



Esterification of glycerol with acetic acid over dodecamolybdophosphoric acid encaged in USY zeolite

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ABSTRACT

The esterification of glycerol with acetic acid was carried out over dodecamolybdophosphoric acid (PMo) encaged in the USY zeolite. The products of glycerol acetylation were monoacetin, diacetin and triacetin. A series of PMo encaged in the NaUSY zeolite with different PMo loading from 0.6 to 5.4 wt.% were prepared. It was observed that the catalytic activity increases with the amount of PMo immobilized in the NaUSY zeolite, being the PMo₃-NaUSY (with 1.9 wt.%) the most active sample. However, at high loading of heteropolyacid encaged in the NaUSY zeolite, a decrease on the catalytic activity was observed, which can be explained, probably, due to the internal diffusion limitations.

Good values of selectivity to diacetin were obtained with all the catalyst.

Catalytic stability of the PMo₃-NaUSY was evaluated by performing consecutive batch runs with the same catalyst sample. After the second batch, it was observed a stabilization of the catalytic activity.

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1. Introduction

Glycerol is the main by-product of the biodiesel production by transesterification of oil with methanol or ethanol. The increasing use and production of biodiesel has resulted in an increase of glycerol production and a price decline, which makes glycerol a particularly attractive molecule for the synthesis of other value chemical products [1,2].

The esterification of glycerol with acetic acid can be a good alternative for the glycerol produced by biodiesel. The products of glycerol acetylation are monoacetin, diacetin and triacetin (Scheme 1), which have great industrial applications. The triacetylated derivative is known as triacetin, and has applications going from cosmetics to fuel additive [3–5]. The mono and diacetylated esters are also known as mono and diacetin, and have applications in cryogenics and as raw material for production of biodegradable polyesters [6].

Traditionally, mineral acids have been used as catalysts in the esterification of glycerol with acetic acid, but the effluent disposal leads to environmental problems and economical inconveniences. These problems can be overcome by the use of heterogeneous catalysts. Only a few reports have been found dealing with solid acid catalysts including zeolites, amberlyst and niobic acid [7], mesoporous silica with sulfonic acid groups [8] and Starbon[®] [9].

Heteropolyacids (HPAs) with Keggin structure are widely used as acid catalysts, due to their very strong Brønsted acidity and their structural properties [10–12]. HPAs have low specific surface area (1–10 m²/g). In order to increase the specific area of HPAs or even better to increase the number of accessible acid sites of the HPAs, a variety of supports like, activated carbon [13–17], silica [18–23], zeolite [24–28] and polymeric matrix [29–33] have been used as support to immobilize HPAs.

Industrially, the HPAs have been used as catalysts in the oxidation of methacrolein to methacrylic acid, oxidation of ethylene to acetic acid and hydration of olefins [12].

In this work, we describe the use of the dodecamolybdophosphoric acid (H₃PMo₁₂O₄₀) encaged in USY zeolite, as catalysts for the esterification of glycerol with acetic acid.

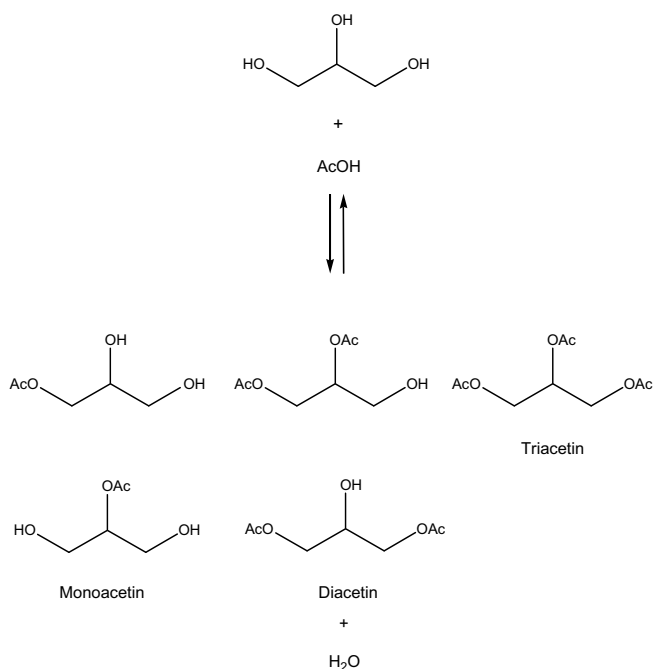
2. Experimental

2.1. Preparation of the catalysts

In order to neutralize the commercial HUSY zeolite (CBV 720, Si/Al = 30, A_o = 24.28 Å, Zeolyst International) before the encapsulation of the dodecamolybdophosphoric acid (PMo), the zeolite was exchanged to the sodium form, by three consecutive treatments with 2 M NaCl at 80 °C, washed with distilled water and finally dried at 120 °C. The sample will be denoted as NaUSY.

