followed by filtering, washing with anhydrous ether, drying at 50 °C for 6 h. After repeating this procedure once again, followed by filtration, washed with anhydrous ether, and dried at 50 °C for

6 h, the MPM-C_6V-SO_3CF_3-IL sample was obtained, where SO_3CF_3 stands for the treatment of acid.

2.4. Catalyst characterizations

Transmission electron microscopy (TEM) experiments were conducted on a JEM-1230 with an acceleration voltage of 100 kV. Scanning electron microscopy (SEM) images were recorded on a JEOL JSM-5600L SEM instrument. Fourier transform infrared (FT-IR) spectra were recorded on a BRUKERALPHA FT-IR spectrometer.Thermo Gravimetric Analysis (TGA) was performed using a Rigaku ThermoPlus TG8120 system at a rate of 10 °C min^{-1} under air. The nitrogen adsorption-desorption isotherms were measured on an ASAP 2020 (Micromeritics, USA). Specific surface area was calculated by Brunauer-Emmett-Teller (BET) algorithm, and the pore size and pore volumes distributions were calculated using the Barrett-Joyner-Halenda (BJH) method. The X-ray photoelectron spectroscopy (XPS) spectra were performed on a Thermo ESCALAB 250 with Al Kα radiation, and the binding energies were calibrated using the C1s peak at 284.8 eV.

2.5. The alkylation of *o*-xylene with styrene

The catalytic activities of the as-prepared samples were evaluated through alkylation of *o*-xylene with styrene to produce 1,2-diphenylethane (PXE). In a general procedure, *o*-xylene (30 g), styrene (4 g), and 0.17 g catalyst (0.5 wt%, relative to the weight of *o*-xylene and styrene) were mixed in a 250 ml flask. The reactant mixture was heated to

120 °C in an oil bath with magnetic stirring for 3 h under autogenous pressure.-After this reaction, catalyst was recycled by vacuum filter. Cross-linked poly acidic ionic liquids catalyst was synthesized in three steps as shown in Fig. 1.
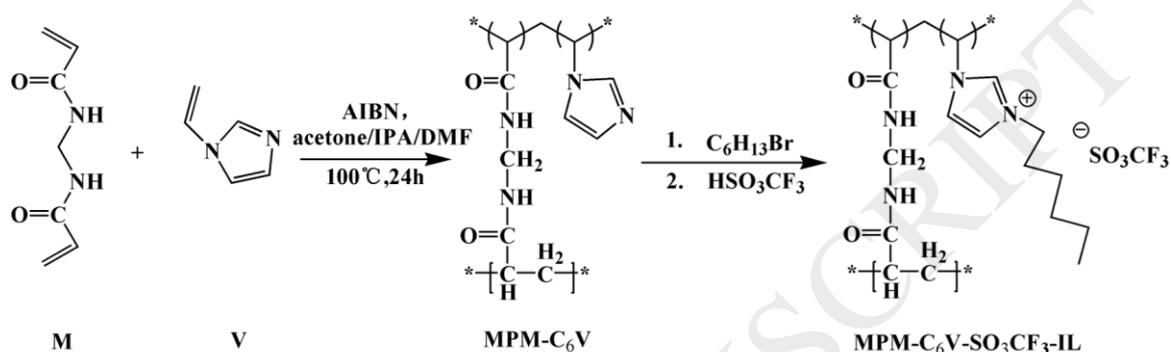
Fig. 1. Synthesis of cross-linked poly acidic ionic liquids catalyst

3. Results and discussion

3.1. Catalysts characterization

FT-IR was used to evaluate the special functional group of samples and the results were exhibited in Fig. 2. For Fig.2a-c, peaks at 1668 cm^{-1} and 1533 cm^{-1} were attributed to C=O, N-H and C-N stretching vibration of amide group, suggesting amide group structure had been embedded in the mesoporous and macroporous polymers. The FT-IR spectrum of MPM-C$_6$V-SO$_3$CF$_3$-IL clearly showed the new bands at 641 cm^{-1}, 1031 cm^{-1}, and 1175 cm^{-1} (Fig. 2c-e), which was attributed to the presence of S−O and C−F. It was noteworthy that different solvent exhibited different peak intensity. Especially, the peak intensity of Fig. 2c was stronger than Fig. 2 (a, b), which indicates that there existed many SO$_3$CF$_3$.
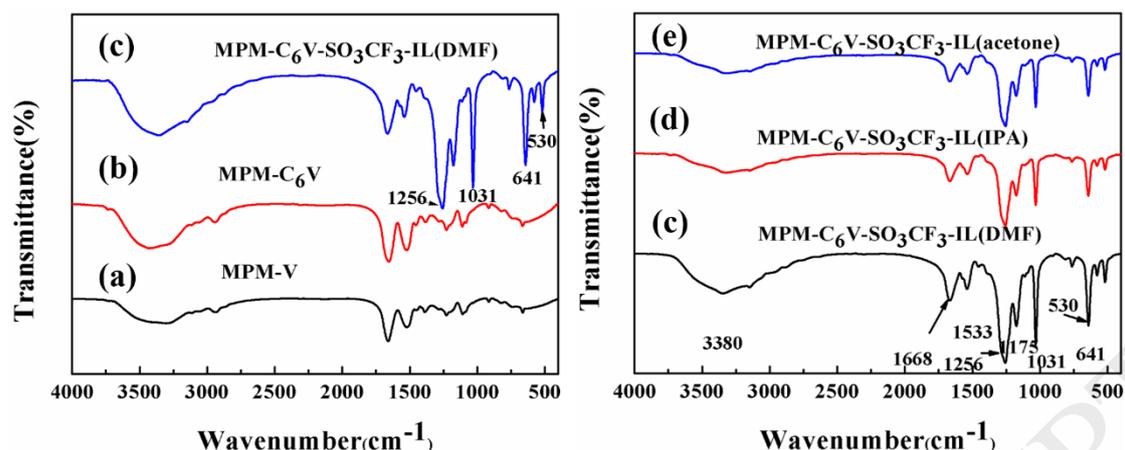
Fig. 2. FT-IR spectra of (a) MPM-V, (b) MPM-C$_6$V, and (c) MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF), (d) MPM-C$_6$V-SO$_3$CF$_3$-IL (IPA), (e) MPM-C$_6$V-SO$_3$CF$_3$-IL (acetone).

