RESEARCH ARTICLE

Fabrication of HPA-ZSM-5 and their successful application to the recyclable heterogeneous catalyst for the smooth synthesis of spiro-pyrido-pyrimidine indoline derivatives

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ABSTRACT

A beneficial and efficient one-pot three-component approach for the synthesis of spiro cyclic 2-oxindole derivatives has been described by the reaction of isatins, cyclic-1,3-diketones and 6-amino-1,3-dimethyluracil in the presence of highly active HPA-ZSM-5 microporous catalyst. The zeolite catalyst has been synthesized and the catalyst has been thoroughly characterized by X-ray diffraction (XRD), field emission scanning electronic microscopy (FE-SEM), Fourier transform infrared (FT-IR), energy dispersive spectroscopy (EDS) and N2-adsorption analysis. HPA-ZSM-5 catalyst exhibited exceptional recyclability at least for 6 times and the surface acidity was not significantly changed. The best results were gained in H2O and we found the convincing results in the synthesis of spiro-pyrido-pyrimidine in the presence of HPA-ZSM-5 (10 mg) under ultrasound irradiation (40W). Experimental simplicity, wide range of products, excellent yields in short reaction times and low catalyst loading are some of the substantial features of this procedure. The present catalytic method is extensible to a wide diversity of substrates for the synthesis of a variety-oriented library of spiro-pyrido-pyrimidine indoline derivatives.

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INTRODUCTION

Nowadays, solid acid catalysts, which are recyclable and readily separable from the reaction system, offers the opportunity to reduce the impact on the environment and increase industrial interest for the liquid phase acid catalytic process [1-3]. Heteropolyacids (HPAs) have polyoxometalate inorganic cage structures, which may adopt the Keggin form with the general formula $H_3MX_{12}O_{40}$, where M is the central atom and X the heteroatom. Typically M can be either P or Si, and X = W or Mo [4]. Heteropolyacids have proved to be the alternative of traditional acid catalysts, such as sulfuric acid and aluminum chloride, due to their strong acidity and harmless for environmental. The low surface area (~5 m^2/g), high solubility in polar systems, which thus results in separation problems and the lower thermal stability of pure HPA, have severely hindered its applications [5, 6]. It is necessary to have a support in which they can be structurally incorporated with uniform shapes, sizes and specific surface area. Immobilization of HPAs on a silica support gives more stability and enhanced catalytic activity [7, 8]. Among the common known Keggin-type HPAs, we selected Phosphomolybdic acid ($H_3PMo_{12}O_{40}$; PMA), in anhydrous acid form. Its effectiveness as a catalyst has been explored in various organic transformations including aza-Diels–Alder reactions [9]. deprotection of ethers [10], Hydrolysis of Acetonides [11], Acetylation of Alcohols, Phenols, and Amines [12], Ferrier rearrangement [13], polymerization reaction [14] and aza-Piancatelli rearrangement [15]. There are various carriers such as amorphous silica [16] or a porous supports including zeolite Y and ZSM-5 [17, 18] ordered mesoporous silica [19, 20] (e.g.

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SBA-15 or MCM-41). In this context, among different solid supports, nanocrystalline ZSM-5 zeolite is most preferred because of its many advantageous properties such as high surface area with different active sites, small pore sizes, a short diffusion path, excellent chemical and thermal stability, and good accessibility [21]. ZSM-5 zeolites are used in a variety of applications in industry, environment and medicine [22, 23]. In general, the surface of ZSM-5 zeolites has two types of active sites, Bronsted acid sites and Lewis acid sites. The Bronsted acid sites include the terminal silanol groups on the external surface and the bridging hydroxyl groups (Si-OH-Al), which are located at the channel intersections, while the Lewis acid sites, which are electron acceptors, refer to extra-framework aluminum species [24-26].

These days, there has been considerable growth of interest in the synthesis of spirooxindole derivatives (Fig. 1) because of the wide-ranging biological activity associated with them such as antibacterial, antifungal, anti-inflammatory, and antipyretic activities [27, 28].

As well as, a large number of pyrimidine derivatives consist of barbituric acid and 2-aminouracil have attracted great interest for their biological activities and applications in medicine and therapeutics [29, 30]. In this context, the synthesis of this important ring system fused with spirooxindole remains a topic of current interest. Various methods for the preparation of spirooxindole derivatives have been reported [30-35]. However, some of these methods suffer from tedious synthetic routes, long reaction time, drastic reaction conditions, toxicity, corrosiveness, cost, as well as unrecoverable of catalyst. Thus, we want to develop an alternative protocol for the preparation of these spiro-pyrido-pyrimidine indoline derivatives with enhanced synthetic scope and better reaction profiles, thereby satisfying several green chemistry aspects. Ideally, utilizing environmental and green catalysts which can be easily recycled at the end of reactions has obtained great attention in recent years [36-39]. Accordingly, we herein report an ultrasound-promoted expedient and green practical method to access functionalized spiro-pyrido-pyrimidine indoline derivatives from the one-pot multicomponent reaction between 6-amino-1,3-dimethyluracil (**1**), isatin (**2**) and 1,3-diketone (**3,4,5,6**) using HPA-ZSM-5 catalysis in aqueous system (Scheme 1). The notable advantages of this present protocol compared to the earlier method are broader substrate scope, reduced reaction time in minutes, energy-efficiency occurring at ambient temperature, use of H_2O as solvent, reusability of reaction media and large-scale synthetic applicability.

