Accepted Manuscript

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S1381-1169(14)00149-6
http://dx.doi.org/doi:10.1016/j.molcata.2014.04.011
MOLCAA 9073
Journal of Molecular Catalysis A: Chemical
16-11-2013
4-4-2014
4-4-2014

Please cite this article as: J. Liu, Y. Liu, </sup>,Wu Yang, H. Guo, F. Fang, Z. Tang, Immobilization of phosphortungstic acid on amino-functionalized bimetallic Zr-La-SBA-15 and its highly catalytic performance for acetylation, *Journal of Molecular Catalysis A: Chemical* (2014), http://dx.doi.org/10.1016/j.molcata.2014.04.011

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Immobilization of phosphortungstic acid on amino-functionalized bimetallic Zr-La-SBA-15 and its highly catalytic performance for acetylation

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Abstract: Phosphotungstic acid (PW) catalysts supported on amino-functionalized Zr and La incorporated SBA-15 mesoporous materials(PW/H₂N-ZLS) were prepared by an impregnation procedure and their physicochemical properties were characterized by FT-IR, XRD, TEM, TG and N₂ adsorption-desorption isotherm techniques. It was found that the modified materials still preserved a desirable ordered two-dimensional P6 mm hexagonal structure and possessed high specific surface area, large pore volume and narrow pore size distribution and meanwhile the Keggin structure of heteopolyaniona could be retained. Moreover, these catalysts were found to be efficient heterogeneous catalysts for acetylation of anisole with acetic anhydride under microwave irradiation. High yields, short reaction times, easy work-up, easy availability and handling, eco-friendliness and reusability of the catalysts were the main aspects of the present method.

Keywords: PW; H₂N-ZLS; mesoporous materials; supported catalysts; microwave irradiation; acetylation

1. Introduction

The Friedel–Crafts acetylation reaction is a classical method for the preparation of aromatic ketones and it has been one of the most important basic reaction types in organic chemistry. It is a key step in the synthesis of numerous pharmaceuticals, natural products and versatile synthetic intermediates [1]. Traditionally, various homogeneous catalysts including Lewis or Brønsted acids, such as, H₂SO₄, BF₃, HF, AlCl₃ or FeCl₃, zirconia sulphated, have been used in this reaction, [2].

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However, most catalysts suffer from drawbacks of difficult separation after the reaction, therefore, they are incapable of recycling and reusing. Furthermore, some of them are corrosive and volatile and often cause the environment problems. Many efforts have been made to exploit the environmental-friendly catalytic technology for the target reaction. In recent years, use of heterogeneous catalysts in liquid phase reactions has received great attention due to their advantages such as high activity, selectivity, reusability, ease of separation, no corrosion or disposal of effluent problems, etc.

The applications of heteropoly acids (HPA) catalysts have attracted extensive interest in the last decade as solid acid catalyst [3-7]. Heteropoly acids (HPA), especially phosphotungstic acid (PW), have received great attention among the acid catalysts because of their high acid strength and selectivity properties [8, 9]. However, the main disadvantage of bulk PW is their very low surface area (< 10 m²·g⁻¹) and hence it becomes necessary to disperse PW on supports that possess large surface area. The use of SBA-15 mesoporous materials is attractive because it possesses well-ordered pore structures, high thermal stability and high surface area [10]. This would make the material become a suitable host for acid catalysts. There are some reports available on the modification of SBA-15 with HPA and its applications [11-20]. However, weak interaction between the PW and the support resulted in its leaching in polar media [21]. The reaction stabilities of the catalysts are still not satisfactory. Thus, it is necessary to further develop novel and facile methods to prepare supported PW catalysts, which could be applied in acetylation of organic compounds with high performance. Some important issues are considered, e.g. to improve the dispersion of the active species and the interaction between the active species and the supporter, to minimize the leaching of active species and to boost the reusability of catalysts.

