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A Novel Gemini Sulfonic Ionic Liquid Immobilized MCM-41 as Efficient Catalyst for Doebner-Von Miller Reaction to Quinoline

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A novel 2,2'-bipyridine-based gemini sulfonic ionic liquid was first synthesized and then immobilized on MCM-41 support (named IL1/MCM-41), which was further characterized using XRD, FT-IR, SEM, TEM, N₂-physisorption, XPS and TG techniques. These characterization results revealed that the IL1/MCM-41 presented a whole ordered mesoporous structure, excellent thermal stability as well as the interaction between ionic liquid with MCM-41. Catalytic activity of the obtained IL1/MCM-41 was systematically evaluated for the Doebner-Von Miller reaction to generate quinoline. Compared to conventional imidazole-type

single sulfonic ionic liquid supported on MCM-41 (named IL2/MCM-41), IL1/MCM-41 exhibited higher catalytic activity and better reusability, which was probably due to the synergistic catalytic effect of the dual sulfonic acid group on IL2 and the stronger interaction between dipyrindine ring of ionic liquid with MCM-41 support, respectively. Meanwhile, a plausible reaction routes for the synergistic catalytic action of dual sulfonic acid to quinoline over the IL1/MCM-41 catalyst was also proposed in this paper.

1. Introduction

Ionic liquids (IL) are a class of liquid salts, which consist of organic cations and anions counterparts.^[1–4] Nowadays, the functionalization of ionic liquids have been attracted more and more attention and utilized for various reaction as novel and environmental-friendly catalysts, due to their attractive properties, such as, negligible vapor pressure, superior solubility property, efficient catalytic activity, excellent recyclability and so on.^[5–10] However, ILs also exists several weaknesses, involving expensive synthesis cost, large consumption and troublesome separation. More importantly, because of ionic liquids exiting observable property of high viscosity, the mass transfer decreases during the reaction and the difficulty of separation handing increases after the reaction.^[11,12] As a result, the practical applications of ILs are significantly restricted in industrial production. In this regard, the immobilization of IL into solid carriers provides a good strategy to solve the mentioned-above drawbacks.^[12–15] Through the immobilization of ILs with solid carriers, the IL membranes on the surface of solid carriers could create homogeneous surroundings during

the reaction, and also these ILs-based heterogeneous catalysts could realize simplified separation and recyclability after reaction.

To dates, ordered mesoporous materials (such as SBA-15 and MCM-41) have been received great attention and widely employed for various application fields.^[16,17] These ordered mesoporous materials exhibit excellent structural features, including high surface area, large pore volume, adjustable pore size as well as good chemical/thermal stabilities.^[18,19] Meanwhile, their catalytic properties can be flexibly adjusted via the immobilization with various active components over the inactive surface of mesoporous silica.^[20–22] Thus, ordered mesoporous materials are regarded as the ideal solid carriers for versatile heterogeneous catalysts. Up to now, the preparation and application of MCM-41-type mesoporous catalysts, via utilizing MCM-41 as the solid carrier to immobilize ILs, have been widely investigated. For instance, Henni et al reported that the imidazolium based ILs-immobilized on mesoporous MCM-41 showed high-efficiency adsorptive property, rapid sorption rates and stable regenerability for carbon dioxide capture.^[23] Hu et al showed a series of copper-doped MCM-41 supported dual acidic ILs catalysts, which exhibited efficient catalytic activity in Biginelli reaction and could be readily separated via filtration.^[24] Besides, Hu et al also displayed that the acidic IL immobilized on Sn-modified MCM-41 presented excellent activity and recyclability in Mannich reaction.^[25] Therefore, the ILs-immobilized MCM-41 catalysts have significant potentiality as efficient and eco-friendly heterogeneous catalysts for the wide application in numerous chemical processes.

Quinoline and its derivatives, as an important class of aza-heterocyclic compounds, exhibit excellent therapeutic as well as biological properties.^[26–28] Doebner-Von Miller reaction is one of the most valuable C-heteroatom bond forming route to build

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versatile quinoline skeletons among various synthetic routes to quinolines, undergoing aza-heterocyclic and subsequent aromatization processes.^[29] In general, traditionally homogeneous catalysts were usually employed in quinolines synthetic reactions, such as, sulfuric acid, muriatic acid, metal salt and ionic liquids.^[30–33] Nevertheless, the homogeneous catalytic process caused several significant problems. For example, a larger amount of acid wastewater is brought out and the complicated separation of homogeneous catalysts after reaction is required. Alternatively, heterogeneous catalysts are easier separated from the reaction system, which is more environmentally-friendly than the homogeneous ones. In recent years, just several heterogeneous catalysts, like $\text{InCl}_3/\text{SiO}_2$, montmorillonite and phosphotungstic acid, have been explored for the reaction of Doebner-Miller reaction to quinolines,^[34–37] and these catalysts existed short lifetimes because of the loss of active ingredients and/or rapid inactivation during quinolines synthetic reaction. Therefore, the further development of a novel type of green heterogeneous catalysts owning high activity as well as excellent stability for Doebner-Von Miller reaction to quinoline is still highly desired.

In this work, a novel gemini sulfonic ionic liquid immobilized on MCM-41 was prepared as effective and recyclable heterogeneous catalyst, and employed to catalyze the domino reaction of aniline and acrolein dimethyl acetal to quinoline, via hydrolysis-heterocyclic-aromatization processes. Accordingly, 2,2'-bipyridine-based gemini sulfonic ionic liquid was firstly prepared and then immobilized on MCM-41 mesoporous materials. The obtained IL-immobilized MCM-41 materials were characterized, and the catalytic activities were evaluated systematically in Doebner-Von Miller reaction. Further, the reusability of the IL-immobilized MCM-41 catalysts were also investigated.