Newly, ultrasound irradiation has been in broad use as a green tool in organic synthesis due to its several interest, for instance energy savings, enhancement of reaction rates, and the enhancement in the mass transfer and product selectivity [40, 41]. The use of aqueous system as green solvent, effective application of ultrasonication in expediting reaction rate, employing reusable catalyst for the smooth synthesis, beneficial application of one-pot multicomponent reaction (MCR) strategy, and ambient reaction conditions are, thus, the steps forward to the cause of green and sustainable chemistry.

EXPERIMENTAL SECTION

Materials

NMR spectra were recorded on Bruker Avance-400 MHz spectrometers in the presence of tetramethylsilane as internal standard. The IR spectra were recorded on FT-IR Magna 550 apparatus using KBr discs. Melting points were

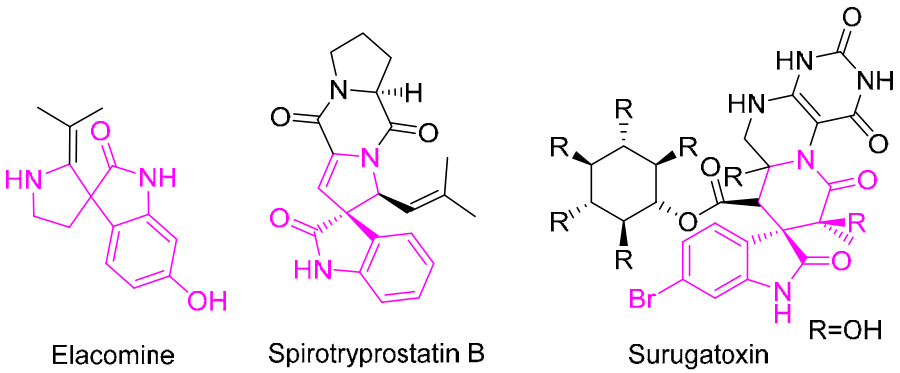
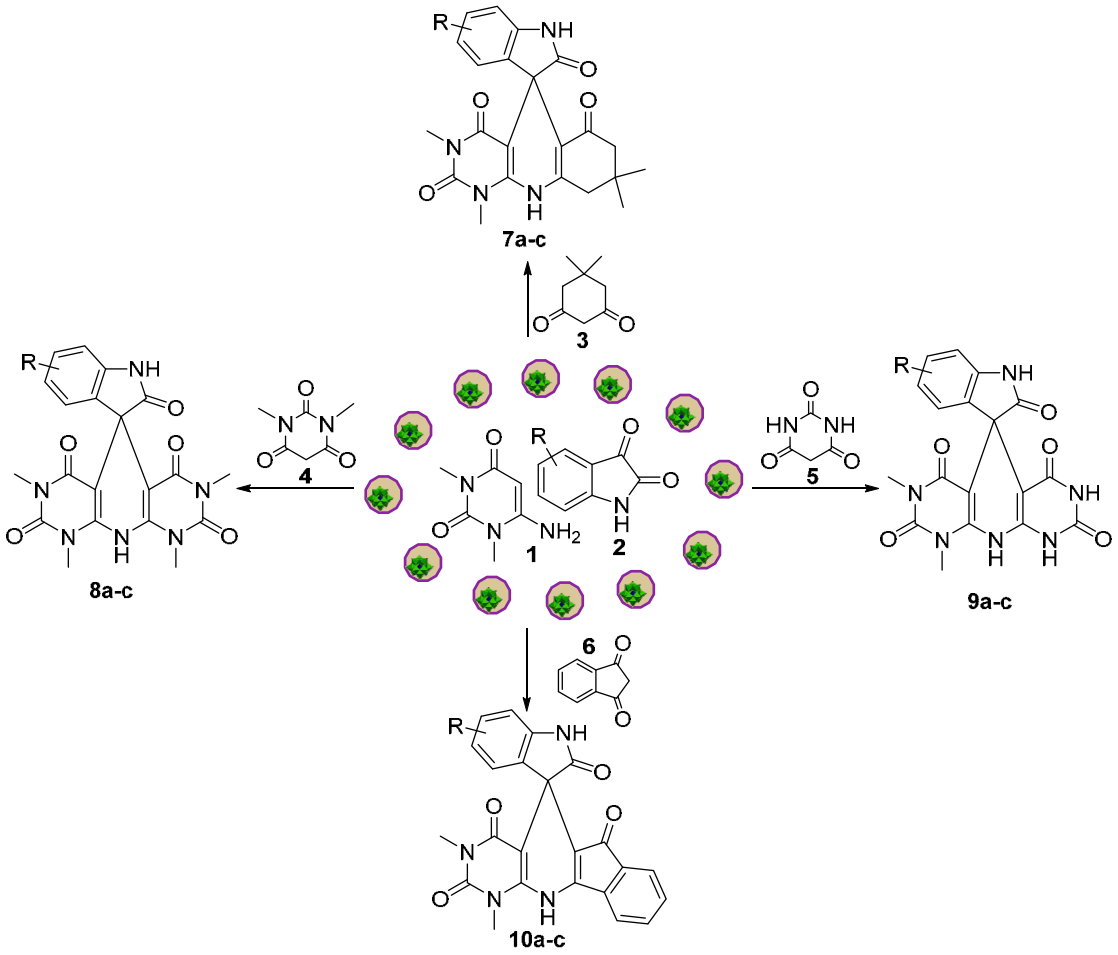