In this present work, zirconium and lanthanum elements, at first, have been successfully incorporated into SBA-15 mesoporous material framework by a direct synthesis method. Then, PW was successfully anchored to amino- functionalized Zr and La incorporated SBA-15 mesoporous material (PW/H₂N-ZLS). The prepared catalyst (PW/H₂N-ZLS) showed a high catalytic performance for the acetylation of anisole with acetic anhydride. PW of various loadings supported on H₂N-ZLS were prepared by an impregnation method and characterized by Fourier-transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD), transmission electron microscopy (TEM), N₂ adsorption-desorption isotherm and thermo gravimetry (TG).

2. Experimental

2.1 Catalyst preparation

2.1.1 Mesoporous materials ZLS preparation

The catalytic ZLS materials were synthesized by the following procedures. 2 g of pluronic P123, as a template agent, was dissolved in 100 g of deionized water under vigorous stirring at 35 for 2h. The appropriate amount of tetraethyl orthosilicate TEOS (silica source), $ZrOCl_2\cdot8H_2O$ and La(NO₃)₃·6H₂O (precursors) were added into above solution under vigorous stirring. The molar ratio of P123/TEOS/H₂O/ ZrOCl₂·8H₂O/ La(NO₃)₃·6H₂O was maintained as 0.01: 1: 170: 0.05: 0.05. The mixed solution was continuously stirred for 20h, and finally crystallized in a teflon-lined autoclave at 100 for 24h. The white product was filtered, washed abundantly with deionized water and absolute ethanol to pH 7 respectively, and then dried at 60 in vacuum oven for 8h. The template agent was removed from the as-synthesized product through solvent extraction using HCl/EtOH solution (1g of sample in 5mL/150mL) for 24h. The obtained sample was dried at 60 in vacuum oven for 6h. For comparison, conventional SBA-15 was also prepared according to Zhao's synthesis procedure [10].

2.1.2 Different amino-functionalized ZLS (H₂N-ZLS) preparation

The preparation of amino-functionalized mesoporous materials H₂N-ZLS was performed by post-grafting procedure. Two different aminosilanes were used: 3-(trimethoxysilyl)propylamine $[(H_2N-(CH_2)_3-Si(OCH_3)_3)](APTS)$, N-[3-(trimethoxysilyl)propyl]ethylenediamine $[(H_2N-(CH_2)_2-NH-(CH_2)_3-Si(OCH_3)_3)](AAPTS)$. Typically, 1 g of ZLS sample was suspended in 60 mL of dried toluene and then 8 mmol·g⁻¹ of organosilane (APTS or AAPTS) was added under the strong stirring. This suspension system was then stirred under refluxing at 75 for 24 h. The resulting solid material was filtered and washed abundantly with dried toluene and isopropyl alcohol. After drying at 80 in vacuum oven overnight, the resulting solid was re-suspended in 0.2M HCl for 6 h at room temperature for protonation followed by filtering and vacuum drying at 50 for 12 h. The obtained samples were named as H₂N-ZLS-N and H₂N-ZLS-NN, respectively.

2.1.3 Immobilization of PW on H₂N-ZLS (PW/H₂N-ZLS)

The supported PW catalyst was prepared by a method of incipient wetness. A typical process was as follows: 2 g of amino-functionalized mesoporous material (H₂N-ZLS-N or H₂N-ZLS-NN) was stirred in 5 mL of deionized aqueous solution containing 6.5×10^{-4} mol (1.87g) of PW at 60

for 8h. The resulting solid catalysts, PW/H₂N-ZLS-N or PW/H₂N-ZLS-NN, were then filtered and washed with methanol three times to remove unanchored PW and dried at 95 for 3h. The catalyst loading capacity of H₂N-ZLS was calculated to be about 30wt%. The obtained samples were denoted as 30%PW/H₂N-ZLS-N and 30%PW/H₂N-ZLS-NN, respectively. The supported catalysts PW/H₂N-ZLS-N and PW/H₂N-ZLS-NN with 20% and 40% loading capacity were prepared according to the above steps. They were denoted as 20%PW/H₂N-ZLS-N, 40%PW/H₂N-ZLS-N , 20%PW/H₂N-ZLS-NN and 40%PW/H₂N-ZLS-NN, respectively. PW supported on unmodified ZLS was also synthesized through incipient wetness under similar conditions, the resulting material was denoted by 30%PW/ZLS. The preparation process of the catalyst was showed as Scheme 1.

