

Preparation and Characterization of Some Solid Acidic Catalysts and Their Catalytic Application

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Received: April 2011, Revised: April 2011, Accepted: July 2011

Abstract: The objective of this study was to prepare dibutylphthalate via esterification reaction in the presence of some solid acidic catalysts. The catalysts were some transition metal polyoxometalates as effective and green catalysts with Keggin; $K_3[PMo_6W_6O_{40}]$, $K_3[PMo_{12}O_{40}]$, $K_4[SiMo_{12}O_{40}]$, $K_4[SiW_{12}O_{40}]$, $Na_7[PW_{11}O_{39}]$, Wells-Dawson; $K_6[P_2W_{18}O_{62}]$, and Preyssler structures; $K_{14}[NaP_5W_{30}O_{110}]$. In the first step, the above-mentioned polyoxometalates were prepared, and then characterized. Consequently, the reactivity of those catalysts have been studied and compared in the preparation of dibutylphthalate. Among various acidic catalysts which were used, $K_3[PMo_6W_6O_{40}]$ showed the best reactivity and efficiency compared to the other catalysts.

Keywords: Polyoxometalate, Keggin, Wells-Dawson, Preyssler, Preparation, Characterization, Esterification, Dibutylphthalate

Introduction

In the past decades, Greenpeace groups and NGOs in various countries have increasingly addressed the environmental impact of the chemical substances, fully recog-

nized as a global issue. As a consequence, this awareness is pushing governments toward more stringent legislation, which promotes the preservation and protection of the quality of the environment for future gen-

erations. To overcome the problem at the source, the chemical industry must develop cleaner chemical processes or materials by the design of innovative and environmentally benign chemical reactions. Green chemistry offers the tools for this approach. In other words, green chemistry is the chemical products and processes that reduce or eliminate the use and generation of hazardous substances [1].

The drive to develop green processes has led to the development of solid acid catalysts. These materials can replace the corrosive liquid acids currently used in many industries. A variety of materials have been used as solid acid catalysts such as clays, zeolites, sulfated metal oxides, polyoxometalates (POMs), etc. [2, 3]. Each of these materials offers unique properties that can influence the catalytic activity. Among these solid acids, polyoxometalates (POMs) represent a well known class of structurally well-defined clusters with an enormous variation in size, metal-oxygen framework topology, composition, and function. The preparation of POMs is based on the programmed self-assembly of metal oxide building blocks [4-6]. In recent years, POMs are widely used in a variety of acid catalyzed reactions for both homogeneous and heterogeneous reactions due to their high acid strength and high thermal stability such as esterification, etherifi-

cation, hydration of olefin and polymerization of tetrahydrofuran [7-19].

In the present study, initial preparation of some polyoxometalate compounds containing molybdenum and tungsten atoms, as green catalysts, with Keggin, Wells-Dawson and Preyssler structures were investigated. In addition, catalytic application of prepared polyoxometalate compounds in esterification reaction of phthalic anhydride with 1-butanol has been studied. The effects of catalyst amount, various solvents and the reaction time were also investigated in the formation of dibutylphthalate.

Experimental

Materials and Methods

All solvents and materials were analytical grade, commercially available and used without further purification. Infrared spectra were recorded using KBr disks on a Tensor 27 Bruker spectrophotometer. The electronic spectra were obtained with a Cary 100 Bio UV-Vis spectrophotometer. The NMR spectra were recorded on a Bruker spectrometer at 300 MHz (CDCl_3 solution). Elemental analysis was performed on a Perkin-Elmer 2400 CHN elemental analyzer. Mass spectra were recorded on an Agilent technologies 5973 network mass selective detector (MSD) operating at an ionization potential of 70 eV.

Preparation of polyoxometalates with Keggin structure

For the preparation of $K_3[PMo_6W_6O_{40}]$, sodium tungstate (0.05 mol), sodium molybdate (0.05 mol), and sodium dihydrogen phosphate (0.02 mol) were dissolved in deionized water (60 ml). The solution was kept at 80 °C for 3 h with agitation and then concentrated to 30 ml. subsequently, hydrochloric acid 24 % (30 ml) was added, while the solution color was yellow. After extraction with diethyl ether at room temperature, crystals were obtained. The product was characterized by IR and UV-Vis spectroscopic methods.

The $K_3[PMo_{12}O_{40}]$ was prepared by the reaction between disodium hydrogen phosphate (0.01 mol) and a solution of sodium molybdate (0.04 mol) in water (30 ml). The solution was stirred while it was heated to boiling point. Then, hydrochloric acid 37% (8 ml) was added. The purification procedure was performed by extraction with diethyl ether in two stages.