Fig. 1. Reported biologically active spirooxindole-based molecules.



Scheme 1.Synthesis of spiro-pyrido-pyrimidine indoline derivatives

determined on Electro thermal 9200 and are not corrected. The elemental analyses (C, H, N) were obtained using a Carlo ERBA Model EA 1108 analyzer. The XRD patterns were recorded on an X-ray diffractometer (PHILIPS, PW 1510, Netherland) using Cu-Kα radiation (λ = 0.154056 nm) in the range 2θ = 0.8–10°. Field Emission Scanning electron microscope (FE-SEM) of nanocatalyst was visualized by SEM (MIRA3). Energy-Dispersive X-ray Spectroscopy (EDS) measurement was carried out with the SAMX analyser. The N_2 adsorption/desorption analysis (BET) was performed using an automated gas adsorption analyzer (BEL SORP mini II).

Methods

Preparation of ZSM-5

Zeolite precursor was prepared by adding tetrapropylammonium hydroxide (TPAOH), tetraethyl orthosilicate (TEOS) to a mixed aqueous solution of aluminium isopropoxide [Al(*i*Pro)$_3$] and NaOH with stirring. The mixture was converted to gel. The gel was stirred for 20 h. The mole composition of the gel was $1Al_2O_3$:$46SiO_2$:$4TPA$:$5Na_2O$:$2500H_2O$. The resulting gel was sealed in Teflon-lined autoclaves and heated at 165 °C for 72h. The solid product was recovered by filtration, washed by deionized water for several times, dried in an oven at 100 °C overnight. The as-synthesized material was then calcined at 550 °C for 8h to remove the templates.

Preparation of HPA-ZSM-5

ZSM-5 Zeolites (1 g) was added to the solution of 0.3 g of phosphomolybdic acid (HPA) in ethanol (25 mL) and the reaction mixture was stirred for 24 h. The mixture was filtrated, washed by deionized water for several times, dried in an oven at 100

°C overnight. The as-synthesized material was subjected at 400 °C for 2h to product HPA-ZSM-5.

General procedure for the preparation of spiro-pyrido-pyrimidine indoline derivatives

A mixture of isatins (1 mmol), 6-amino-1,3-dimethyluracil (1 mmol), cyclic-1,3-diketones (1 mmol) and water (10 ml) in the presence of highly active HPA-ZSM-5 microporous catalyst (10 mg) was sonicated at 40 W. After completion of the reaction, progress of reaction was monitored using TLC (eluent EtOAc/n-hexane, 1:3), the formed precipitate was isolated by filtration. The product was dissolved in hot CH_3OH and the catalyst was filtered. After cooling, the crude products were precipitated. The precipitate was washed with EtOH to afford the pure product and then dried well under vacuum pump.

Spectra data

1',3',8',8'-Tetramethyl-8',9'-dihydro-1'H-spiro[indoline-3,5'-pyrimido[4,5-b]quinoline] 2,2',4',6'(3'H,7'H,10'H)-tetraone (**7a**): Yellow crystals, mp: 320-322 °C. IR (KBr): ν =3280, 3210, 3090, 2959, 1690, 1644, 1499 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ=0.91 (3H, s, CH_3), 1.02 (3H, s, CH_3), 1.90-2.13 (2H, m, CH_2), 2.50-2.55 (2H, m, CH_2), 2.97 (3H, s, CH_3), 3.45 (3H, s, CH_3), 6.61-7.01 (4H, m, ArH), 8.94, 10.07 (2H, br s, 2NH, exchangeable with D_2O) ppm. Anal. Calcd. for $C_{22}H_{22}N_4O_4$: C, 65.01; H, 5.46; N, 13.78. Found: C, 64.98; H, 5.36; N, 13.68.