X-ray photoelectron spectroscopy measurement was carried out to study the valence state of different elements of MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF). Fig. 3a displayed three peaks at binding energies of 292.2, 288.5 and 284.8 eV, which were assigned to C−F, C−N, and C−C bonds, respectively. It confirmed the ionic liquid functionalized on the mesoporous and macroporous polymers. As shown in Fig. 3b, F1s peak was located at 688.1 eV, besides, N1s peaks at 401.4 and 400.1 eV were associated with N−C bonds (Fig. 3c). The O1s exhibited a single peak at around 531.7 eV (Fig. 3d), which corresponds to O atoms in SO$_3$CF$_3$. As shown in Fig. 3e, S2p peaks at 168.4 eV were assigned to S–O bonds. These data were in good agreement with the presence of C$_6$V-SO$_3$CF$_3$ in the sample [31-34].
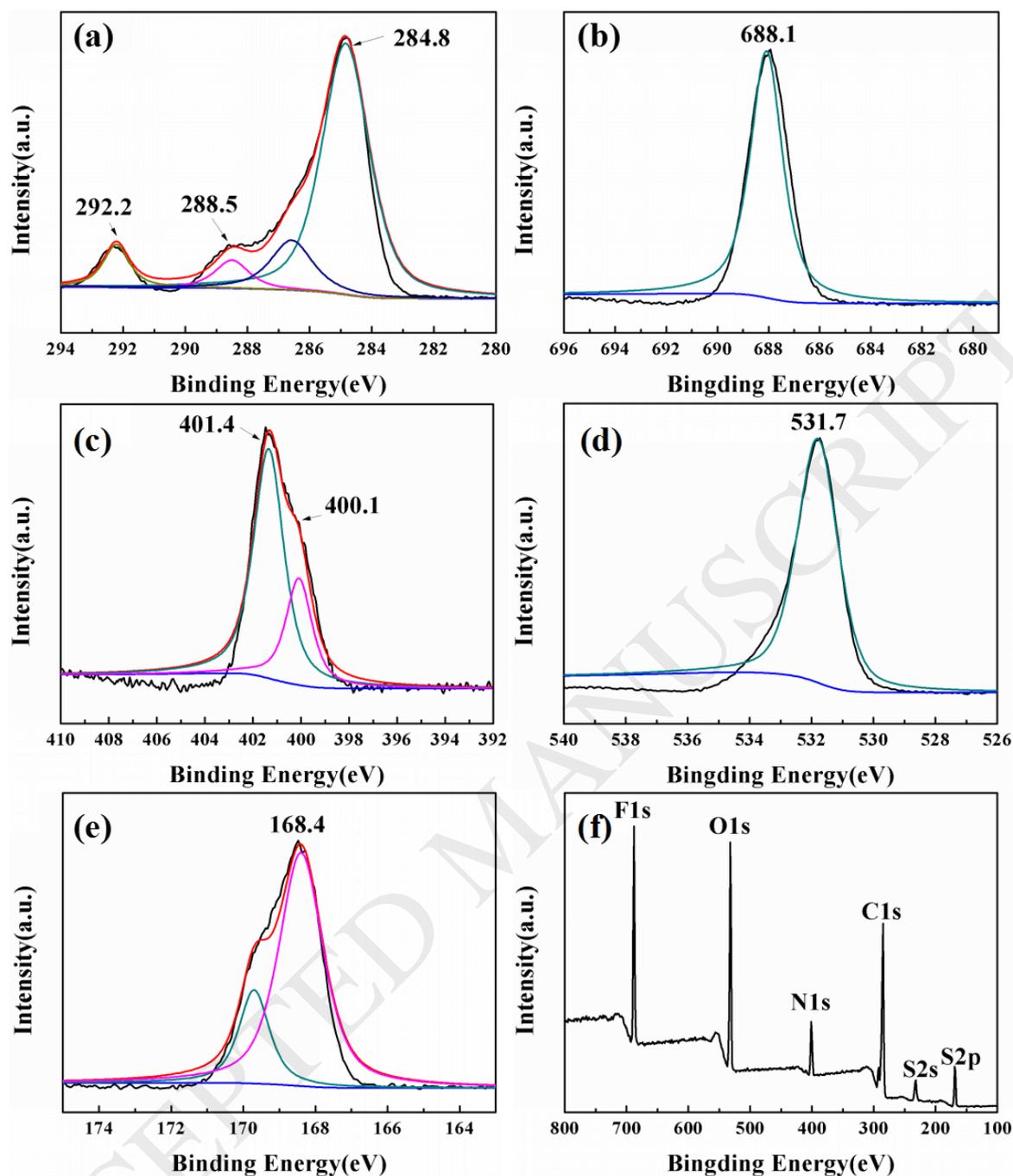
Fig. 3. XPS spectra of (a) C1s, (b) F1s, (c) N1s, (d) O1s, (e) S2p, (f) wide-scan

survey in MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF)

According to above analysis, the purity of the product was ascertained by various compositional techniques (FT-IR and XPS)，and results indicated that alkyl and ionic liquid groups have been incorporated on the copolymer of N,N'-Methylenebis (acrylamide) and vinylimidazole.