Experimental

Chemicals

All the chemicals, tetraethoxysilane (Sinopharm Chemical Reagent Co., Ltd; TEOS), cetylpyridinium chloride (Sinopharm Chemical Reagent Co., Ltd. CPCI), acetic acid and sodium hydroxide (Sinopharm Chemical Reagent Co., Ltd.), 2,2'-bipyridine, 1-methylimidazole and 1,4-butane sultone (Aladdin Chemical Reagent Co., Ltd.); aniline and Acrolein diethyl acetal (Xilong Chemical Co., Ltd.), were commercially available and had an analytic purity.

Catalyst Preparation

Preparation of MCM-41

The synthesis method of MCM-41 was used as in previous literatures.^[38,39] In a typical preparation, the aqueous solution containing cetylpyridinium chloride (CPCI) and ammonia ($\text{NH}_3\cdot\text{H}_2\text{O}$, 25 wt. %) was stirring for 30 min, and then tetraethoxysilane (TEOS) was dropwise into the aqueous solution. The mixture was further stirring at room temperature for 30 min to form an expectant homogenization gel. The synthesis gel had the molar composition: 1TEOS: 9.2 $\text{NH}_3\cdot\text{H}_2\text{O}$: 0.5CPCI: 130 H_2O . Subsequently, the formed-gel

was transferred into the teflon-lined autoclave to crystallization for 24 h at 100 °C. The resultant solid was collected by filtration, washing with distilled water and then vacuum drying at 60 °C. Finally, the mesoporous MCM-41 material was obtained via calcining for 6 hours at 550 °C in an air flow.

Preparation of Gemini Sulfonic Ionic Liquid

A typical procedure of gemini sulfonic ionic liquid' synthesis is given, as depicted in Figure 1S(a). 2,2'-bipyridine and 1,4-butane sultone were mixed completely without using solvent; and stirred violently for 24 h at 60 °C. Subsequently, the sulfuric acid (98%) was added slowly into the reaction system and then kept stirring magnetically for 12 h at room temperature. The forming liquid was washed repeatedly with ethyl acetate and dried in vacuum condition at 60 °C for 24 h. the as-obtained ionic liquid was named as IL1. As comparison, a typical imidazole-type sulfonic ionic liquid was also ready according to the above method, using N-methyl imidazole and 1,4-butane sultone as reagents, as showed in Figure 1S(b), which was defined as IL2.

Immobilization of Ionic Liquid on MCM-41

Immobilization of ionic liquid on MCM-41 was prepared using the convenient impregnation method. In a typical preparation, the as-prepared IL1 or IL2 was dissolved into absolute ethyl alcohol. Then, the MCM-41 powder was added into and the formed suspension kept strongly stirring for 12 h at room temperature. After that, the resulting suspension was dried at 60 °C for 24 h in the vacuum environment to remove absolute ethyl alcohol. The obtained IL-immobilized catalysts were denoted respectively as IL1/MCM-41 and IL2/MCM-41.

Catalysts Characterization

X-ray diffraction (XRD) spectroscopy for catalysts was performed with a Bruker D8-Advance diffractometer, using the conditions as follow: Cu target $K\alpha$ radiation ($\lambda = 1.54187 \text{ \AA}$), scanning voltage (40 kV), scanning speed (0.5 s), scanning current (40 mA); scanning step (0.02°).

Fourier transform infrared (FT-IR) spectra for catalysts was recorded on a Varian 3100 spectrometer, equipped with a DTGS detector. The sample and KBr were initially mixed thoroughly and then positioned in the holder to mount in sample cavity of the spectrometer. The data were recorded at a scanning number of 32 as well as a resolution of 2 cm^{-1} .

Scanning electron microscopy (SEM) for catalysts was conducted on a JEOL JSM 6700F apparatus, using an accelerating voltage of 10 kV. The sample was initially dispersed adequately in alcohol via ultrasonication and then placed on the silicon chip.

Transmission Electron Microscope (TEM) for catalysts was recorded with a JEM-2100F apparatus, using an accelerating voltage of 200 kV. The sample was firstly ultrasonic treated to disperse in ethanol and then dropped on the carbon-coated copper grid.

N_2 -physisorption for catalysts was measured on a Quantachrome Autosorb-1 apparatus at liquid nitrogen temperature. Prior to measurement, the sample was firstly outgassed at 300 °C for 8 h under a 10^{-8} Torr vacuum. The specific surface area was obtained via the multipoint BET equation, and the average mesopore size was calculated via BJH method using desorption isotherms.

X-ray photoelectron spectroscopy (XPS) for catalysts was performed on a PHI Quantum 2000 apparatus, using the Al $K\alpha$ radiation source.

The sample was firstly compressed into a wafer before measurement.

Thermogravimetry (TG) for catalysts was conducted on a Diamond apparatus. The fresh and used catalysts were heated with 5 °C/min from room temperature to 800 °C in air atmosphere.

Catalytic Performance Evaluation

Domino reaction of acrolein diethyl acetal and aniline to quinoline was conducted, employing IL-immobilized MCM-41 as heterogeneous catalyst. The general procedure was as follows: acrolein diethyl acetal and aniline were firstly mixed adequately at room temperature, and then the heterogeneous catalyst was added into the above reaction system. The mixtures were put into Aika reactor to react under strongly stirring. After the reaction finished, the products mixtures were identified by mean of the Varian Saturn 2200/CP-3800 gas chromatography-mass spectrometry, which was equipped with two CP8944 chromatographic columns (VF-5, 30 m × 0.25 mm × 0.25 μm). The yield and selectivity of quinoline were calculated, according to the converted acrolein diethyl acetal.