2.2 Catalysts characterization

FT-IR spectra were recorded on a Digilab FTS3000 FT-IR spectrometer using the KBr wafer technique. XRD patterns were obtained with an X'Pert/PRO diffractometer in the reflection mode using Cu K α radiation source with a resolution of 0.02° and scanning speed of 0.5°/min. N₂ adsorption–desorption isotherms were measured on a Micromeritics ASAP 2020 analyzer. The samples were first degassed at 110 for 5h before adsorption measurements. TEM images of the samples deposited on carbon–copper grids were taken on a JEM 1200EX microscope. TGA were performed by means of a PerkinElmer PE6300 series instrument, in the temperature range from 25 to 800 , with a heating rate of 10 /min under nitrogen atmosphere.

2.3 Catalytic tests

In a round-bottomed flask (50mL), anisole (1.08g, 10mmol), acetic anhydride (2.04g, 20mmol), dichloromethane (10mL) and PW/H₂N-ZLS or PW/ZLS (0.6g) were added respectively. Then the flask was transferred into the modified microwave oven fitted with a condenser and subjected to microwave irradiation at the power of 450W for 8 min. The progress of the reaction was monitored by TLC (petroleum ether:ethyl acetate=5:1 as eluent). After completion of the reaction, the catalyst was filtered off and the filtrate was evaporated to remove the solvent under reduced pressure. Finally, the selectivities and conversions were determined by a shimadzu GC 2010 equipped 15m-0.5mm, RTX-1 capillary column and FID detector.

3. Results and discussion

3.1 Characterization of the catalysts

3.1.1 XRD patterns

Fig. 1 showed small angle XRD patterns of the 3-aminopropyl-functionalized ZLS (H₂N-ZLS-N and H₂N-ZLS-NN) and heterogeneous catalysts with different PW loading (PW/H₂N-ZLS-N, PW/H₂N-ZLS-NN and PW/ZLS) in the 20 range of 0.6-5°. Three XRD peaks corresponding to (100), (110) and (200) reflections were exhibited, which can be indexed to a two-dimensional hexagonal lattice of the mesoporous material ZLS. Although the relative intensities of the reflections had slight decrease, the well-resolved reflections at (110) and (200) of H₂N-ZLS-N and the PW-supported H₂N-ZLS-N indicated that they remained mesoporous structural characterizations. Generally, the appearance of the main reflection (100) suggested the existence of mesopore in PW/H₂N-ZLS-N sample. Therefore, this finding demonstrated that the mesoporous structure of ZLS was not destroyed after the aminosilylation and immobilization of PW. In contrast, the intensities of all the peaks of the N-[3-(trimethoxysilyl)propyl] ethylenediamine modification (H₂N-ZLS-NN) and PW immobilization (PW/ H₂N-ZLS-NN) decreased obviously. It indicated that the regularity of the structure H₂N-ZLS-NN and PW/ H₂N-ZLS-NN became rather poorer. The channels in the ordered hexagonal arrangement were partially collapsed, in some degree, into disordered and wormhole-like packings. These findings demonstrated that the long-range mesoporous ordering of the parent support ZLS was much affected by the N-[3-(trimethoxysilyl)propyl]ethylenediamine modification (H₂N-ZLS-NN) and PW immobilization (PW/ H₂N-ZLS-NN). The immobilization of PW inside ZLS (PW/ZLS) channels resulted in a slight decrease in the intensity of all diffractions, which was probably attributed to the pore filling of the host material with PW.