1′,3′,7′,9′-Tetramethyl-1′H-spiro[indoline-3,5′-pyrido[2,3-d:6,5-d′]dipyrimidine]-2,2′,4′,6′,8′ (3′H,7′H, 9′H,10′H)-pentaone (**8a**): Yellow crystals, mp: 320-322 °C. IR (KBr): ν = 3442, 3291, 3146, 1700, 1536 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ= 2.99 (3H, s, CH_3), 3.07 (3H, s, CH_3), 3.34 (3H, s, CH_3), 3.39 (3H, s, CH_3), 6.88-7.56 (4H, m, ArH), 9.35, 11.57 (2H, br s, 2NH, exchangeable with D_2O) ppm. Anal. Calcd. for $C_{20}H_{18}N_6O_5$: C, 56.87; H, 4.30; N, 19.90. Found: C, 56.78; H, 4.25; N, 19.89.

1',3'-Dimethyl-1'*H*-spiro[indoline-3,5'-pyrido[2,3d:6,5d']dipyrimidine]2,2',4',6',8' (3'*H*, 7'*H*, 9'*H*,10'*H*)-pentaone (**9a**): White crystals, m.p. >300 °C. IR (KBr): 3264, 3286, 1685, 1617, 1536, 1495 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ 3.10 (s, 3H, CH_3), 3.37 (s, 3H, CH_3), 6.87-7.16 (4H, m, ArH), 9.09 (s, NH, D_2O exchangeable), 10.44 (s, NH, D_2O exchangeable), 10.60 (s, NH, D_2O exchangeable), 11.56 (s, NH, D_2O exchangeable). ^{13}C NMR (100 MHz, DMSO-d_6): δ 26.2, 32.6, 56.7, 117.4, 121.5, 123.4, 126.8, 128.8, 134.2, 145.5, 150.1, 150.8, 152.5, 155.9, 159.6, 173.7, 180.4; Anal. Calcd. for $C_{18}H_{14}N_6O_5$: C, 54.82; H, 3.58; N, 21.31; Found: C, 54.72; H, 3.48; N, 21.14.

1,3-dimethyl-1*H*-spiro[indeno[1,2-*b*]pyrido[2,3-*d*]pyrimidine-5,3'-indoline]-2,2',4,6(3'*H*,10'*H*)-tetraone (**10 a**): Orange powder, mp 290-292 °C. IR (KBr): 3237, 3200, 1759, 1697, 1633, 1615 cm^{-1}. ^1H NMR (400 MHz, DMSO-d_6): δ (ppm) 3.02 (3H, s, CH_3), 3.44 (3H, s, CH_3), 7.01-7.65 (8H, m, H-Ar), 10.95 (1H, s, NH), 11.65 (1H, s, NH). ^{13}C NMR (100 MHz, DMSO-d_6): δ (ppm) 27.4, 31.6, 50.2, 97.4, 100.4, 118.2, 119.6, 120.6, 123.7, 124.9, 128.3, 129.1, 131.2, 131.2, 135.1, 136.4, 136.9, 151.7, 152.8, 156.4, 157.3, 180.6, 188.8. Anal. Calcd for $C_{23}H_{16}N_4O_4$ C, 66.99; H, 3.91; N, 13.59. Found: C, 66.90; H, 3.82; N, 13.48.

RESULTS AND DISCUSSION

The prepared catalyst was characterized by spectral techniques including FT-IR, XRD, FE-SEM, EDX, BET analyses.

FT-IR studies on zeolite ZSM-5 and its immobilized catalysts were carried out (Fig. 2). Unmodified product has bands at the following wavenumbers (cm^{-1}): 548 (δSi-O-Si), 796 (νsSi-O-Si), 1096 (νasSi-O-Si), 1630 (adsorbed H2O) and 3448 (νOH). The 796 band was shifted in PMA-modified sample to 787 cm^{-1} that is the result of overlapping with bands δ Mo-O-Mo (754 cm^{-1}) [42]. The band of silanol groups shifted in the case of PMA-containing sample only. In addition, the new strong band at 962 cm^{-1} appeared in the spectra of modified ZSM-5. This band is typical for Keggin's structure of heteropolyacids and corresponds to νasMo-O-Mo or νasW-O-W vibrations [43].

FE-SEM images of ZSM-5 and its immobilized catalyst are provided in Fig. 3. After the immobilization, the surfaces of the catalyst (b) were covered with a white translucent substance, and the surfaces became smoother. The particles became larger in size and their profiles became clearer, indicating that HPA was immobilized on the surface of ZSM-5. The evaluation of the used catalyst structure by FE-SEM evidences that the morphology of the catalyst remained unchanged after the 5th cycle (Fig. 5e, 5f).