2. Results and Discussions

2.1. Catalyst Characterization

The XRD patterns in low 2θ region of the parent and IL-supported MCM-41 samples are shown in Figure 1. The MCM-41 sample displays three characteristic diffraction peaks at 2.10°, 3.64° and 4.22°, which are assigned to (100), (110) as well as (200) planes of the ordered mesoporous structure of the MCM-41 material. The result demonstrates that the prepared MCM-41 sample exists the well-defined p6m hexagonal structure with uniform mesopore distribution.^[40] the IL1/MCM-41 and IL2/MCM-41 samples exhibit the similar diffraction peaks to the parent MCM-41 one, showing that the ordered mesopore

structure of MCM-41 was retained well even after immobilization of acidic ionic liquid on MCM-41. Apparently, the intensity of diffraction peak of (100) decreases slightly over the IL1/MCM-41 and IL2/MCM-41 samples, relative to the pure MCM-41 material. This is possibly due that the decreasing intensity of XRD peak over IL-supported MCM-41 is attributed to the adsorption influence to the X-ray by the layer of ionic liquid supported on the outside and inner surface of MCM-41.^[41] In addition, the diffraction peak of (100) shift slightly toward higher 2θ over the IL-supported MCM-41 samples, compared to the parent MCM-41 one. This may be resulted from the decreasing mesopore size over IL-supported MCM-41 samples, according to the rule of Bragg ($\lambda = 2d \cdot \sin\theta$).^[12] As a result, the ordered hexagonal mesopore structure of MCM-41 preserved intact after the immobilization of acid ionic liquid.

The FT-IR spectra of the parent and IL-supported MCM-41 sample are displayed in Figure 2. Generally, the peaks centred at ca. 3434 and 1639 cm⁻¹ are assigned to the stretching and bending vibration of adsorbed water molecules.^[40] The peaks at ca. 1080, 805 and 454 cm⁻¹ are related to the asymmetric vibrations, symmetric stretching vibrations and bending vibration of Si–O–Si units. The peak at ca. 952 cm⁻¹ is associated to the asymmetric vibrations of Si–OH units.^[42] Obviously, the parent and IL-supported MCM-41 show typical characteristic structure of MCM-41. Interestingly, the characteristic peak intensities of MCM-41 decrease scarcely after modifying with acid ionic liquid, further implying that the ordered mesoporous structure is remained well. Furthermore, the FT-IR spectra of pure IL1, fresh IL1/MCM-41 and used IL1/MCM-41 are also depicted in Figure 2S. For the IR spectra of pure IL1, the peak at 1046 cm⁻¹ and 1194 cm⁻¹ is due to the S=O symmetric and asymmetric stretching vibrations of –SO₃H group, and the peak at 886 cm⁻¹ should be assigned to the stretching vibrations of S–O group.^[7,43, 44] While the peak at 1602 cm⁻¹, 1541 cm⁻¹, 1434 cm⁻¹ could be related to the bending vibration of N–H,

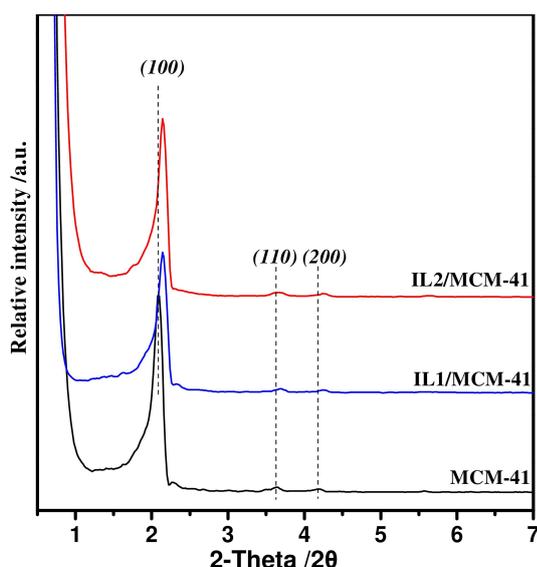


Figure 1. XRD patterns for catalysts.

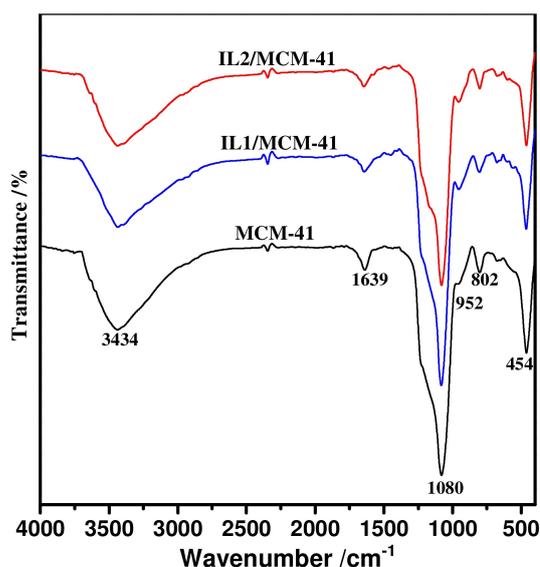


Figure 2. FT-IR spectra for catalysts.

stretching vibration of C=N as well as C=C of pyridine ring.^[45,46] However, for the fresh and used IL1/MCM-41, some IR peak of IL1 are disappeared, which is probably overlapped by those of MCM-41.^[7] It is worth noting that the peaks at 1432 cm^{-1} and 1514 cm^{-1} are shift toward to 1446 cm^{-1} and 1524 cm^{-1} after the immobilization of IL1 on MCM-41 support. This blue-shift is attributed to the interionic interactions between the IL and the surface of MCM-41.^[23,47] Besides, the characteristic peaks of used IL1/MCM-41 is consistent with that of the fresh one, and The peak intensities decrease slightly, which may indicate the slight deactivation of catalyst.^[44]

The SEM images of the parent and IL-supported MCM-41 samples are shown in Figure 3. The parent MCM-41 sample shows the coralline-like aggregated external morphology, which consisting of irregular particles with different diameter of 100–200 nm. Obviously, both of IL1/MCM-41 and IL2/MCM-41 exist the similar coralline-like morphology as well as particle sizes, compared to the MCM-41 one, indicating the preserving intact of MCM-41.