3.1.2 Nitrogen sorption isotherms

For the N₂ adsorption-desorption isotherms of the ZLS, 3- aminopropyl-functionalized ZLS (H₂N-ZLS-N and H₂N-ZLS-NN), 3- aminopropyl-functionalized ZLS loaded PW catalysts (PW/ H₂N-ZLS-N, PW/H₂N-ZLS-NN) and PW/ZLS (Fig. 2a), typical irreversible type IV adsorption isotherms with a H1 hysteresis loop as defined by IUPAC [22] were observed. As we can see, the surface modified and PW immobilized samples retained the same shape of the isotherms as that of ZLS and the adsorption isotherm showed a sharp inflection of the relative pressure between 0.65 and 0.85, which was a characteristic capillary condensation for mesoporous materials. On the other hand, the BJH pore size distribution was showed in Fig. 2b. The corresponding textural parameters calculated by N₂ adsorption-desorption isotherms were presented in Table 1. The results showed that aminosilylation of the surface and follow-up immobilization of PW accounted for the decrease in pore volume and surface area. This loss of specific surface area can be the result of strong adsorption of PW that did not block the pores and did not contribute to the surface area of the supports. The surface area of the samples up to 30% loaded PW was more than

123m².g⁻¹ and the pore volume was 0.44cm³·g⁻¹ (Table 1), which was sufficient for catalytic performance. The above characterization results confirmed that PW were located inside the channels and the mesoporous channels were still preserved. In all cases, correlation coefficients above 0.999 were obtained.

3.1.3 FT-IR analysis

FT-IR spectra could be used to investigate the structure characteristics of the samples and to monitor the essence of surface interaction between PW and H₂N-ZLS or ZLS. Fig. 3 showed IR patterns of ZLS (a), H₂N-ZLS-N (b), PW/H₂N-ZLS-N (c) and PW/ZLS (d). ZLS showed IR bands at ca. 457 cm⁻¹, 795 cm⁻¹, 1074 cm⁻¹ corresponding to the rocking, bending (or symmetric stretching) and asymmetric stretching of the inter-tetrahedral oxygen atoms in SiO₂ of ZLS, respectively. In the spectrum of H₂N-ZLS-N, the bands approximately at 2933 cm⁻¹ and 1486 cm⁻¹ could be assigned to CH stretching vibration and asymmetric stretching vibration of the methylene groups. Two other IR bands at 1512 cm⁻¹ and 687 cm⁻¹ belonged to N-H deformation vibration and bending vibration of protonated amino groups, which indicated that part of the amino groups of 30%PW/H₂N-ZLS-N were protonated. From the FT-IR analysis, it was found that no structural collapse of pore structures occurred by the incorporation of PW into Si-O bonds. The IR bands at approximate 987 cm⁻¹ (terminal W=O), 890 cm⁻¹ and 808 cm⁻¹ (W–O–W) were clearly observed for 30%PW/H₂N-ZLS-N catalyst. This indicated that the primary structure of PW was preserved even after being supported on H₂N-ZLS-N, which was in accordance with the XRD analysis. *3.1.4 TEM morphologies*

TEM images provided further evidence of the stability of the mesostructure samples after modification of ZLS. In Fig. 4, the exemplified TEM images of the 30%PW/H₂N-ZLS-N further demonstrated that the hexagonal ordered channel structure of ZLS had no significant change after aminosilylation of ZLS and immobilization of PW into the channels. The polyoxometalates filled in the pores of ZLS were shown by the highly contrast lines in comparison with pure ZLS. Fig.4(d) was a TEM image of deactivated 30%PW/H₂N-ZLS-N. It illustrated that the regularity of the structure of 30%PW/H₂N-ZLS-N became disordered to some extent and wormhole-like packings. However, porestructure was still preserved.

3.1.5 TGA profiles

The thermal stability of 30%PW/H₂N-ZLS-N, H₂N-ZLS-N and 30%PW/ZLS, ZLS mesoporous materials was determined by TGA and their TG curves were illustrated in Fig. 5. The weight loss of H₂N-ZLS-N was about 7.5% from 150 to 350 , which was caused by the complete decomposition and combined combustion of protonated amino groups. It was obvious that 30%PW/H₂N-ZLS-N possessed a higher thermal stability than 30%PW/ZLS. The weight losses above 300 s in 30%PW/H₂N-ZLS-N and H₂N-ZLS-N were possibly due to further framework condensation, as observed in other mesoporous silica [23]. The synthesized sample possessed a weight loss about 13.8% in the range of 100-800 that was attributed to the decomposition of organic groups incorporated in the material. The obtained results were in good agreement with the organic content determined by elemental analysis.