EDX analysis (Fig. 4) of the catalyst showed the presence of Al, P, O, Si, and Mo elements confirming the formation of the catalytic system as visualized. Elemental mapping images (Fig. 4) of the catalyst

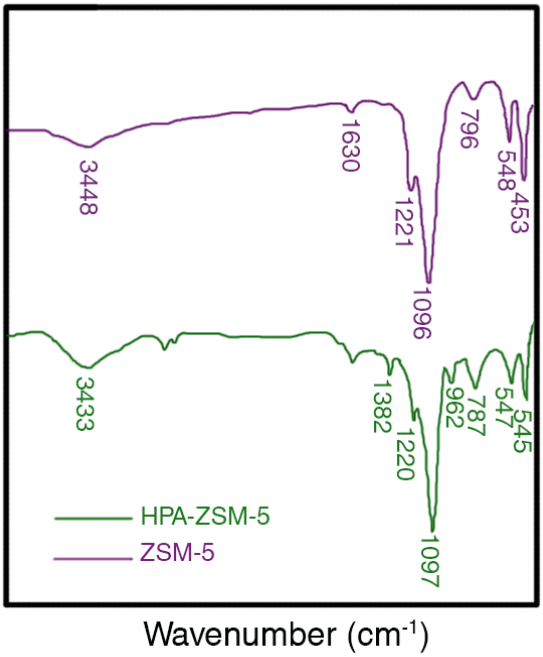


Fig. 2. Fourier transform infrared spectroscopy spectra of ZSM-5, HPA-ZSM-5

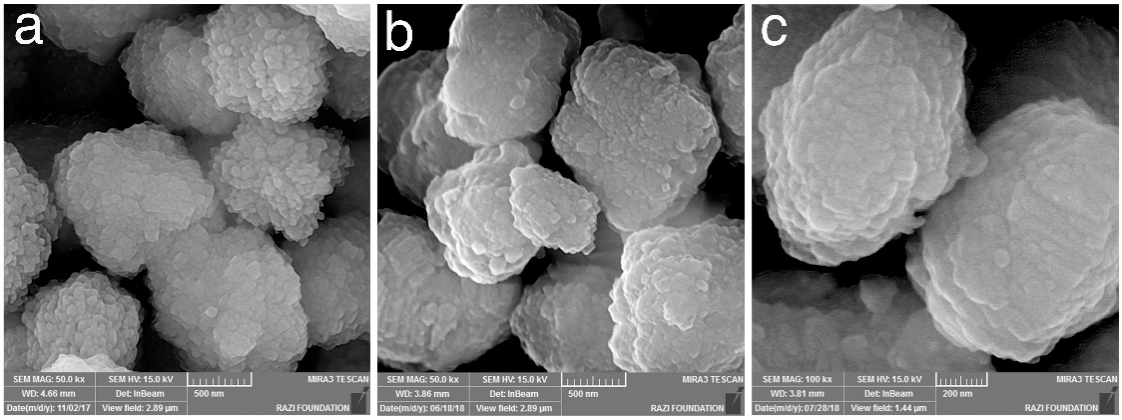


Fig. 3. FE-SEM images of (a ZSM-5, (b) HPA-ZSM-5, (c) the used HPA-ZSM-5

showed uniform distribution of the elements P and Mo in the desired catalytic system.

The XRD patterns of ZSM-5 and its immobilized catalyst are shown in Fig. 4. In pattern (a), the peaks of high intensity at 23.4°, 24.1°, and 24.6° are the characteristic diffraction peaks of ZSM-5, indicating good crystallinity of our synthesized ZSM-5. Compared with ZSM-5 pattern, HPA-ZSM-5 pattern exhibit all the diffraction peaks of ZSM-5, and the shape and intensity of the diffraction peaks have negligible changes, indicating that the prepared catalysts maintained the good crystallinity of ZSM-5 after immobilization of the HPA onto ZSM-5.

N_2-sorption isotherms at 77 K of ZSM-5 and HPA-ZSM-5 were indicated in Fig. 6. As shown in Fig. 4, all the isotherms exhibited a typical type IV isotherm with an H1 hysteresis loop starting from $P/P0 = 0.5$. The results presented that the BET specific surface area of ZSM-5 was increased from 170 to 240 m^2/g after modification with HPA.