The TEM images of the parent and IL-supported MCM-41 samples are displayed in Figure 4. Obviously, the TEM images of MCM-41 provide the visible evidence for a well-ordered hexagonal array in mesoporous structure. Moreover, after immobilizing of acid ionic liquid on MCM-41 support, the ordered arrays are clearly observed in the IL1/MCM-41 and IL2/MCM-41 samples. This result indicates that the ordered mesoporous structure of MCM-41 is still highly retained after supporting with acidic ionic liquids. Therefore, it could be

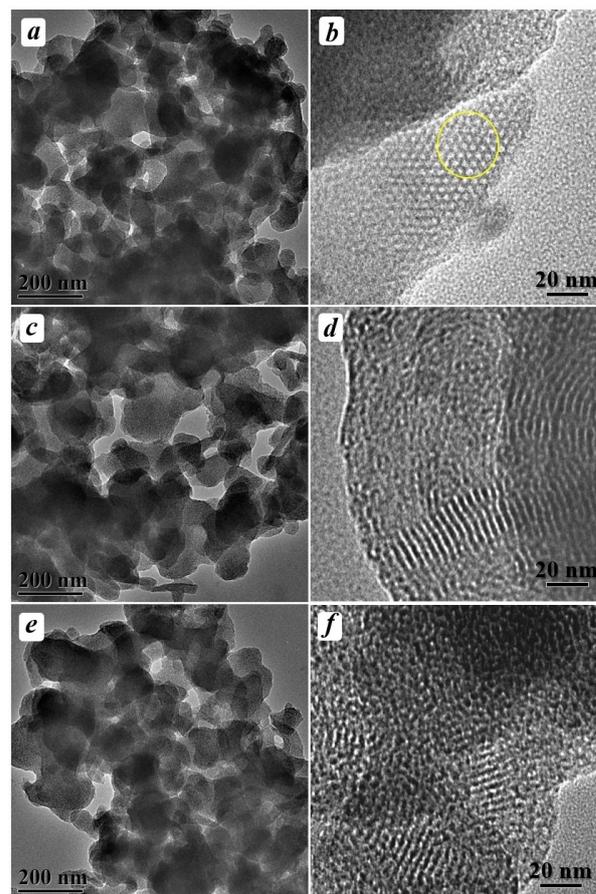


Figure 4. The TEM images for catalysts. MCM-41(a, b); IL1/MCM-41(e, d) and IL2/MCM-41(e, f).

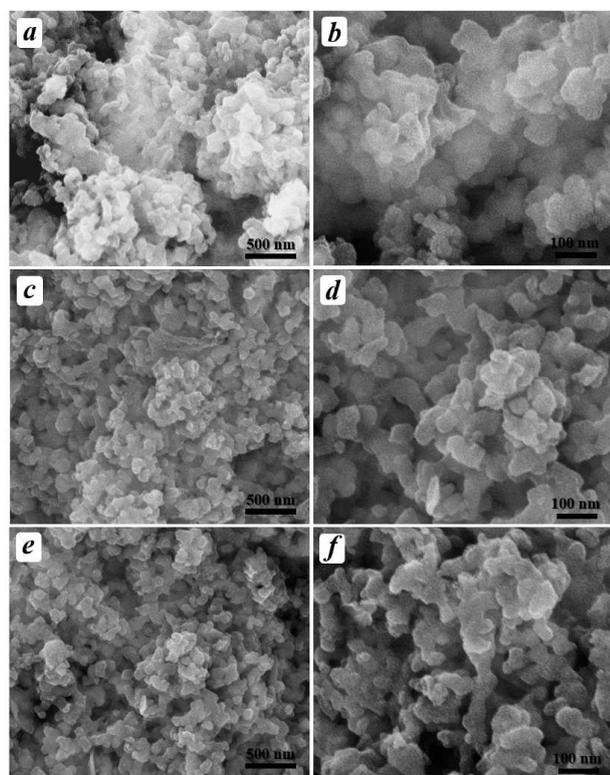


Figure 3. The SEM images for catalysts. MCM-41(a, b); IL1/MCM-41(e, d) and IL2/MCM-41(e, f).

demonstrated that the immobilization of acid ionic liquid does not destroy mesopore structure of the parent MCM-41 support.

The N_2 -physisorption isotherms of the parent and IL-supported MCM-41 samples and corresponding pore size distributions are shown in Figure 5. Obviously, the parent MCM-41 sample presents the typical IV-type isotherms, based on the IUPAC classifications, illustrating the existence of mesopores. It should be noted that the hysteresis loop is present well over all the samples, although the hysteresis loop is weakened over the IL1/MCM-41 and IL2/MCM-41 samples. The intact retainment of hysteresis loop indicates that the mesopores structure of the MCM-41 support is reserved well after the modification of acid ionic liquid. Moreover, relative to the parent MCM-41 sample, the adsorption volume of N_2 decreases sharply over the IL1/MCM-41 and IL2/MCM-41 ones. This is possibly due to the attachment of ionic liquid on the wall of mesopore. From the pore size distribution in Figure 5, one can see that the mesopore size decrease clearly over the IL1/MCM-41 and IL2/MCM-41 ones, which could further imply that ionic liquid was immobilization into the surface of mesopore channels of MCM-41 support.

The textural properties of the parent and IL-supported MCM-41 samples are showed detailedly in Table 1. The specific

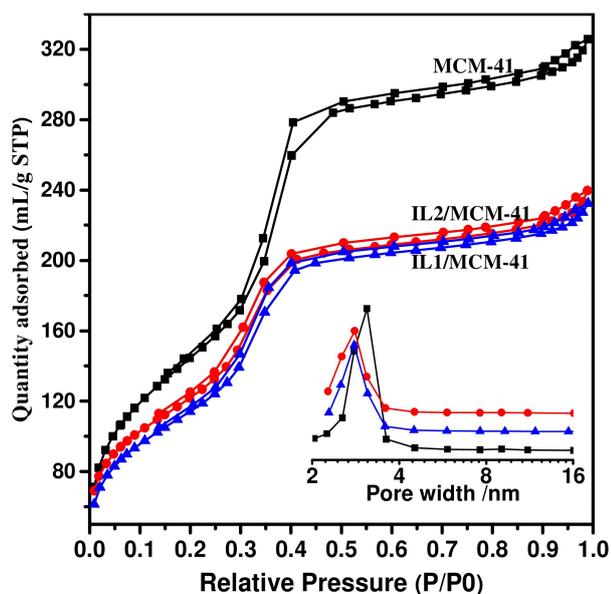


Figure 5. The N_2 adsorption-desorption isotherms and pore size distribution for catalysts.