3.2 Catalytic performance

Catalytic activities of the materials in acetylation of anisole and acetic anhydride with microwave irradiation were given in Table 4. The detailed reaction scheme was shown in Scheme 2. Lately, the use of microwave irradiation in synthesis organic chemistry has become more popular [24] and microwave irradiation has been used for many organic reactions. The acceleration of the reactions by microwave mainly resulted from two effects: thermal effect and specific microwave effect [25, 26]. Thermal effect (dielectric heating) resulting from material-microwave interaction allowed fast and uniform distribution and conversion of microwave energy into heat. Specific microwave effect can be expected for the polar mechanism, when the polarity was increased during the reaction from the ground state (GS) towards the transition state (TS). For the reactions under investigation, it seemed that stabilization of the transition state was more effective than that of the ground state and therefore, the reactivity was enhanced as a result of decreased activation energy.

In order to select approximate microwave power, the reaction was conducted at different power level from 65 W to 650 W (Fig. 6). It was observed that 455 W of power level was the most promising for the reaction because lower power level gave poor yield and higher power lead to destroy of the substrate. In this work, we could find that the oil-bath heating method took much longer to complete the reactions and the selectivities were often lower than the corresponding microwave irradiation reactions. These clearly showed that microwave irradiation improved the results.

The solvent effect on the acetylation was also investigated (Table 2). Several solvents were tested for the reaction such as CH_3CN , DMF, CH_2Cl_2 and THF. For CH_3CN , the conversion was very low though selectivity was better. The reaction can not proceeded in DMF. CH_2Cl_2 and THF could exhibit higher selectivity and conversion. Considering the environment effect, CH_2Cl_2 was chosen in the experiment.

The optimal reaction time was also investigated. It was found that the acetylation of anisole with acetic anhydride could be completed within 8 min under microwave irradiation to give the corresponding p-methoxy acetophenone in excellent yield.

The effect of anisole to acetic anhydride mole ratio was studied at 1:1, 1:1.5, 1:2 1:2.3,1:2.5 and 1:2.8 by keeping the catalysts loading constant. The conversion of anisole increased with an increase of the amount of acetic anhydride, whereas, selectivity towards *p*-methoxy acetophenone was found to decrease with an increase in concentration of acetic anhydride. 1:2 was found to be the optimal mole ratio of anisole to acetic anhydride for the acetylation (Fig. 7). Therefore, all further experiments were studied by keeping a mild anisole: acetic anhydride mole ratio of 1:2.

The results of acetylation with different catalysts were shown in Table 3. The catalytic activities of Lewis acids such as AlCl₃/SBA-15 was first tested, but little product was observed. The PW/H₂N-ZLS-N could efficiently catalyze Fries-Crafts reaction to give the satisfying selectivity and high yield compared with the data of literature [27-30]. In contrast, the PW exhibited an intermediate level of activity, which was significantly lower than the PW/H₂N-ZLS-N. Thus, the current catalysts were much better than others.

As listed in Table 4, the 30%PW/H₂N-ZLS-N sample exhibited the highest product yield and good selectivity, meaning that suitable concentration of PW was advantageous to the reaction. In this case, a significant difference was found among these catalysts as a function of the PW loading. The *p*-methoxy acetophenone yield decreased in the following order: 30%PW/H₂N-ZLS-N (86.4%)>40%PW/H₂N-ZLS-N (82.9%)>20%PW/H₂N-ZLS-N (68.8%). This increase in yield can be ascribed to their higher acidity. Due to the less amounts of active site in the sample, 20%PW/H₂N-ZLS-N showed less product yield. In the case of 40%PW/H₂N-ZLS-N the product yield was found to be less compared to 30%PW/H₂N-ZLS-N catalyst, which was probably due to the blocking of active sites by the dense Keggin structure, thereby giving diffusional constraints [31]. It was noteworthy that in all the reactions the region-selectivity and conversion using the