Fig. 4 showed transmission electron microscopy (TEM) images of specific synthesize step of MPM-C_6V-SO$_3$CF$_3$-IL and cross-linked poly acidic ionic liquids synthesized from different solvent. Abundant net-like hierarchical mesopores and macropores can be found in the sample. It is obviously that following acidification had little destruction on the multiporous structure of original sample. In addition, multiporous network could be clearly found by introducing cross-linking agent M. Notably, the solvent of MPM-V played an important role in controlling the structure of final catalyst. In other words, heterogeneous catalysts cross-linked poly acidic ionic liquids showed different morphology in different solvents. Specifically, MPM-C_6V-SO$_3$CF$_3$-IL (acetone) occupied blocky-shaped particles and heaped up together to form interspaces. MPM-C_6V-SO$_3$CF$_3$-IL (DMF) showed stable and multilayer network, while, cross-linked poly acidic ionic liquids synthesized from IPA displays irregularly network. Morphology of different cross-linked poly acidic ionic liquids had enormous effects on catalyst performance. In contrast with blocky-shaped particles structure, the net-like mesoporous and macroporous structure not only facilitated the diffusion of reactants and heat, but also provided high exposition degree of active sites. Moreover, network with uniform pore distribution, promoting the dispersion of reactant molecules. It could be seen that MPM-C_6V-SO$_3$CF$_3$-IL (DMF) with stable network, meanwhile, possessing abundant mesopores and macropores (Fig. 4e).
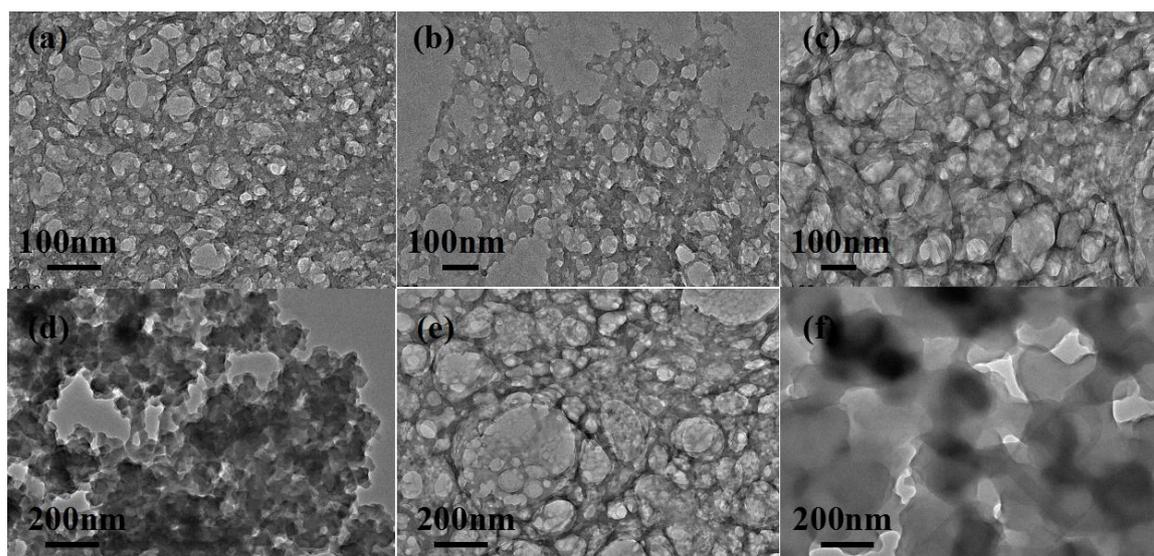
Fig.4. transmission electron microscopy (TEM) images of specific synthesize step of MPM-C$_6$V-SO$_3$CF$_3$-IL and cross-linked poly acidic ionic liquids synthesized from different solvent: (a) MPM-V (DMF), (b) MPM-C$_6$V (DMF), (c) MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF), (d) MPM-C$_6$V-SO$_3$CF$_3$-IL (IPA), (e) MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF), (f) MPM-C$_6$V-SO$_3$CF$_3$-IL (acetone)

Fig. 5 shows scanning electron microscope (SEM) images of specific synthesize step of MPM-C$_6$V-SO$_3$CF$_3$-IL and cross-linked poly acidic ionic liquids synthesized from different solvents, which were in good agreement with TEM results. From a level of relatively macroscopical micron order, it can be clearly found the differences among the cross-linked poly acidic ionic liquids synthesized in different synthesize solvents. The network of cross-linked poly acidic ionic liquids kept stable during the whole synthesis process. Multilayer and pores were related to the introduction of cross-linking agent M, and can be demonstrated by Fig.5 (a-c). Fig.5 (d-f) give differences on morphology of final sample synthesized in various solvent, certifying the solvent had