Table 1. The textural properties of catalysts.

Catalyst	BET Surface Area [m^2/g]	Pore Volume [cm^3/g]	Average pore size ^[a] [nm]
MCM-41	588.42	0.59	3.15
IL1/MCM-41	412.98	0.37	3.10
IL2/MCM-41	414.40	0.37	3.09

[a] Average pore size was calculated via BJH method using desorption isotherms.

surface area is calculated via BET method, and the distribution of mesopore size is determined via BJH method using the isotherm of adsorption branch. The parent MCM-41 sample possesses as high as $588.42 m^2/g$ of surface area, $0.59 m^3/g$ of pore volume and *ca.* 3.15 nm of pore size. However, after the

immobilization with ionic liquid, the surface area decreases significantly to $412.98 m^2/g$ and $414.40 m^2/g$ respectively over the IL1/MCM-41 and IL2/MCM-41 samples. Meanwhile, their pore volume as well as pore size also decreases in different degree. Because the mesopore structure of MCM-41 support is not varied in the process of the immobilization with acid ionic liquid, such a result should be attributed to the adhesion of ionic liquid in mesopore channels. This phenomenon could also indicate that the wall thickness of MCM-41 support would be increased after immobilizing with ionic liquid, which may strengthen the stability of MCM-41 support via protecting the surface of MCM-41 wall via the immobilized ionic liquid.

The S_{2p} and N_{1s} XPS spectra of the parent and IL-supported MCM-41 samples are shown in Figure 6. From the S_{2p} XPS spectra in Figure 6, one can see that an evident peak of binding energy at 168.90 eV is appeared over the IL1/MCM-41 and IL2/MCM-41 samples but absent over the parent MCM-41 one, which is assigned to the $S(+6)$ from the sulfate radical (SO_4^{2-}) and sulfonic acid group ($-SO_3H$) of ionic liquid supported on the surface of MCM-41.^[48] This result further demonstrates that the ionic liquids are immobilized indeed on MCM-41. From the N_{1s} XPS spectra in Figure 6, one can see that, no peak of binding energy is appeared over the parent MCM-41 sample, whereas a distinct peak of binding energy is emerged over the IL1/MCM-41 and IL2/MCM-41 ones, respectively, further confirming the effective immobilization with N-containing ionic liquid on MCM-41 support.

It was reported that the imidazole derivatives could generate the effective chemical interaction with the support to inhibit the corrosion of surface.^[49,50] Similarly, the dipyrindyl compounds as ligands could form the noncovalent interactions with various metal ions, in which N element played an important effect in the formed interaction.^[51,52] Moreover, Huang et al. reported that the binding energy of N_{1s} could shift toward the lower BE value because of the forming interaction through chemical adsorption, when the pure N-containing organic compounds were supported on the carrier.^[48] Obviously, the binding energy of 400.1 eV over the IL1/MCM-41

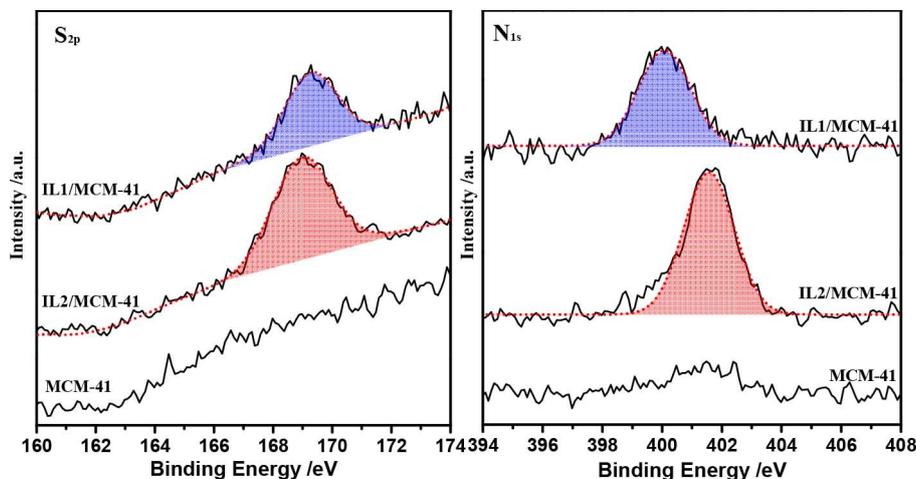


Figure 6. The S_{2p} and N_{1s} XPS spectra for catalysts.

sample is lower than that of 401.6 eV over the IL2/MCM-41 one, it could be suggested that the IL1/MCM-41 sample exists stronger interaction between ionic liquid with MCM-41 support than the IL2/MCM-41 one. Considering imidazole and dipyriddy derivatives acting as N-containing ligands, we just guess that the interaction between ionic liquid with MCM-41 is possibly attributed to the noncovalent coordination effect from N element of ionic liquid with support, as seen in Figure 3S. Due to the IL1 molecule existing double N atom, the IL1 possesses stronger interaction with the support via the synergetic double coordination, relative to the IL2. Certainly, the true interaction between ionic liquid with the support is still unclear and needs further investigated. To sum up, it is considered that the IL1/MCM-41 sample possesses the enhanced interaction between ionic liquid with MCM-41 support, relative to the IL2/MCM-41 one.