H₂N-ZLS-N supported PW catalytic system were the highest, whereas, 30%PW/ZLS, as a catalyst, which contained mainly Brønsted acidic sites, only showed moderate yield (81.4%) and lower selectivity than that of the H₂N-ZLS-N-based catalyst. It was intriguing that introducing protonated amino groups into ZLS framework would promote the reaction between anisole and acetic anhydride in terms of higher yield and high selectivity. The reaction with the present H₂N-ZLS-N based catalysts was improved effectively as compared to PW/ZLS catalysts. From these reasons, it can be deduced that high dispersion of PW onto H₂N-ZLS-N and the large surface area with suitable pore size might account for the high catalytic activity. In addition, the introduction of lanthanum and zirconium into SBA-15 framework to create a lot of new activity sites, which can also enhance the catalytic activity and selectivity of the current catalysts[32,33].Since 30%PW/H₂N-ZLS-N catalyst exhibited the highest *p*-methoxy acetophenone yield in our experiments, this sample was chosen for the further study.

In addition, it could be found that when a higher content of PW/H_2N -ZLS-NN was used, the total nitrogen content increased, but the BET surface area decreased (Fig. 2 and Table 1). The higher packing of aminated organosilanes prevented the interaction of amino groups and nearby chains, and consequently decreased the efficiency of the process (Table 4).

The reuse ability of catalysts was also studied. The catalyst could be so easily separated by filtering that the recovery and reuse of the catalyst could be very convenient. The selectivity and conversion with the current catalyst only decreased a little as shown in Fig. 8. This is because that the protonated amino group on ZLS effectively improved the stability of the immobilizing PW. As a comparison, even though PW supported unmodified ZLS catalyst showed the same anisole conversion and *p*-methoxy acetophenone yield as 30%PW/H₂N-ZLS-N in the first run, the leaching of PW from 30%PW/ZLS was significant. 30%PW/ZLS after the fourth run almost showed no catalytic activity.

4. Conclusion

Phosphotungstic acid supported bimetallic mesoporous material Zr-La-SBA-15 was successfully synthesized with a simple impregnation method and this material maintained a good inherent ordered hexagonal channel structure of SBA-15. Under microwave irradiation, the prepared material showed a high catalytic activity and selectivity for the acetylation of anisole and acetic anhydride. Besides, this new methodology still had some outstanding advantages, such as

the reusability of the catalysts, the operational simplicity, fast reaction and green synthesis avoiding toxic reagents. Thus, it provided a better and more practical alternative to the existing methodologies for the synthesis of p-methoxy acetophenone.

Acknowledgements

The authors gratefully acknowledged the financial support from the National Nature Science Foundation of China (No. 20873101) and Key Lab of Eco-Environment Related Polymer Materials of MOE, China.

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Figure captions

Scheme 1 The preparation scheme of the mesoporous materials PW/H2N-SBA-15

Scheme 2 Catalytic acetylation of anisole with acetic anhydride by phosphotungstic acid supported on amino-functionalized Zr-La-SBA-15

Fig. 1. Small angle XRD patterns of (a) H2N-ZLS-N, 30%PW/H2N-ZLS-N, 20%PW/H2N-ZLS-N, 40%PW/ H2N-ZLS-N and 30%PW/ZLS (b) H2N-ZLS-NN, 30%PW/H2N-ZLS-NN, 20%PW/H2N-ZLS-NN and 40%PW/ H2N-ZLS-NN

Fig. 2. (a) N2 adsorption-desorption isotherms and (b) pore size distributions of ZLS, H2N-ZLS-N,

30%PW/H2N-ZLS-N, 30%PW/H2N-ZLS-NN and 30%PW/ZLS

Fig. 3. FT-IR spectra of ZLS, H2N-ZLS-N, 30%PW/H2N-ZLS-N, 30%PW/ZLS

Fig. 4. TEM Images of 30%PW/H2N-ZLS-N (a) perpendicular channel, (b) parallel channel (c) live FFT and (d) deactivated 30%PW/ZLS-N