The optimum reaction conditions were obtained by using a model reaction (Scheme 2) to show the effect of various parameters such as

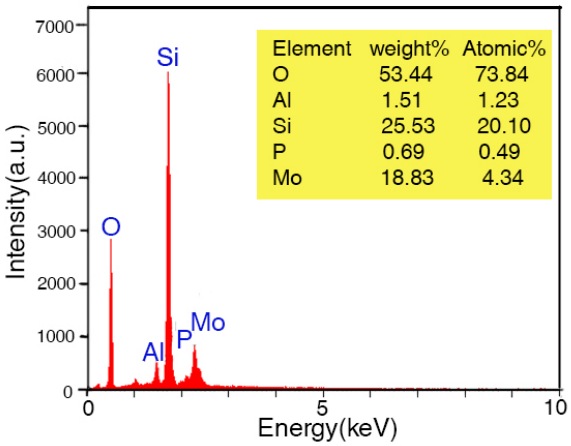


Fig. 4. EDS of HPA-ZSM-5

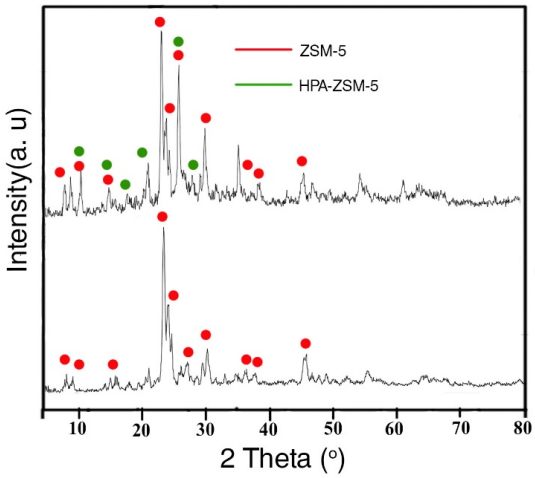


Fig. 5. XRD of ZSM-5 and HPA-ZSM-5

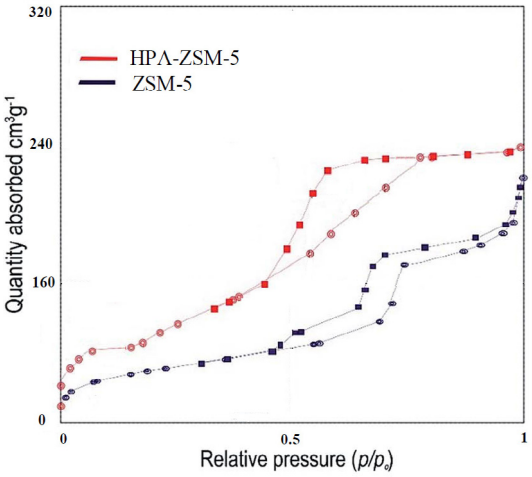
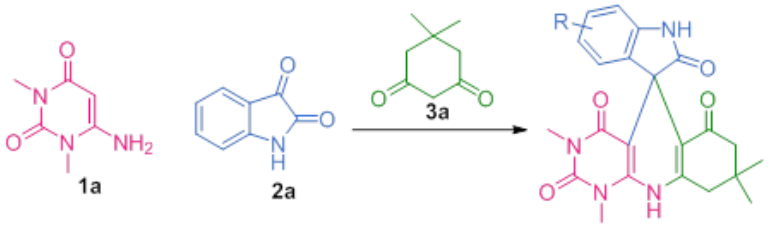


Fig. 6. N_2 adsorption–desorption isotherms of ZSM-5 and HPA-ZSM-5



Scheme 2. Synthesis of 7a

Table 1.

Entry	Catalyst	amount	Solvent/ Condition	Time (min)	Yield (%)	Ref
1	Free-Catalyst		EtOH	180	89	32
2	MA Ionic Liquid	(10 mol%)	H_2O	300	89	30
3	PTSA	(5 mol%)	H_2O	300	90	34
4	SBA-15-$PhSO_3H$	15 mg	H_2O:EtOH	300	95	33
5	SBA-Oxime-Zn	15 mg	H_2O	30	91	35
6	$AlCl_3$	20 mg	H_2O	300	65	-
7	CH_3COOH	10 mol%	H_2O	300	70	-
8	$H_3PMo_{12}O_{40}$	10 mol%	H_2O	300	80	-
9	ZSM-5	15 mg	H_2O	300	60	-
10	HPA-ZSM-5	15 mg	H_2O	180	90	-
11	HPA-ZSM-5	15 mg	EtOH	300	87	
12	HPA-ZSM-5	10 mg	H_2O/US (30 W)	20	85	
13	HPA-ZSM-5	10 mg	H_2O/US (40 W)	15	92	-
14	HPA-ZSM-5	10 mg	H_2O/US (50 W)	15	92	
15	HPA-ZSM-5	8 mg	H_2O/US (40 W)	15	90	
16	HPA-ZSM-5	15 mg	H_2O/US (40 W)	15	92	

the effect of different catalysts and solvents, HPA-ZSM-5 loading, amount of HPA-ZSM-5, and different temperatures.