inevitable influence on the synthesis of cross-linked poly acidic ionic liquids. Only MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF) shows special network among all the samples. And a net-like structure with rough and loose surfaces of MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF) may be ascribed to the presence of abundant mesopores and macropores in the catalyst, which benefited the exposure of active sites and finally enhanced the catalytic activity. In contrast, most active sites of the blocky-shaped of cross-linked poly acidic ionic liquids, focus on the interspace between particles, which provided passage for reactant molecules at the same time. Thus, synthesis solvents of cross-linked poly acidic ionic liquids influenced the morphology of catalysts and catalytic activity.
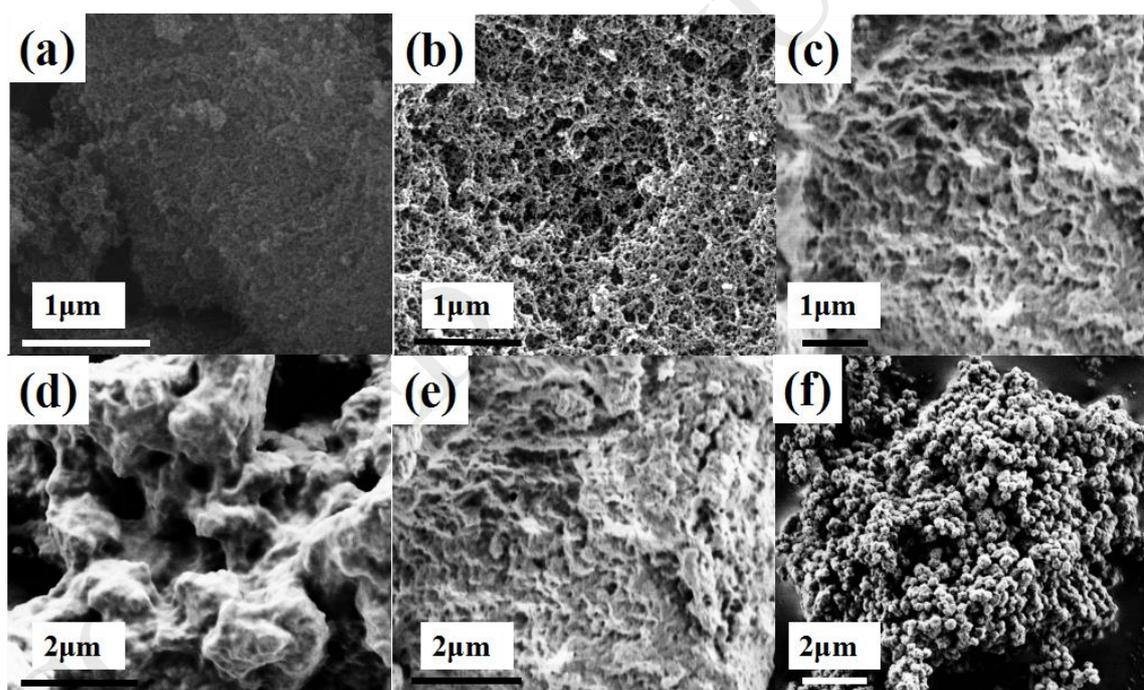
Fig.5 scanning electron microscope (SEM) images of specific synthesize step of MPM-C$_6$V-SO$_3$CF$_3$-IL and cross-linked poly acidic ionic liquids synthesized from different solvent: (a) MPM-V (DMF), (b) MPM-C$_6$V (DMF), (c) MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF), (d) MPM-C$_6$V-SO$_3$CF$_3$-IL (IPA), (e) MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF), (f) MPM-C$_6$V-SO$_3$CF$_3$-IL (acetone)

From the image of TG curves of different cross-linked poly acidic ionic liquids, which was showed in Fig. 6, we can have a clear recognition that thermal decomposition of catalyst was generally divided into three parts. Every part of down trend represents the decomposition of a kind of monomer. At the original part, decomposition probably referred to solvent, and then monomer of polymer began to decompose at about 150 °C. From then on, major bond between cross-linking M and V started to decompose at 300 °C. Finally, the whole cross-linked poly acidic ionic liquids were decomposed thoroughly over 600 °C. Overall, the synthesized catalyst occupied heat stability to some extent, specifically, keep stable under relatively lower temperature (below 300 °C), which definitely fits to the alkylation of o-xylene and styrene.
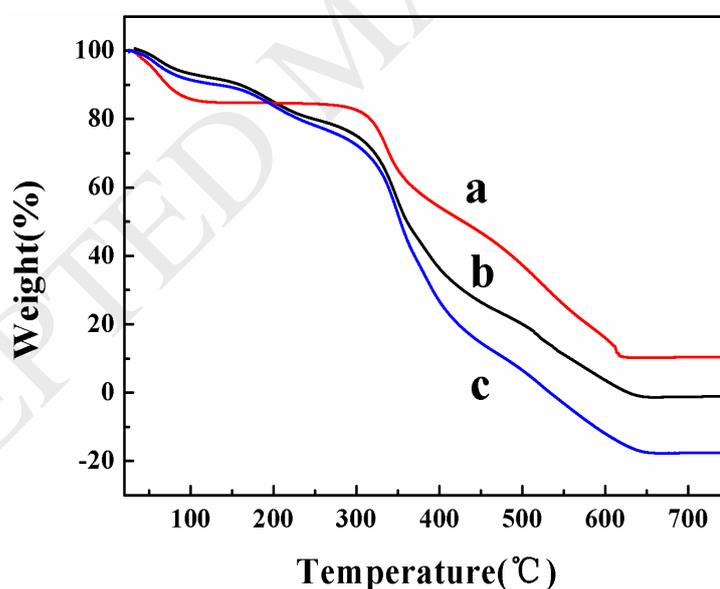
Fig.6. TG curves of (a) MPM-C$_6$V-SO$_3$CF$_3$-IL (DMF), (b)MPM-C$_6$V-SO$_3$CF$_3$-IL (acetone), (c) MPM-C$_6$V-SO$_3$CF$_3$-IL (IPA)