Fig. 5. TG curves of (a) ZLS and 30%PW/ZLS and (b) H2N-ZLS and 30%PW/ H2N-ZLS

Fig. 6. Effect of microwave power on the yield of acetylation of anisole with acetic anhydride catalyzed by 30%PW/H2N-ZLS-N

Fig. 7. The effect of mole ratio of acetic anhydride to anisole on yield of p-methoxy acetophenone Fig. 8. Comparison the reuse ability of 30%PW/H2N-ZLS-N and 30% PW/ZLS in acetylation of anisole with acetic anhydride

	BET surface	Pore size	Pore	Ŀ
Sample name	area	diameters ^a	volume ^b	d ₁₀₀
	(m^2/g)	(nm)	(cm^3/g)	(nm)
ZLS	898	6.65	1.34	6.64
H ₂ N-ZLS-N	346	5.86	0.62	5.67
30%PW/H2N-ZLS-N	123	5.16	0.44	5.09
30%PW/H2N-ZLS-NN	16	3.45	0.57	3.54
PW/ZLS	932	6.95	1.4	6.93

Table 1 Textural properties of the samples.

a, b. Calculated from the $N_{\rm 2}$ adsorption branch of the isotherms by the BJH method with

Halsey equation.

F actor	Q.1t	$C_{\rm eff}$	Selectivity of <i>p</i> -methoxy		
Entry	intry Solvent	Conversion(%)	acetophenone (%) ^b		
1	CH ₃ CN	50.0	85.1		
2	DMF	30.0	50.2		
3	CH_2Cl_2	88.2	96.5		
4	THF	88.0	95.2		

Table 2 PW/H₂N-ZLS-N catalyzed the acetylation of anisole with acetic anhydride in different solvents^a.

a. All reactions of anisole (10mmol), acetic anhydride (20mmol) were carried out under

microwave irradiation for 8 min.

b. Conversion and selectivity were measured by GC.

Entry	Catalyst	Amount of	Time	Yield of <i>p</i> -methoxy	
		Catalyst(mmol%)	(min)	acetophenone $(\%)^{b}$	
1	AlCl ₃ /SBA-15	10	8	44.2	
2	PW	10	8	62.5	
3	PW/NH ₂ -ZLS-N	10	8	86.4	
4	0.5K/Beta [29]			32.2	
5	19-WO ₃ /ZrO ₂ [30]			82.0	

Table 3 The acetylation of anisole with acetic anhydride catalyzed by different catalysts^a.

a. All reactions of anisole (10mmol), acetic anhydride (20mmol) were carried out in a solution of

CH₂Cl₂ under microwave irradiation.

b. Yields refered to the isolated products and were measured by GC.

Reaction conditions	T	Anisole	<i>p</i> -methoxy acetophenone	
	Time	conversion(%) ^a	Selectivity (%) ^a	
30%PW/H2N-ZLS-N	4min	54.2	81.2	
30%PW/H2N-ZLS-N	6min	70.3	87.8	
30%PW/H2N-ZLS-N	8min	87.5	98.7	
30%PW/H2N-ZLS-N	10min	88.2	96.5	
20%PW/H2N-ZLS-N	8min	72.3	95.2	
40%PW/H2N-ZLS-N	8min	84.3	98.3	
20%PW/H2N-ZLS-NN	8min	28.7	88.5	
30%PW/H2N-ZLS-NN	8min	43.2	90.4	
40%PW/H2N-ZLS-NN	8min	40.3	90.1	
30%PW/ ZLS	8min	87.3	93.2	

Table 4 Catalytic performances of various catalysts for acetylation of anisole with acetic anhydride with microwave irradiation method.

Anisole conversion and *p*-methoxy acetophenone selectivity were determined by GC.

Highlights :

- 1. PW/H_2N -ZLS is synthesized with a simple impregnation method.
- 2. The material has a good inherent ordered hexagonal channel and Keggin structure.
- 3. The acetylation of anisole with acetic anhydride was studied under MW condition.
- 4. The material shows superior catalytic activity.





(b)



(b)







(c)

Cook Cook

(d)









Scheme 1

ACCEPTED MANUSCRIPT