First, the model reaction was employed on 1a, 2a and 3a to give 4a without any catalyst, and a small quantity (89%) of the product was formed after prolonged heating [32] (Table 1, entry 1). The model reaction was then examined with different catalysts such as MA Ionic Liquid, PTSA, SBA-15-$PhSO_3H$ and SBA-Oxime-Zn. It was observed that MA Ionic Liquid, PTSA, SBA-15-$PhSO_3H$ and SBA-Oxime-Zn afforded a moderate yield of the product after a longer time period (Table 1, entries 2, 3, 4, 5)

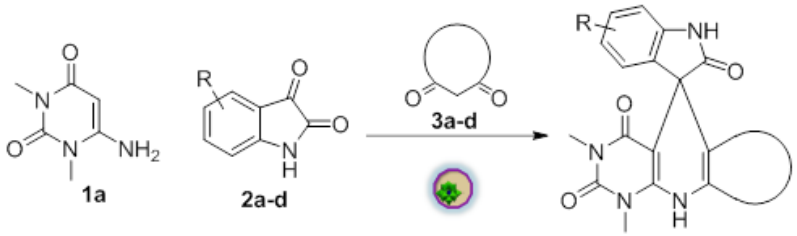
With Lewis acid and Brønsted–Lowry acid (Table 1, entries 6, 7) small amounts of the product were obtained. However, the reaction with heteropoly acid such as $H_3PMo_{12}O_{40}$ afforded an improved yield of the product (Table 1, entry 8). When the reaction was conducted with HPA–doped ZSM-5 the rate of reaction was enhanced and time period reduced giving good yield of the product (Table 1, entries 10 and 11). However, using HPA supported on ZSM-5 (HPA-ZSM-5), the reaction completed in a relatively shorter reaction time (180 min) affording an excellent yield of the product (90%; Table 1, entry 10) showing the effect of doped HPA on the catalytic activity of the catalyst, whereas, for the model reaction carried out with ZSM-5 alone as a catalyst, small amounts of the product were obtained (Table 1, entry 9).

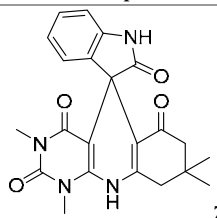
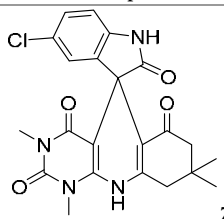
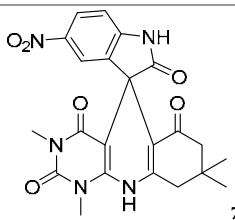
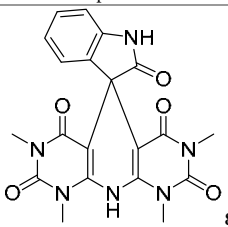
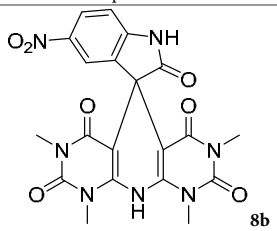
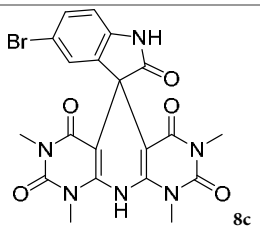
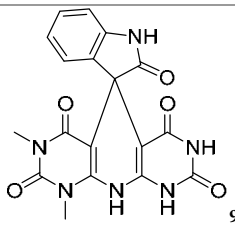
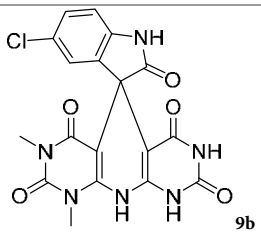
For a demonstration of the superiority of ultrasound-assisted method the model reaction was carried out in H_2O as solvent and the result is shown in entry 13. As observed, when the reaction was carried out under ultrasound irradiation (40 W), the maximum yield of the product was obtained in the minimum time period (Table 1, entry 13).

A mixture of 6-Amino-1,3-dimethyluracil (1a), isatin (2a) and 1,3-diketone (3a) in presence of HPA-ZSM-5 as catalyst in H_2O for about 15 min, afforded 1',3',8',8'-tetramethyl-8',9'-dihydro-1'H-spiro[indoline-3,5'-pyrimido[4,5-b]quinoline]-2,2',4',6'(3'H,7'H,10'H)-tetraone (7a) in good