To measure the specific pores distribution of final cross-linking poly acidic ionic liquid, BET analysis was carried out and the results were exhibited in Fig. 7. As demonstrated in Fig. 7b, the sample MPM-C_6V-SO_3CF_3-IL (DMF) shows a type-IV curve with a sharp capillary condensation step at p/p$_0$ of 0.5-1.0, indicating the existence of mesopores and macroporous in the sample. Correspondingly, its pore size was mainly distributed at 40 nm and 5 nm (Fig. 7a), besides, parts of pore size distributed at over 80 nm. To a great extent, the smaller pores were formed due to cross-linking. Compared with cross-linking poly acidic ionic liquids synthesized from different solvents, the sample synthesized in DMF exhibited a relatively higher surface area (103.83 m^2/g) and larger pore volume (0.72 cm^3/g) than that of samples synthesized in acetone and IPA (surface area 13.19 m^2/g and 80.96 m^2/g, pore volume 0.16 cm^3/g and 0.65 cm^3/g, respectively), which was favorable for good catalytic activity.
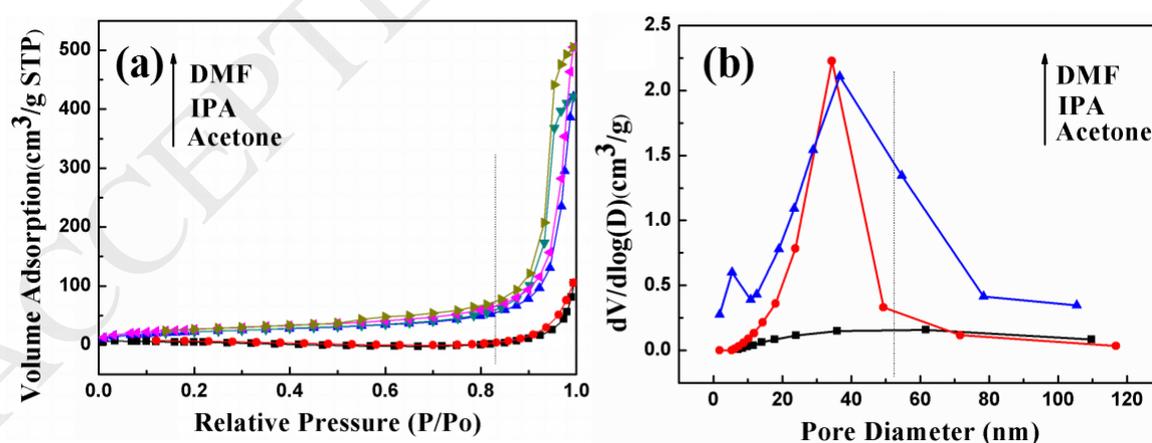
Fig.7. N$_2$ adsorption-desorption isotherm (a) and Pore size distribution (b) of

MPM-C_6V-SO_3CF_3-IL

3.2. Catalytic performace evaluation

3.2.1 Effect of the reaction temperature

A serious of factors optimization have been made in following for evaluating catalyst performance, moreover, specific procedure of alkylation of *o*-xylene and styrene was show on Fig. 8. Temperature of reaction was confirmed as principal factor. In a specific routes of optimization, the addition of catalysts were indentical controlled in a certain amount of 0.05 g, and then change the temperature of reaction，40 °C，60 °C, 80 °C, 100 °C, 120 °C，respectively. Styrene conversion rate (%) was confirmed as one of standard of catalyst performance, which was detected by gas chromatograph, GC 9890A. The results showed that styrene conversion rate (%) gradually increased as the temperature went up. Even at the temperature of 120 °C，styrene conversion rate (%) reached 100 %. On the one hand, it can be concluded that the alkylation of *o*-xylene and styrene suit a relatively higher temperature condition, and styrene can achieve almost conversion under this temperature. On the other hand, the yield of PXE advanced by the addition of catalyst, but still is not good enough under a relatively lower addition of catalyst cross-linked poly acidic ionic liquids, with the best PXE yield just 72.17 %. Naturally, it is needed to make deeper discussion on other factors which have a connection with PXE yield (%).

(1) *o*-xylene + styrene $\xrightarrow{\text{Cat}}$ 1,2-diphenylethane **(PXE)**

(2) Styrene $\xrightarrow{\text{Cat}}$ Styrene Oligomer

(3) *o*-xylene + styrene $\xrightarrow{\text{Cat}}$ bis(1-phenyl ethanyl) ortho-xylene **(BPXE)**
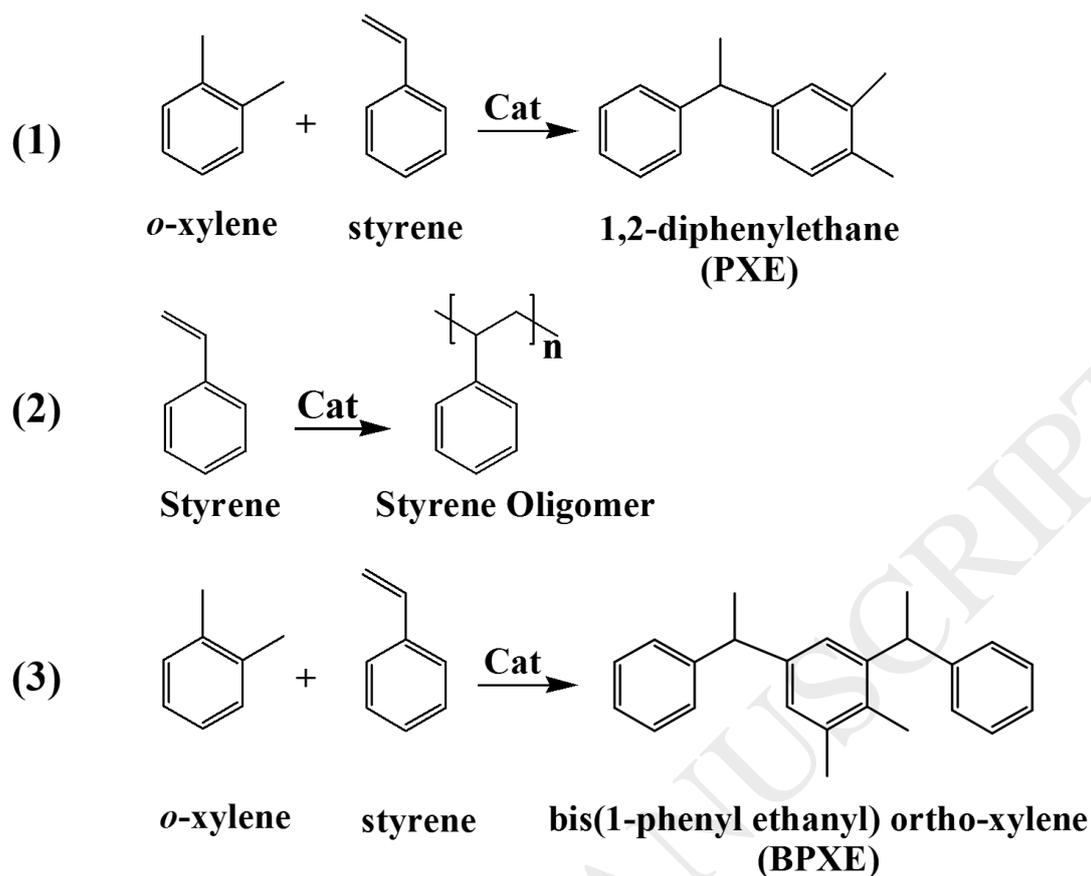
Fig. 8. Reaction scheme of alkylation of o-xylene with styrene over a