For the preparation of $Na_7[PW_{11}O_{39}]$, sodium tungstate (0.07 mol) and disodium hydrogen phosphate (0.01 mol) were dissolved in water (50 ml). The solution was heated to 80 °C and titrated exactly with concentrated nitric acid with vigorous stirring to pH 4.8. The volume was reduced to half by evaporation and the polyoxometalate

separated in a dense lower layer by liquid-liquid extraction with acetone. The extraction was repeated until the acetone extract shows no nitric ions (ferrous sulfate test). The solid sodium salt was obtained as the hydrate by evaporation to dryness of the acetone extracts.

The $K_4[SiMo_{12}O_{40}]$ was synthesized by addition of sodium silicate (0.5 mL) to a solution of sodium molybdate (0.02 mol) in water (10 ml). The solution was stirred and heated to boiling point. Subsequently, hydrochloric acid (4 ml) and diethyl ether (10 ml) was added. After 7 days, colorless cubic crystals were obtained by vaporization of solvent in room temperature.

The experimental procedure for preparation of $K_4[SiW_{12}O_{40}]$ was similar to that of $K_4[SiMo_{12}O_{40}]$ with a replacement of the sodium tungstate (0.02 mol) by sodium molybdate (0.02 mol).

It should be noted that some Keggin salt such as $K_3[PMo_6W_6O_{40}]$, $K_3[PMo_{12}O_{40}]$, $K_4[SiMo_{12}O_{40}]$ and $K_4[SiW_{12}O_{40}]$ were prepared by passing an aqueous acidic solution through a column of ion-resin.

Preparation of polyoxometalate with Wells-Dawson structure

For the preparation of $K_6[P_2W_{18}O_{62}]$, phosphoric acid (2 ml) was added to a solution of sodium tungstate (0.01 mol) in water (30 ml). The solution was refluxed for 8 h. The

salt was precipitated by adding potassium chloride (1 g), subsequently purified by recrystallization and cooled overnight to 5 °C. The product was filtered, washed and then vacuum-dried for 8 h.

Preparation of polyoxometalate with Preyssler structure

The $K_{14}[NaP_5W_{30}O_{110}]$ was synthesized by dissolving sodium tungstate (0.01 mol) in water (30 ml). Subsequently, the solution was added to phosphoric acid 85% (3 ml). In the next step, the mixture was sealed into a Teflon bottle at 120 °C for 18 h. Following, a solution of potassium chloride (1 g) were added into the above mixture to form the precipitate. The precipitate was obtained by filtration and washed successively using aqueous solution of potassium acetate (2 M) and methanol. The white precipitate was dried and recrystallized twice to obtain the potassium salt of Preyssler type POM.

General procedure for esterification reaction

The esterification was carried out in a round-bottom flask equipped with a magnetic stirrer, reflux condenser and Dean-Stark trap. All catalysts were dried prior to use. The temperature was maintained with an oil bath. To prepare dibutylphthalate ester, phthalic anhydride (0.1 mol), 1-butanol (0.2 mol) and POMs were added to solvent (15

ml) and the mixture was refluxed. The water formed in the reaction was removed by azeotropic distillation with the solvent, and then solvent was reverting back to the reaction vessel. After completion of reaction, the catalyst was extracted from reaction mixture by aqueous solution of sodium carbonate. The reaction mixture was distilled under reduced pressure for removing the excess of alcohol and distillation continued to obtain the main product. The formation of ester was monitored by TLC, IR, ¹HNMR, Mass Spectroscopy and CHN analysis. The reaction conversions were calculated from the amount of collected water in Dean-Stark trap.

Results and Discussion

Characterization by FT-IR and UV-Vis

The FT-IR and UV-Visible spectra of 7 POMs compound are summarized in Tables 1 and 2. The $[XM_{12}O_{40}]_n^-$ structure (Keggin structure), where X is the heteroatom and M is the d0 metal consists one XO_4 tetrahedron surrounded by four M_3O_{13} sets formed by three edge-sharing octahedral. The M_3O_{13} sets are linked together through oxygen atoms. Thus, there are four kinds of oxygen atoms in $[XM_{12}O_{40}]_n^-$, four X–O_a in which one oxygen atom connects with heteroatom (X), 12 M–O_b–M oxygen-bridges (corner-sharing oxygen-bridge between

different M_3O_{13} sets), 12 M–Oc–M oxygen bridges (edge-sharing oxygen-bridge within M_3O_{13} sets) and 12 M=Od terminal oxygen atoms. For example, in the IR spectrum of $K_3[PMo_6W_6O_{40}]$ (Table 1), there are four characteristic bands (vas, cm^{-1}): 1072 (X–O); 972 (M=Od); 877 (M–Ob–M) and 790 (M–Oc–M). In the Keggin structure, intense absorption bands at 220 and 270 nm are caused by charge-transfer of the terminal oxygen and bridge-oxygen to metal atoms, respectively (Table 2).