The encapsulation of PMo in the supercages of the NaUSY sample was performed according to the method reported by Mukai et al. [26]. Briefly, 2.0 g of NaUSY and 7.2 g of molybdenum (VI) oxide

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Scheme 1.

were mixed in 70 g of deionized water. This mixture was stirred for 24 h at room temperature. 0.48 g of phosphoric acid was added, and the obtained mixture was stirred for 3 h, at a temperature of 368 K. The synthesized sample (PMo encaged NaUSY) was filtrated and dried at 383 K. The obtained PMo_NaUSY catalyst was thoroughly washed with hot water.

2.2. Characterization of the catalysts

The textural characterization of the catalysts was based on the nitrogen adsorption isotherm, determined at 77 K with a Micromeritics ASAP 2010 apparatus.

FTIR spectra were recorded on a Bio-Rad FTS 155 FTIR spectrometer at room temperature in KBr pellets over range of 400–4000 cm^{-1} under atmospheric conditions.

X-ray diffraction (XRD) patterns were recorded on the catalyst, NaUSY zeolite and heteropolyacid. The equipment used to this end was a Bruker powder diffractometer with built-in recorder, using Cu K α radiation, nickel filter, 30 mA and 40 kV in the high voltage source, and scanning angle between 5° and 40° of 2 θ at a scanning rate of 1°/min. The amount of dodecamolybdophosphoric acid encaged in NaUSY zeolite was measured by dissolving the catalyst in H₂SO₄/HF 1:1 (v/v) and analyzing the obtained solution using inductively coupled plasma analysis (ICP), which was carried out in a Jobin-Yvon ULTIMA instrument.

2.3. Catalytic experiments

The catalytic experiments were carried out in a stirred batch reactor at reflux conditions. In a typical experiment, the reactor was loaded with 20 mL of acetic acid, 2 g of glycerol and 0.2 g of catalyst.

Stability tests of the PMo₃-NaUSY were carried out by running four consecutive experiments, in the same reaction conditions. Between the catalytic experiments, the catalyst was separated from the reaction mixture by centrifugation, washed with water and dried at 120 °C overnight.

Samples were taken periodically and analyzed by GC, using a KONIC HRGC-3000C instrument equipped with a 30 m × 0.25 mm DB-1 column.

3. Results and discussion

3.1. Catalysts characterization

Table 1 shows the textural characterization of the catalysts. The specific surface area (S_{BET}) was determined using the BET method while microporous volume (V_{micro}) was determined by the *t*-method, using a standard isotherm proposed by Greeg and Sing [34]. It was observed that the immobilization of dodecamolybdophosphoric acid in the NaUSY zeolite leads a decrease of the surface area and the microporous volume. The reduction in the surface area and microporous volume of the catalysts may be due to the inclusion of heteropolyacid in supercages of the NaUSY zeolite. A similar result was also observed by Mukai et al. [26].

Fig. 1 shows the IR spectra of the PMo (Fig. 1A), PMo₃-NaUSY (Fig. 1B) and NaUSY (Fig. 1C). The bands at $\sim 1100 \text{ cm}^{-1}$, 954–975 cm^{-1} , 869–880 cm^{-1} and 785–810 cm^{-1} , respectively, assignable to the bending vibrations P–O, Mo–O (terminal), Mo–O–Mo (corner-sharing oxygen) and Mo–O–Mo (edge-sharing oxygen) [26] was observed in the IR spectra of PMo (Fig. 1A). However, only the band at 954–975 cm^{-1} appears in the IR spectra of PMo₃-NaUSY catalyst (Fig. 1B). The other peaks are overlapped or partially overlapped with the peaks of framework of NaUSY zeolite matrix. However, the differential spectrum of PMo₃-NaUSY (Fig. 2B) shows the presence of typical peaks characteristic of Keggin structures. These results suggest that the dodecamolybdophosphoric acid was synthesized in the supercages of NaUSY zeolite [28].

The XRD patterns of the NaUSY zeolite and catalysts are shown in Fig. 3. No diffraction peaks assigned to PMo were detected for the catalysts. The XRD patterns of the catalysts are similar to the XRD pattern of the NaUSY, suggesting the framework structure of zeolite was maintained after the PMo immobilization. Tran et al. also made a similar observation from XRD analysis of PMo_NaUSY catalysts [28]. Consequently, the heteropolyacid encaged in USY zeolite is highly dispersed into supercages, and its structure was not identified clearly by XRD.

Table 1
Physicochemical characterization of catalyst sample.

Sample	Amount HPA ^a ($\text{g}_{\text{HPA}}/\text{g}_{\text{zeolite}}$)	Surface area ^b (m^2/g)	Microporous volume ^c (cm^3/g)
NaUSY	–	854	0.31
PMo1_NaUSY	0.006	853	0.29
PMo2_NaUSY	0.013	738	0.28
PMo3_NaUSY	0.019	713	0.17
PMo4_NaUSY	0.054	544	0.10

^a ICP.

^b BET.

^c *t*-Method.

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