heterogeneous catalyst.

3.2.2 Effect of the MPM-C$_6$V-SO$_3$CF$_3$-IL amount

After confirm the adequate reactant temperature 120 °C，a deeper discussion on

the PXE yield (%) from the aspect of addition of catalyst MPM-C$_6$V-SO$_3$CF$_3$-IL have

been made. It is noteworthy that addition of catalyst made a great effect on the whole

alkylation of *o*-xylene and styrene. PXE yield (%) increased with the increasing of

catalyst amount. There is no doubt that active sites increased by the addition of catalysts.

Under same react temperature, more catalysts provide more active sites for the

transformation of both reactants and products. In comparison with different addition of

cross-linked poly acidic ionic liquids MPM-C$_6$V-SO$_3$CF$_3$-IL, it can be found that PXE

yield almost achieve 100 % with 0.17 g catalyst.

3.2.3 Effect of the solvent system

Solvents of precursor mesoporous polymer make enormous effects on the whole structure of final sample, which can be proved by TEM and SEM of MPM-C_6V-SO_3CF_3-IL (Fig. 4 & Fig. 5). DMF as an excellent solvent can dissolve kinds of organics, similarly, M and V can be dissolved completely in DMF, and then cross-linking polymerization can be carried definitely through hydrothermal method. The radical of cross-linking reaction decided the stability of network of cross-linked poly acidic ionic liquids. In other words, more radically of the cross-linking reaction have been carried, more stable and pyknotic network was formed. Compared with other different solvents, the solubleness of M and V in IPA and acetone were far from DMF, which results in abnormal structure, partly network and blocky-shaped, respectively. These two kinds of structure possess intuitively less active sites compared with network, leading not good enough catalytic performance during the alkylation of o-xylene and styrene. Styrene was transformed during the reaction with catalyst MPM-C_6V-SO_3CF_3-IL (DMF), with yields of PXE up to 99.67 % (Table 1). In contrast, the yields of PXE catalyzed by MPM-C_6V-SO_3CF_3-IL (IPA) and MPM-C_6V-SO_3CF_3-IL (acetone) were relatively lower, with the yield of PXE at 91.68 % and 90.43 %, respectively. Finally, the results was collected as following (Table1), and the optimum conditions (reaction time was 3h, reaction temperature was 120 °C, catalyst amount was 0.17 g (0.5 wt %), and o-xylene/styrene mass ratio was 7.5:1) was obtained.

Table1 yield of 1,2-diphenylethylane and conversion of styrene in the alkylation of *o*-xylene and styrene catalyzed by various cross-linked poly acidic ionic liquids

Catalyst	addition(g)	Temperature (°C)	Styrene conversion rate (%)[a]	1,2-Diphenylethylane yield (%)[a]
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.05	40	36.78	29.31
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.05	60	57.5	33.49
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.05	80	82.73	43.78
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.05	100	93.46	58.84
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.05	120	100	72.86
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.003	120	100	25.55
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.02	120	100	32.15
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.08	120	100	90.05
MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF)	0.17	120	100	99.67
MPM-C$_6$V-SO$_3$CF$_3$-IL(IPA)	0.17	120	100	91.68
MPM-C$_6$V-SO$_3$CF$_3$-IL(acetone)	0.17	120	100	90.43

[a] Measured by gas chromatograph, detection condition: initial temperature 150°C, hold time was 2 min, heating rate was 5 °C /min, final temperature was 250 °C, hold time was 2 min, the whole detection time was 0.5 h. Styrene conversion rate (%) and 1,2-diphenylethylane yield (%) was calculated by area normalization method.

According to our previous work and as listed in Table 2, Sheng et al. [35] found that pure HPW showed high catalytic performance for the reaction, however, it was difficult for separation and recovery. Furthermore, HPW/SBA-15 catalyst exhibited high conversion, while, showed the low product yield (68.3%) in their work. Besides, Zhao et. al [36] found that HPW/PIL-30-393 with large pore size of the support exhibited excellent catalytic performance, but styrene conversion and PXE yield still not high enough. From Table 2, it is found that MPM-C$_6$V-SO$_3$CF$_3$-IL(DMF) shows much higher conversion (100%) and higher yield (99.7%) than those of other catalysts. It is

noteworthy that the addition of catalyst is only 0.5wt% much fewer than other catalysts

with 2wt%

Table 2 Activity of HPW catalysts[a] and MPM-C_6V-SO_3CF_3-IL(DMF) in alkylation of

o-xylene with styrene

Catalyst	Styrene Conversion(%)	PXE Yield[b] (mol/g cat)
HPW[c]	100	1.86
HPW/SBA-15-PS	91	1.30
HPW/SBA-15-DS	100	1.74
HPW/PIL-30	95.9	1.73
MPM-C_6V-SO_3CF_3-IL(DMF)	100	7.59

[a] Reaction conditions: o-xylene : styrene = 7.5 : 1, reaction temperature=393 K, reaction

time = 3.0 h, catalyst loading = 20% (w/w of styrene).