In the IR spectrum of $K_6[P_2W_{18}O_{62}]$ ($[X_2M_{18}O_{62}]_n^-$, Wells-Dawson structure), there are four characteristic bands (vas, cm^{-1}): 1091(X–O); 962 (M=Od); 912 (M–Ob–M); 780 (M–Oc–M) (Table 1). In the

UV spectrum of $K_6[P_2W_{18}O_{62}]$, there are two characteristic bands: 203 nm (Od to metal charge transfer) and 250 nm Ob/Oc to metal charge transfer (Table 2).

The Preyssler anion $[NaP_5W_{30}O_{110}]_{14}^-$, consist of a cyclic assembly of five PW_6O_{22} units, each derived from the Keggin anion, $[PW_{12}O_{40}]_3^-$, by removal of two sets of three corner-shared WO_6 octahedral. In the IR spectrum of $K_{14}[NaP_5W_{30}O_{110}]$, displayed vibrations (vas, cm^{-1}): 1165, 1082, 1021 (X–O); 788 (M=Od); 940 and 913 (M–Ob–M) (Table 1). In the UV spectrum of $K_{14}[NaP_5W_{30}O_{110}]$, there are two characteristic bands: 201 nm, Od to metal charge transfer; 278 nm Ob/Oc to metal charge transfer.

Table 1 FT-IR data of prepared polyoxometalates.

Structure	Compound	X–O(cm^{-1})	M=Od (cm^{-1})	M–Ob–M (cm^{-1})	M–Oc–M (cm^{-1})
	$K_3[PMo_6W_6O_{40}]$	1072	972	877	790
	$K_3[PMo_{12}O_{40}]$	1064	964	868	797
Keggin	$K_4[SiMo_{12}O_{40}]$	1020	978	910	780
	$K_4[SiW_{12}O_{40}]$	1016	984	914	787
	$Na_7[PW_{11}O_{39}]$	1096, 1055	956	894	814
Wells-Dawson	$K_6[P_2W_{18}O_{62}]$	1091	962	912	780
Preyssler	$K_{14}[NaP_5W_{30}O_{110}]$	1165,1082,1021	788	940	983

Table 2 UV-Vis spectra for prepared polyoxometalates

Structure	Compound	Absorption (max, nm)
	$K_3[PMo_6W_6O_{40}]$	220, 270
	$K_3[PMo_{12}O_{40}]$	212, 309
Keggin	$K_4[SiMo_{12}O_{40}]$	250, 260
	$K_4[SiW_{12}O_{40}]$	250, 260
	$Na_7[PW_{11}O_{39}]$	202, 257
Wells-Dawson	$K_6[P_3W_{18}O_{62}]$	203, 250
Preyssler	$K_{14}[NaP_5W_{30}O_{110}]$	201, 278

Esterification studies

Esterification of phthalic anhydride by alcohol takes place in two stages. The first stage is so rapid that it can be carried out in the absence of catalyst. However, esterification of the second carboxylic group is very slow and needs to be facilitated by acid catalyst and the resulting water must be removed from the reaction mixture.

In this work, the effects of three variable factors namely amount of catalyst, reaction time and solvent type on the percentage conversion for the reaction of phthalic anhydride with 1-butanol has been studied. The reaction time and amount of catalyst were varied in the range of 2-6 h and 0.1-0.9 g, respectively. Furthermore, the reaction was carried out in toluene and xylene as solvent. The data show that increasing the amount of catalyst (>0.7 g) and reaction time (>5 h) did not show remarkable effect on the reaction conversion (Table 3). It is to be noted that the effect of solvent should not be ignored. Esterification yields in xylene solvent in the present work are higher than that of toluene

solvent due to the higher boiling point and influence of refluxing temperature and consequently higher reaction rate.

In summary, among the investigated catalysts, $K_3[PMo_6W_6O_{40}]$ with Keggin structure with amount of 0.7 g and the reaction time of 5 h in xylene solvent show the best reactivity and efficiency (97%), while, the lowest conversion percent using $K_{14}[NaP_5W_{30}O_{110}]$ catalyst is 20% in toluene solvent (Table 3). Also, results clearly demonstrated that $K_3[PMo_6W_6O_{40}]$ was a better catalytic system when compared to conventional acid catalysts such as H_2SO_4 .