The TG profiles of the parent and IL-supported MCM-41 samples are shown in Figure 7. Obviously, the weight loss appears distinctly over the IL1/MCM-41 and IL2/MCM-41 samples. Meanwhile, the difference value of weight losses between the MCM-41 and IL-supported MCM-41 is approximately equal to the loading amount of ionic liquid on MCM-41, as presented in Table 1S. Thus, the distinct decreasing of weight over IL-supported MCM-41 mainly belongs to the decomposition and burning of the ionic liquid substances. Moreover, the temperature of weight loss over IL1/MCM-41 occurs at *ca.* 324 °C, which is significantly higher than that of weight loss over IL2/MCM-41 (*ca.* 205 °C). This result demonstrates that the IL1/MCM-41 sample possesses more excellent thermal stability than the IL2/MCM-41 sample.

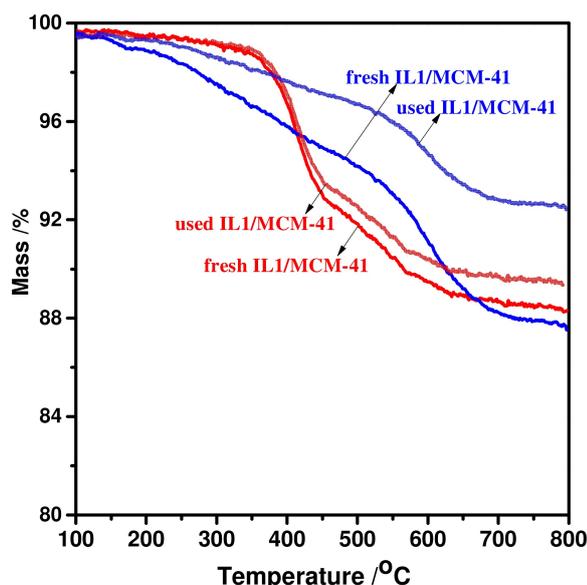


Figure 7. The TG profiles for the fresh and used catalysts.

2.2. Catalytic Activity

In the reaction of synthesizing quinoline, acid site is one of the most effective catalytic active sites for the process of hydrolysis as well as cyclization. As showed in Table 2, the catalytic activities of pure MCM-41, pure ionic liquid and IL-supported MCM-41 catalysts for synthesis of quinoline are evaluated. Obviously, few yield of quinoline is obtained over the pure MCM-41. This is mainly due that MCM-41 lacks sufficient acid sites as catalytic activity sites for the quinoline synthesis. Interestingly, 23.4% yield of quinoline is achieved over pure IL1, while 13.2% yield of quinoline is completed over pure IL2, indicating that IL1 shows better catalytic activity than IL2. However, the relatively low yield of quinoline over IL1 and IL2 is possibly ascribed to the poor compatibility between hydrophilic ionic liquid with lipophilic reactants. Apparently, yield of quinoline increase significantly after immobilization of ionic liquid on MCM-41; 70.2% and 48.4% yield of quinoline could be obtained over IL1/MCM-41 and IL2/MCM-41, respectively. This result illustrates that the immobilization of ionic liquid on the carrier improve catalytic activity of ionic liquid effectively. In addition, the addition of solvent could further increase the yield of quinoline. This is probably due that the reactants could form the homogeneous system, which favors the hydrolysis process of acrolein diethyl acetal with H₂O to acrolein as well as subsequent cyclization process. From the above results, it is concluded that the IL1/MCM-41 exhibits enhanced catalytic activity for synthesizing quinoline.

The effect of reaction temperature and time for quinoline are also investigated over IL1/MCM-41, as shown in Figure 8. From the Figure 8(a), one can see that the yield of quinoline increases as raising reaction temperature, achieving its maximums value of 73.7% at 120 °C, and then decreases distinctly. This is mainly due that, appropriate raising reaction temperature favors the reaction process of hydrolysis and cyclization, whereas further raising reaction temperature could increase the possibility of side-reactions, such as polymerization of acrolein because of its high chemical activity. Thus, the appropriate reaction temperature could help to promote the generation of quinoline. From the Figure 8(b), one can see that, as prolonging reaction time, conversion of acrolein diethyl acetal increases and reaches up to 100% at 12 h, whereas the yield and

Table 2. The catalytic performance of catalysts for synthesize quinoline.^[a]

Catalysts	Conditions [temperature, time]	Solvent	Yield ^[b] [%]
MCM-41	120 °C, 20 h	MeCN	trace
MCM-41	120 °C, 20 h	–	trace
IL1	120 °C, 20 h	–	23.4
IL2	120 °C, 20 h	–	13.2
IL1/MCM-41	120 °C, 20 h	MeCN	73.7
IL1/MCM-41	120 °C, 20 h	–	70.2
IL2/MCM-41	120 °C, 20 h	MeCN	63.5
IL2/MCM-41	120 °C, 20 h	–	48.4

[a] Reaction conditions: ADA (2 mmol), H₂O (2.5 mmol), aniline (3 mmol) and catalyst (10 wt % of ADA) were mixed and reacted under continuous stirring condition. [b] Quinoline determined by GC and its yield was calculated based on ADA.