[b] Isolated yield based on the amount of styrene.

[c] Homogeneous catalyst, 0.30 g.

3.2.4 Recyclability of MPM-C_6V-SO_3CF_3-IL (DMF) catalyst

Recycling utilization of catalyst could be another effective way to judge the

performance of catalysts, besides the heat stability showed by TGA. Although the

activity of catalyst showed great performance during the alkylation of o-xylene and

styrene, which can be proved by both the styrene conversion rate (%) and 1,2-

diphenylethylane yield (%), stability still need to be considered. It is noteworthy that

the recycling of the catalyst that we made was not stable as we expected. Take the

MPM-C_6V-SO_3CF_3-IL (DMF) as an example, it has a rapid decline since the first

catalyst reaction, with the yield of PXE from 99.67 % down to 46.11 % after 4 times recycling. After reaction of alkylation of o-xylene and styrene, structure of catalyst was destroyed, for the reason that amido bond in poly acidic ionic liquid can be destroyed under higher temperature. In addition, part of acidic group SO_3CF_3 may stay in the solvent of reactants, which can be proved by the directly orange color of reaction product and weaker transmittance reflect on the FT-IR compared with sample which before catalyst reaction (Fig. 9). This may be the reason for the lower recycling utilization.
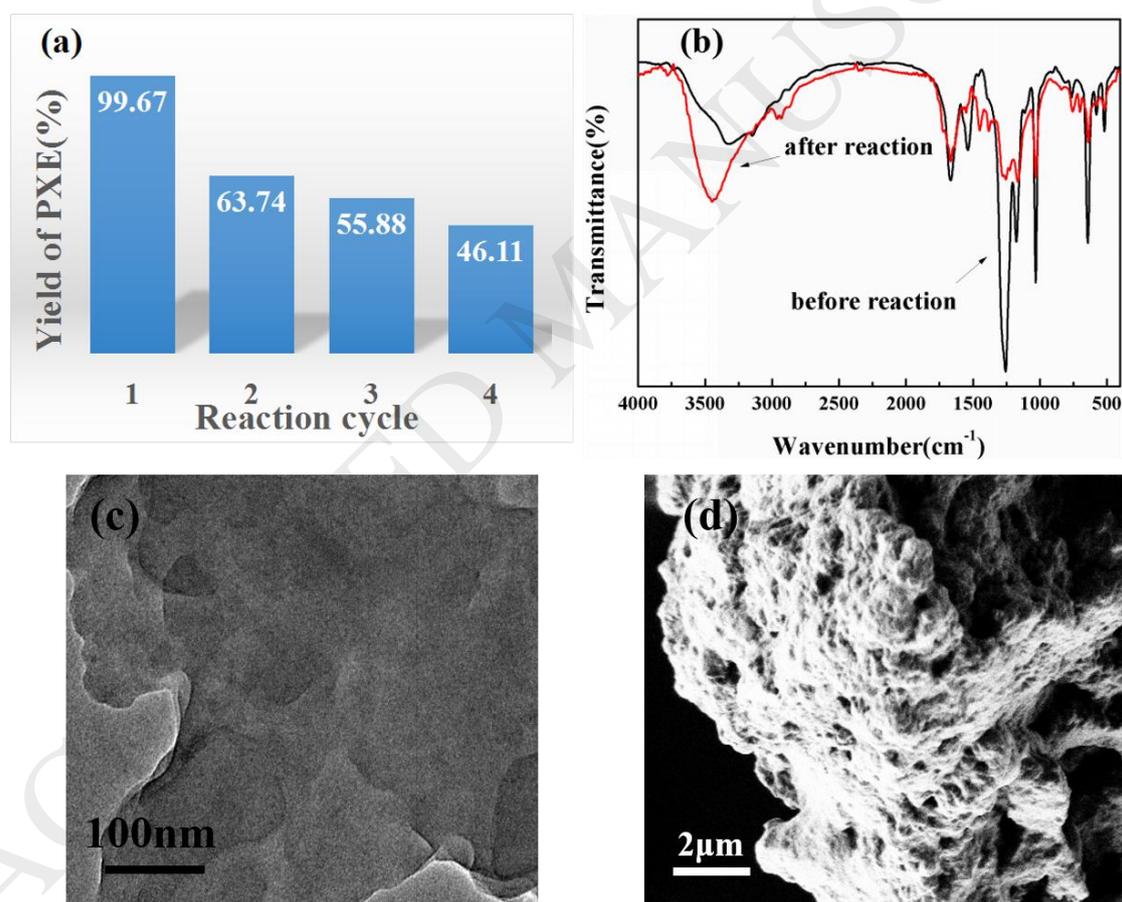
Fig. 9. Recycling of catalyst (MPM-C_6V-SO_3CF_3-IL(DMF)) (a); FT-IR spectrum of before reaction and after reaction(b)；TEM of MPM-C_6V-SO_3CF_3-IL(DMF) after alkylation of o-xylene and styrene (c); SEM of MPM-C_6V-SO_3CF_3-IL(DMF) after

alkylation of *o*-xylene and styrene (d)

