C. R. Chimie 17 (2014) 1136–1143

Contents lists available at ScienceDirect

Comptes Rendus Chimie

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Star-shaped Keggin-type heteropolytungstate nanostructure as a new catalyst for the preparation of quinoxaline derivatives

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ARTICLE INFO

Article history:
Received 18 October 2013
Accepted after revision 28 January 2014
Available online 16 September 2014

Keywords:
Heteropolytungstate
Keggin
Nanostructure
Microemulsion
Quinoxaline
Catalyst

ABSTRACT

In this work, we report the novel successful preparation of the Keggin-type $Cs(CTA)_2PW_{12}O_{40}$ (CTA = cetyltrimethylammonium cation) nanostructure by a microemulsion method. The microemulsion system included the cationic surfactant CTAB, 1-butanol as co-surfactant, isooctane as oil phase, and an aqueous solution containing $CsNO_3$. The $Cs(CTA)_2PW_{12}O_{40}$ nanostructure was formed by the addition of an aqueous solution of phosphotungstic acid to the microemulsion solution. Characterization of the resultant nanostructure was done using FT–IR spectroscopy, X-ray diffraction, scanning electron microscopy, energy-dispersive X-ray analysis, and CHN elemental analysis. The product was found to be a star-shaped nanostructure composed of some nanorods whose diameter and length are about 100 nm and 500 nm, respectively. The prepared nanostructure was used as a recoverable catalyst for the synthesis of quinoxaline derivatives by the condensation of 1,2-diamines with 1,2-dicarbonyl compounds, which afforded the products in good to high yields in short reaction times.

1. Introduction

The synthesis of quinoxaline and of its derivatives played an important role in organic synthesis because of their wide range of biological activities, such as antibacterial [1], antidepressant [2], anti-inflammatory [3], and antitumor [4] ones. Due to their great importance, many synthetic strategies have been developed for the synthesis of quinoxalines [5–9]. However, most of these methodologies involve pollution, long reaction time and difficult work-up and recovery of the catalysts, leaving considerable scope for the development of further clean, facile and efficient catalytic processes for these important molecules. Condensation of a 1,2-diamine with a 1,2-dicarbonyl compound in the presence of Brønsted or Lewis acids, such as montmorillonite K-10 [10], mesoporous silica SBA-15 covalently anchored with copper (II) Schiff base complex [11], alumina [12], and silica-supported perchloric acid [13], Wells–Dawson heteropoly acid ($H_6P_2W_{18}O_{62}\cdot 24H_2O$) [14], iron exchanged molybdophosphoric acid [15], and Keggin-type $H_4SiW_{12}O_{40}$ heteropoly acid [16], is one of the important methods for the preparation of quinoxalines. However, to the best of our knowledge, there is no any example of the use of nanostructured Keggin-type heteropolyanions as catalysts for the synthesis of quinoxaline derivatives.

Heteropoly acids are discrete metal–oxygen clusters built from the connection of MO_x polyhedra in which M is a d-block element in a high oxidation state [17–20]. They possess both acidic and redox properties and thus are of great importance for practical applications, especially in catalysis [21–28]. Pure heteropoly acids have high solubility in polar reaction systems, which hinders their applications as heterogeneous catalysts and so results in

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1631-0748/$ – see front matter
http://dx.doi.org/10.1016/j.crci.2014.01.021

separation problems during the isolation of the product after completion of the reaction. It has been found that water-insoluble salts of heteropoly acids with large cations, such as Cs^+, K^+, NH_4^+, and organic cations can be used as efficient heterogeneous catalysts [28–30]. These compounds are prepared by partial or complete cation exchange with protons in heteropoly acids. For example, a caesium salt of $H_3PW_{12}O_{40}$, $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ has lately gained attention because of strong acidity and insolubility in water and organic solvents, and so can be considered as a solid acid catalyst. This salt was reported to exhibit significantly higher activity than the parent acid in gas-phase acid-catalyzed reactions [28–31].

Polyoxometalate nanostructures have attracted considerable interest owing to their interesting properties and wide range of applications [32–36]. Some methods have been developed for the preparation of polyoxometalate nanostructures, such as homogeneous precipitation using decomposition of urea [35], solid-state chemical reaction [36], and microemulsion methods [37,38].

Recently, we have reported the first successful one-pot preparation and characterization of heteropolymolybdate nanoparticles with a microemulsion method [38]. Microemulsions are systems composed of a mixture of an aqueous phase, an oil phase, a surfactant, and a co-surfactant [39–41]. They are transparent solutions that are thermodynamically stable and optically isotropic. The nanosized water droplets in microemulsions act as nanoreactors for producing the desired nanostructures. The advantage of this method is the good control on the size and morphology of the prepared nanostructure.