The spectra data (IR, 1H NMR) and physical data for dibutylphthalate ester are presented as, IR (KBr, cm^{-1}): 3071 (C-H aromatic), 2960 (C-H aliphatic), 1728 (C=O ester), 1599, and 1465 (C=C aromatic), 1285 (C-O esret), 743 (bending vibration, C-H aromatic); 1H NMR ($CDCl_3$, 300 MHz, ppm): 7.40-7.70 (m, 4H, aromatic ring), 4.25-4.29 (t, J= 6.6, 4H, 2CH₂ aliphatic), 1.63-1.72 (m, 4H, 2CH₂ aliphatic), 1.30-1.46 (m, 4H, 2CH₂ aliphatic), 0.89-

0.98 (t, J=7.35, 6H, 2CH₃ aliphatic). MS, (m/z, %): 278 (10.5), 223 (52.6), 149(100), 76(15.7), 56(36.8), 41(57.8). Anal. Calcd. For C₁₆H₂₂O₄: C, 69.06; H, 7.91. Found: C, 69; H, 8.

Conclusions

Polyoxometalates have several advantages over liquid acid catalysts, including being noncorrosive and environmentally benign. Thus, they present fewer disposal problems and more economically and environmentally attractive. Esterification reactions of phthalic anhydride by 1-butanol catalyzed

by various POMs compounds were investigated. Our results showed that esterification yield depends on several factors, such as reaction time, amount of catalyst and type of solvent. When the amount of catalyst and the reaction time increased, first the conversion percent increased, and then remain unchanged. The highest conversion percent using K₃[PMo₆W₆O₄₀] catalyst in amount of 0.7 g and the duration of 5 h in xylene solvent is 97 %, while, the lowest conversion percent using K₁₄[NaP₅W₃₀O₁₁₀] catalyst is 20% in toluene solvent.

Table 3 Comparison of the efficiency of various polyoxometalates (0.7 g, 5 h) as catalyst under different solvent in esterification

Structure	Compound	Conversion ^a (%)	Conversion ^b (%)
	K ₃ [PMo ₆ W ₆ O ₄₀]	85	97
	K ₃ [PMo ₁₂ O ₄₀]	39	37
Keggin	K ₄ [SiMo ₁₂ O ₄₀]	42	44
	K ₄ [SiW ₁₂ O ₄₀]	40	41
	Na ₇ [PW ₁₁ O ₃₉]	30	42
Wells-Dawson	K ₆ [P ₂ W ₁₈ O ₆₂]	45	64
Preyssler	K ₁₄ [NaP ₅ W ₃₀ O ₁₁₀]	20	27

a Toluene as solvent

b Xylene as solvent

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تهیه و شناسایی چند کاتالیست اسیدی جامد و کاربرد کاتالیتیکی آنها

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دریافت: فروردین 1390 : پذیرش: شهریور 1390

چکیده: هدف از این مطالعه، تهیه دی بوتیل فتالات از طریق واکنش استری شدن در مجاور چند کاتالیست اسیدی جامد بوده است. کاتالیست های مورد استفاده چند پلی اکسومتالات فلز واسطه به عنوان کاتالیست های موثر و دوستدار محیط زیست با ساختارهای کگین: $\text{Na}_7[\text{PW}_{11}\text{O}_{39}]$ $\text{K}_4[\text{SiW}_{12}\text{O}_{40}]$ $\text{K}_4[\text{SiMo}_{12}\text{O}_{40}]$ $\text{K}_3[\text{PMo}_{12}\text{O}_{40}]$ $\text{K}_3[\text{PMo}_6\text{W}_6\text{O}_{40}]$ - : $\text{K}_6[\text{P}_2\text{W}_{18}\text{O}_{62}]$ و پرایسلر: $\text{K}_{14}[\text{NaP}_5\text{W}_{30}\text{O}_{110}]$ هستند. پلی اکسو متالات های یاد شده تهیه و سپس شناسایی شدند. همچنین، واکنش پذیری این کاتالیست ها در تهیه دی بوتیل فتالات مطالعه و مقایسه شد. در میان کاتالیست های اسیدی مورد استفاده، $\text{K}_3[\text{PMo}_6\text{W}_6\text{O}_{40}]$ بهترین واکنش پذیری و بازده را در مقایسه با کاتالیست های دیگر نشان داده است.

واژه های کلیدی: پلی اکسو متالات، کگین، ولز-داوسن، پرایسلر، تهیه، شناسایی، استری شدن، دی بوتیل فتالات.