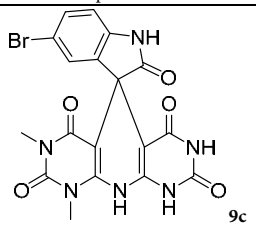
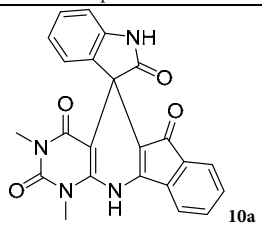
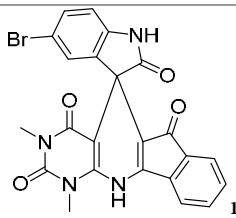
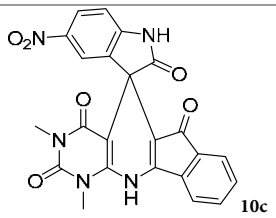
yields (Scheme 2). The scope of the present methodology was investigated by synthesizing structurally different spiro-pyrido-pyrimidine indoline derivatives using the optimized reaction conditions. Various spiro-pyrido-pyrimidine indoline derivatives were obtained in high yields by MCRs of 2-6-Amino-1,3-dimethyluracil (1a), isatin (2a-d) and 1,3-diketone (3a-d) under the

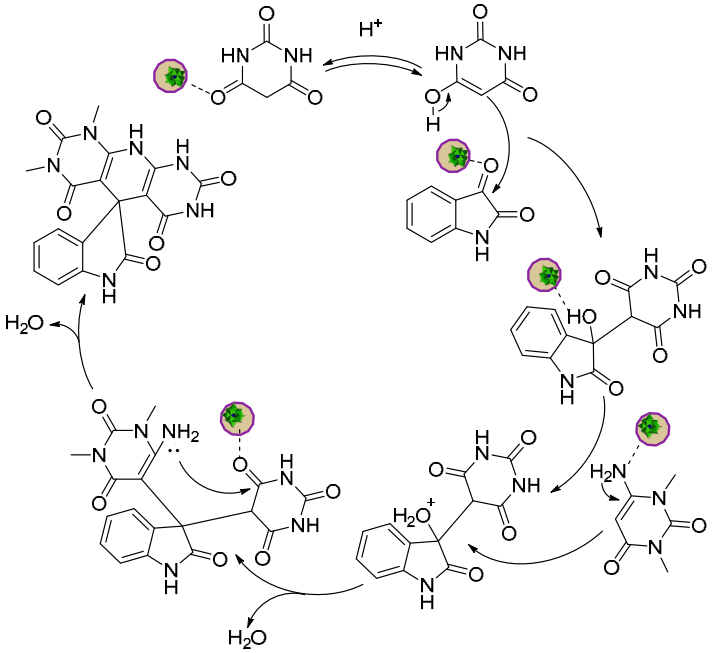
Table 2. Synthesis of spiro cyclic 2-Oxindole derivatives using HPA-ZSM-5



Time/yield% m.p	Time/yield% m.p
 7a	 7b
15 min/ 92 320-322°C	15 min/ 94 mp>300°C
 7c	 8a
15 min/ 94 mp>300°C	20 min/ 90 320-322 °C
 8b	 8c
15 min/ 92 301-303°C	20 min/ 91 296-298 °C
 9a	 9b

Continued Table 2. Synthesis of spiro cyclic 2-Oxindole derivatives using HPA-ZSM-5

20 min/ 88 m.p. >300 °C	20 min/ 90 m.p. >300 °C
 **9c**	 **10a**
20 min/ 90 296-298 °C	15 min/ 90 290-292 °C
 **10b**	 **10c**
15 min/ 92 m.p. >300 °C	15 min/94 294-296 °C



Scheme 3. Plausible Mechanism for the Catalytic Synthesis of spiro-pyrido-pyrimidine indoline derivatives

optimal reaction conditions, and the results are presented in Table 2. To the best of our knowledge, this new procedure provides the first example of use of H_2O green solvent and ultrasound-assisted method of spirooxindole. Overall, this efficient method is applicable for the synthesis of different types of spiro-pyrido-pyrimidine indolines. In addition, the workup of these very clean reactions involves only a filtration and simple washing step with water.

On the basis of the point mentioned above, a reasonable mechanism for the preparation of 1',3'-dimethyl-1'H-spiro[indoline-3,5'-pyrido[2,3-d:6,5-d']dipyrimidine]-2,2',4',6',8'(3'H,7'H,9'H,10'H)-pentaone by the HPA-ZSM-5 is suggested in Scheme 3.

CONCLUSIONS

In conclusion, we have designed a facile method for the synthesis of novel HPA-ZSM-5. The zeolite catalyst has been characterized by XRD, FE-SEM, FT-IR, EDS and N_2-adsorption analysis. The catalyst has been applied for the synthesis of spiro-pyrido-pyrimidine indolines by the reaction of isatins, cyclic-1,3-diketones and 6-amino-1,3-dimethyluracil in presence of highly active HPA-ZSM-5 microporous catalyst (10 mg) under ultrasound irradiation (40 W) in water. This method is applicable for the synthesis of different types of spiro-pyrido-pyrimidine indolines. The catalyst could be recycled for five runs during the course of the reaction. The widespread scope, reusability of the catalyst, clean reaction profile, improved rate of reaction, and product yield are the advantages of the present protocol.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interest regarding the publication of this manuscript.

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