3.3. Plausible catalyst synthesis mechanism
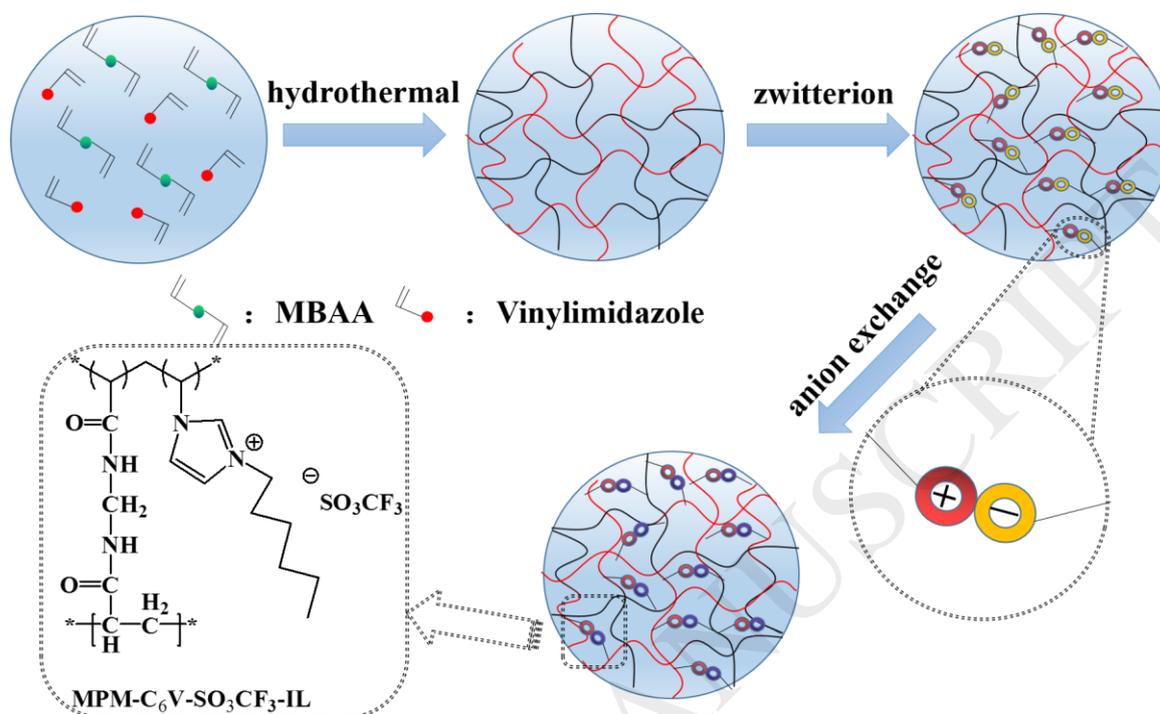
Fig.10. plausible synthesis mechanism for MPM-C_6V-SO_3CF_3-IL catalyst

According to above specific analysis of catalyst from different kinds of aspects, a plausible catalyst synthesis mechanism can be come up with (Fig.10). Cross-linked poly acidic ionic liquids shows excellent catalytic activity in alkylation of *o*-xylene and styrene, due to the special mesoporous and macroporous structure. Acidic functional group SO_3CF_3 was introduced to the acidic condition of alkylation, which provide great possibility for the activity performance of catalyst. With the help of cross-linking regent M, an initial network can be architected through the first strict hydrothermal polymerization, which can be clearly seen from the image (Fig. 4 and Fig. 5). It is noteworthy that the introduction of cross-linking regent M enhanced the stability and compactness of whole network structure to some extent. Moreover, the cross-linking

degree of first step controlled the pore diameter and distribution. Besides energy

between covalent bond, the interaction between cation and anion also enhanced whole

stability of network structure. Anion exchange keeps original network stable after

functionalization of the cross-linking poly ionic liquids, realized the synthesis of acid-

functional catalyst. Mesopores and macropores of MPM-C_6V-SO_3CF_3-IL (DMF) have

little change during the process of synthesis. Moreover, the obtained sample was in

solid and the catalyst after reaction can be easily separated from the solution. Except

for the recycling was not fit to our expectation, catalysts were completely up to the

standard of green chemistry. After reaction of alkylation of o-xylene and styrene, part

of acidic group SO_3CF_3 may stay in the solvent of reactants, which can be proved by

the directly orange color of reaction product and weaker transmittance reflect on the

FT-IR compared with sample which before catalyst reaction. This may be the reason

for the lower recycling utilization.

4. Conclusion

In summary, a novel cross-linked poly acidic ionic liquids catalyst for efficient

alkylation of o-xylene and styrene was synthesized through free radical polymerization

and ionic change. The polymer composite was characterized by different techniques,

and results demonstrated that nanoporous polymeric network was multi-layered and

exhibited repeating units of SO_3CF_3. The combination of mesopores and macropores

would significantly reduce the limitation of mass transfer in alkylation of o-xylene and

styrene and finally promote the catalytic performance compared with other porous solid

acidic catalysts. Besides, cross-linked poly acidic ionic liquids as a heterogeneous acidic catalyst can be easily separated from the solvent. The catalytic performance of the cross-linked poly acidic ionic liquids was discussed from three aspects, temperature, addition of catalyst, solvent, respectively. Under the optimum conditions (reaction time was 3h, reaction temperature was 120°C, catalyst amount was 0.17g (0.5 wt%), and o-xylene/styrene mass ratio was 7.5:1), a high conversion of styrene (100 %) and 1,2-diphenylethane (PXE) yield of 99.67 % was obtained. This study may help develop green routes for reactions under acid condition such as transesterification, esterification, Friedel-Crafts reaction and so on.

Acknowledge

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