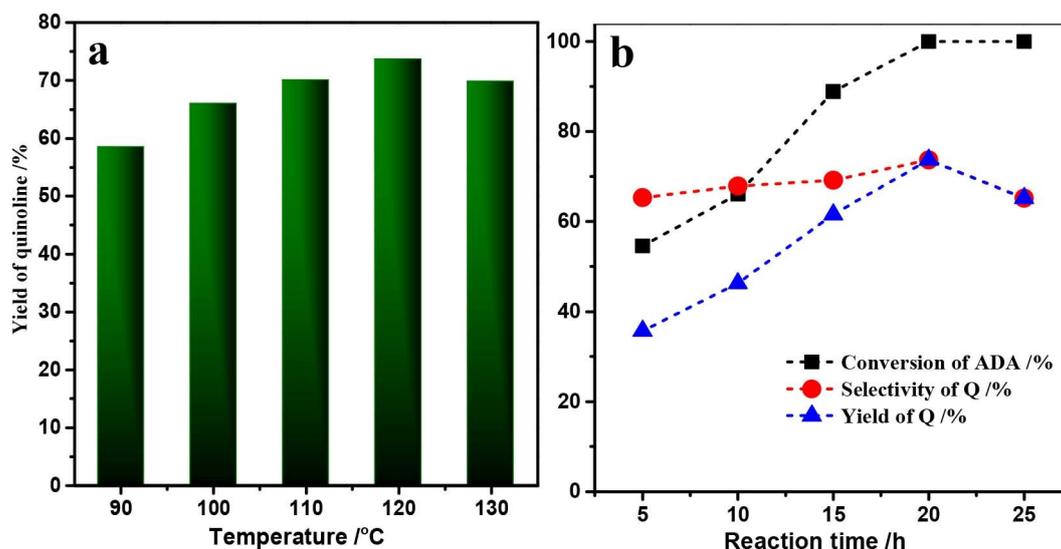


Figure 8. The effect of reaction temperature and time for quinoline.

selectivity of quinoline increases initially and subsequently decreases after 12 h. This result indicates that reaction time has significant influence on the selectivity of quinoline.

The stability of the IL1/MCM-41 and IL2/MCM-41 catalysts are exhibited in Figure 9. The used catalyst is separated from the reaction system, washed with acetone and finally dried in vacuum condition, and then the thus-obtained catalyst is employed in the next reaction. Obviously, the stability of catalytic activity maintains well over the IL1/MCM-41 catalyst while reduces distinctly over the IL2/MCM-41 one, as increasing the cycle times of catalyst. The relative activity could be preserved to 95% over the IL1/MCM-41 catalyst but decreased to 76% over the IL2/MCM-41 one, after using the catalysts for 5 times. The result reveals that the IL1/MCM-41 catalyst exhibits

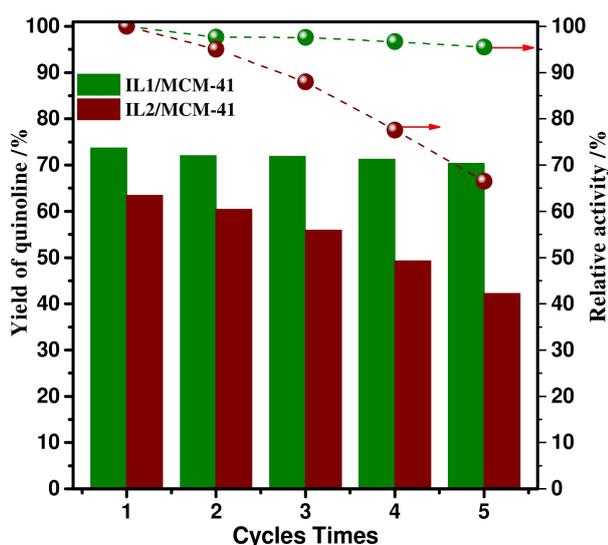


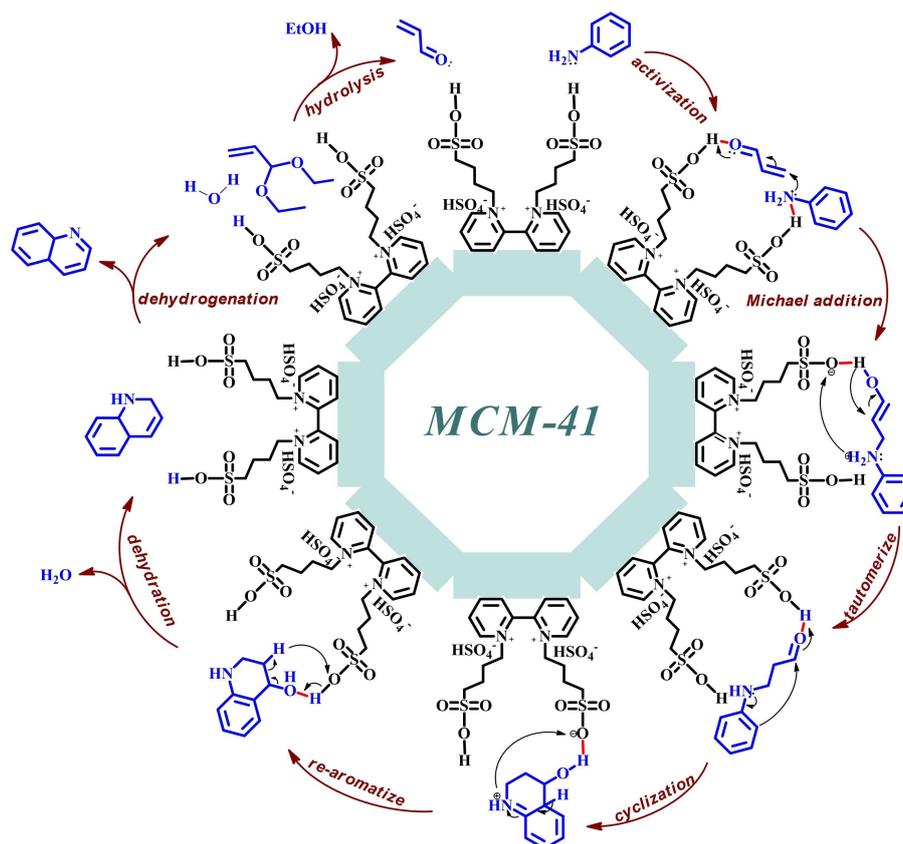
Figure 9. The stability of catalysts.

more excellent stability of catalytic activity than the IL2/MCM-41 one. We approximately estimate the loss rate of ionic liquid from MCM-41 carrier after using 5 times, and the results are listed in Table 1S. It is obvious that the loss rate of ionic liquid over IL1/MCM-41 is noticeably less than that over IL2/MCM-41 after 5 cycle times. Considering the acid sites on ionic liquid serving as effective catalytic active sites, it could be considered that the loss rate of ionic liquid from catalyst is responsible for the decreasing of catalytic activity. The low loss rate of IL1 from MCM-41 is most probably due to the stronger interaction between ionic liquid with MCM-41. As a result, the IL1/MCM-41 catalyst possesses remarkably enhanced stability of catalytic activity in this reaction.