Here, we further explore the potential of microemulsion method for the preparation of a novel $Cs(CTA)_2PW_{12}O_{40}$ nanostructure. The prepared nanostructure acts as a recoverable heterogeneous catalyst for green and efficient synthesis of quinoxaline derivatives in high yields and short reaction times. In comparison with previous catalytic systems for the synthesis of quinoxaline derivatives [10–16], it has the following advantages: easy recoverability, comparable yields with short reaction times, and especially solvent-free conditions that make it an environmentally friendly and cost-effective process.

2. Experimental

2.1. Materials and instrumentations

All chemicals were purchased from Merck Chemicals and used without further purification. Phosphotungstic acid was prepared by a method taken from the literature [28].

FT–IR spectra were recorded with a PerkinElmer Spectrum RXI FT–IR spectrometer using pellets of the materials diluted with KBr. X-ray powder diffraction measurements (XRD) were performed on a SIEFERT XRD 3003 PTS diffractometer using Cu Kα radiation (wavelength λ = 0.154 nm). The patterns were recorded from 5° to 80° with steps of 0.02° every second. Scanning electron microscopy images were taken with a ZEISS-DSM 960A microscope with an attached camera operating at 30 kV. DR UV–Vis spectra were collected using a PG Instrument Ltd T90+ UV–Vis Spectrometer with $BaSO_4$ as a standard. Elemental analyses were performed using a scanning electron microscope equipped with EDX detector INCA Penta FETx3. 1. The carbon and nitrogen contents of the samples were analyzed using a Thermo Finnigan (Flash 1112 Series EA) CHN Analyzer. ^{1}H NMR spectra were recorded on a Bruker AQS AVANCE-300 MHz spectrometer using TMS as an internal standard. All products were well characterized by comparison with authentic samples by TLC, spectral and physical data recording.

2.2. Preparation of the $Cs(CTA)_2PW_{12}O_{40}$ nanostructure

The quaternary microemulsion system consisted of H_2O/CTAB/isooctane/*n*-butanol and had been prepared as follows: CTAB (2 g) in water (2 mL) was added to a stirred solution of *n*-butanol (2 g) and isooctane (4 g). Then, 1 mL $CsNO_3$ (0.5 M) in water was added to the above mixture and stirred for 10 min to give a transparent solution. Under stirring, 1 mL of $H_3PW_{12}O_{40}$ (0.5 M) was added and the reaction continued for another 2 h. The resultant white product was collected by centrifugation and washed several times with water and ethanol to remove the remaining organic residue and dried at 110 °C for 12 h.

2.3. General method for the preparation of quinoxaline derivatives

A mixture of 1,2-dicarbonyl (1 mmol) and 1,2-diamine (1 mmol) derivatives in the presence of an appropriate amount of the $Cs(CTA)_2PW_{12}O_{40}$ catalyst was stirred at a given temperature. The progress of the reaction was monitored by thin layer chromatography (TLC). After completion of the reaction, 5 mL of hot ethanol was added to the reaction mixture and the solid catalyst was filtered. The pure products were obtained after crystallization and analyzed without any further purification. All of the obtained quinoxalines are known compounds and identified by ^{1}H NMR and melting points compared with the literature values. The melting points, spectral (^{1}H NMR) and elemental analysis data for the products are given below.

2.4. 2,3-Diphenyl-quinoxaline

Mp. 120–122 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.20 (d.d, 3.35, 3.35 Hz, 2H), 7.79 (dd, 3.3, 3.35 Hz, 2H), 7.54 (d, J = 6.65 Hz, 4H), 7.38 (m, 6H); FT–IR (KBr): 3059, 1436, 1395, 1341, 707, 695 cm^{-1}. Anal. calcd. for $C_{20}H_{14}N_2$: C, 85.08; H, 5.00; N, 9.92. Found: C, 85.25; H, 5.12; N, 9.98.

2.5. 2,3-Bis (4-methoxyphenyl) quinoxaline

Mp. 140–141 °C; ^{1}H NMR (500 MHz, $CDCl_3$): δ (ppm): 8.14 (m, 2H), 7.73 (m, 2H), 7.51 (d, J = 8.25 Hz, 4H), 6.89 (d, J = 8.25 Hz, 4H), 3.85 (s, 6H); FT–IR (KBr): 2936, 2836, 1603, 1509, 1340, 1293, 1245, 832 cm^{-1}. Anal. calcd. for $C_{22}H_{18}N_2O_2$: C, 77.17; H, 5.30; N, 8.18. Found: C, 76.97; H, 5.21; N, 8.01.