As Comparison, the yield of desired quinoline over various catalysts between in this work and those reported in previous literatures are displayed in Table 2S.^[29,30,53,54] Obviously, among those various catalysts, the IL1/MCM-41 catalyst could obtained the highest yield of pure quinoline. Furthermore, compare to vapor-phase and microwave-assisted modes, the liquid-phase reaction condition is more mild in this work, and the heterogeneous IL1/MCM-41 catalyst can be separated readily and used repeatedly with good relative activity. Therefore, the heterogeneous IL1/MCM-41 catalyst exhibits significant potentiality as efficient and eco-friendly heterogeneous catalysts for the synthesis of desired quinoline.

2.3. Reaction Mechanism

The liquid-phase synthesis of quinoline from aniline and acrolein diethyl acetal actually belongs to the cascade reactions, consisting of the hydrolysis reaction of acrolein diethyl acetal with H₂O to acrolein and subsequent cyclization reaction with aniline to quinoline.^[30] From the catalyst evaluation results, it could be concluded that the gemini sulfonic ionic liquid (IL1)



Scheme 1. The possible reaction pathway of acrolein diethyl acetal and aniline to quinoline catalyzed by IL1/MCM-41 catalyst.

over MCM-41 exhibits more effective catalytic activity to generate quinoline than the single sulfonic ionic liquid (IL2) over MCM-41 under same reaction conditions. Because of the hydrolysis reaction of acrolein diethyl acetal can be easily proceeding over different acid sites, it suggested that the gemini acid sites of ionic liquid is more favorable to promote the cyclization reaction of acrolein and aniline to generate quinoline. Therefore, the possible mechanism relating to the cyclization process from acrolein and aniline to quinoline over IL1/MCM-41 was shown in scheme 1.

Firstly, the hydrolysis of acrolein diethyl acetal is easily proceeded to generate acrolein on acidic sites. Then, the acrolein is adsorbed and activated on the sulfonic acid site of ionic liquid, and meanwhile, the weakly basic aniline also could be adsorbed by the other sulfonic acid site of ionic liquid. As a consequence, the Michael addition could proceed smoothly. Thus, we guess that the synergistic effect of gemini acid site on ionic liquid could contribute to increase the possibility of Michael addition between acrolein with aniline. Subsequently, the cyclization reaction undergoes the tautomerization, ring-closure, re-aromatization, dehydration and dehydrogenation steps to form quinoline.

3. Conclusions

In this work, a novel 2,2'-bipyridine-based gemini sulfonic ionic liquid was firstly synthesized and then immobilized on MCM-41 support as green heterogeneous catalyst (named IL1/MCM-41), which was employed to catalyze the domino reaction of aniline and acrolein dimethyl acetal to yield quinoline via hydrolysis-heterocyclic-aromatization processes. Compared to the imidazole-type single sulfonic ionic liquid supported MCM-41 (named IL2/MCM-41), the IL1/MCM-41 presented higher catalytic activity and better reusability in Doebner-Von Miller reaction. The enhanced catalytic activity of IL2/MCM-41 was probably due to the synergistic catalytic effect of dual sulfonic acid group on IL2. Meanwhile, the superior reusability of IL2/MCM-41 was ascribed to the stronger interaction between dipyridine ring of ionic liquid with MCM-41 support. In conclusion, the heterogeneous IL1/MCM-41 catalyst exhibited good catalytic activity, readily separation and excellent reusability under mild reaction conditions, showing significant potentiality as efficient and eco-friendly heterogeneous catalysts for the synthesis of desired quinoline.

Highlight

1. A novel 2,2'-bipyridine-based gemini sulfonic ionic liquid was synthesized successfully.
2. Ionic liquid-immobilized MCM-41 catalyst exhibited excellent catalytic activity and reusability.
3. The synergistic catalytic action of dual sulfonic acid to quinoline was proposed.

Competing Financial Interest

The authors declare no competing financial interest.

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Conflict of Interest

The authors declare no conflict of interest.

Keywords: heterogeneous catalysis · ionic liquids · liquid phase synthesis · mesoporous materials · ordered mesopore · gemini sulfonic ionic liquid · immobilization · synergistic catalysis · quinoline

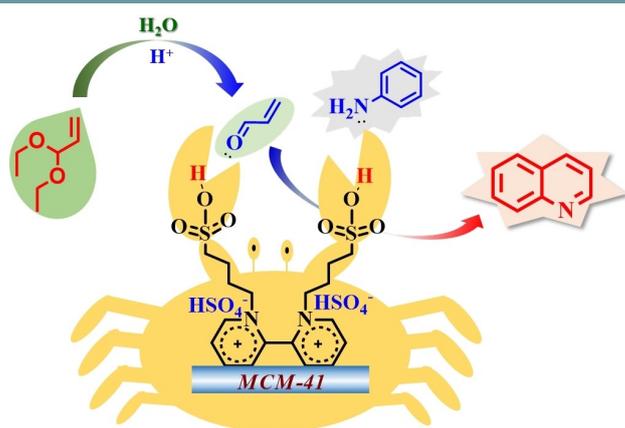
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**A Novel Gemini Sulfonic Ionic
Liquid Immobilized MCM-41 as
Efficient Catalyst for Doebner-Von
Miller Reaction to Quinoline**



Quinoline synthesis: A novel gemini sulfonic acidic pyridinium ionic liquid immobilized MCM-41 was successfully prepared as a green hetero-

geneous catalyst, which exhibited high catalytic activity and excellent reusability in quinoline synthesis.
