

Synthesis of Keggin type vanadophosphomolybdate supported modified clays and their catalytic performance in Cyclohexene epoxidation

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Abstract

The catalytic performance of supported heteropolyacids in various liquid–solid and gas–solid heterogeneous reactions may be affected by the choice of support and/or the method of heteropolyacid deposition. Vanadium substituted polyphosphomolybdate with Keggin structure $H_4[PVMo_{11}O_{40}].13H_2O$ (PVMo) was dispersed throughout acid activated Bentonite (clay from Hammam Boughrara, Maghnia, Algeria). A series of catalysts were prepared via modified impregnation. Modified preparation method used ultrasonication as a means of the dispersion homogenization, followed by freeze-drying. The catalysts were characterized by BET, FT-IR and ³¹P solid-state MAS-NMR spectroscopy. The catalytic performance of PVMo/Hmont was evaluated in the oxidation of cyclohexene. Intact Keggin anions were preserved on Hmont after deposition aided by ultrasonication. The obtained results showed that a better catalytic activity can be obtained with PVMo/Bentonite (98 % of conversion and 89 % of cyclohexene oxide), by drop addition of H₂O₂, for 3 hours.

Keywords: Heteropolyacids; Bentonite; Acid catalyst; Cyclohexene epoxidation; Hydrogen peroxide.

I. Introduction

From an industrial point of view, epoxides are considered as one of the most vital building blocks for the synthesis of perfume materials, anthelmintic preparations, epoxy resins, plasticizers, drugs, sweeteners, etc. and have inspired the invention of numerous methods for their preparation [1, 2]. Although many of these methods have proven to be greatly useful for the construction of a range of important epoxide architectures, much attention has been paid over recent years to the establishment of ecologically acceptable processes in the chemical industries [3, 4].

Though access to a variety of epoxides has been immensely successful due to the remarkable

catalytic activity of d-transition metal complexes, oxidations catalyzed by rare-earth metal derivatives appeared only recently [5-8]. In our study we have chosen the heteropolyacids based vanadium that has been employed as catalyst for the epoxidation of cyclohexene.

Polyoxometalates (POMs) stand for a diverse family of anionic metal oxide molecular species [9, 10]. Among POMs, heteropoly acids (HPAs) have caused great interest of people for a long time. Their excellent properties, such as special structures, unique catalytic performance and stability, promote them to be applied to the catalysis, biomedicine, materials science and so on [11-14]. In particular, the ability of these compounds to act as strong Bronsted acids and

retain water even at high temperatures makes them excellent proton conductors [15, 16]. For this reason, their potential applications in fuel cells, super capacitors, etc., became possible [17, 18].

Heteropolyacids with the Keggin-type structure have been examined in bulk or supported forms in both homogeneous and heterogeneous reactions. Supporting the heteropolyacids on porous solids with high specific surface area may improve their catalytic performance in various liquid–solid and gas–solid heterogeneous reactions. A lot of studies have been published on the immobilization of heteropolyacids on various supports including silica, alumina, titania and zeolites [19–23]. Among them, clay minerals have been also explored as the supports for heteropolyacids. Montmorillonite is one of the most intensively explored catalytic materials in heterogeneous catalysis due to its low cost and eco-friendliness. Also, it possesses some unique properties like cation exchange capacity and swelling ability, thereby accommodating various guest species in its interlayers. Bentonite is a clay mineral, which is mainly composed of montmorillonite with chemical composition of SiO_2 , Al_2O_3 , CaO , MgO , Fe_2O_3 , Na_2O and K_2O . It is a 2:1 aluminosilicate, the unit layer structure of which consists of one Al^{3+} octahedral sheet between two Si^{4+} tetrahedral sheets [24]. Montmorillonite was also used in different fields [25–28].

In this perspective, a series of the catalysts containing Keggin-type heteropolyacids 11-molybdo-vanado-phosphoric acid $\text{H}_4[\text{PVMo}_{11}\text{O}_{40}]\cdot 13\text{H}_2\text{O}$ (PVMo) were prepared according to a new modified impregnation method. Montmorillonite derived from Hammam Boughrara, Maghnia, Algeria and treated by HCl acid activation were used as supports for PVMo. The oxidation of cyclohexene, using hydrogen peroxide as an oxidant was selected to evaluate their catalytic performance.

II. Experimental

A. Catalysts Synthesis

The synthesis of vanadium substituted polyphosphomolybdate with Keggin structure $\text{H}_4[\text{PVMo}_{11}\text{O}_{40}]\cdot 13\text{H}_2\text{O}$ (PVMo) and acid activated clay (Hmont) is reported in the literature [29].

Modified impregnation involved the preparation of dispersion by mixing 1 g of montmorillonite powder (Hmont) with 150 cm^3 of distilled water and stirring the obtained dispersion for 30 min using a magnetic stirrer. Then, the mixture was ultrasonically agitated for 100 min. Ultrasonic treatment was performed with a POLSONIC ultrasonic bath Sonic 2 (100 W, 40 kHz). Next, an appropriate amount of PVMo powder was added to this dispersion. The resulting slurry was mixed for 30 min. and then ultrasonically agitated for 20 min. The final product was dried after immersion in liquid nitrogen in a CHRIST freeze dryer Alpha 1–4/LD (at $-70\text{ }^\circ\text{C}$, in a vacuum 4×10^{-3} Tor). Dried sample was ground using an agate mortar.

B. Characterization

Nitrogen sorption analysis was carried out at $-196\text{ }^\circ\text{C}$ using Quanta chrome Instruments (Nova 1000[®]). Prior to analysis, the samples were degassed at $150\text{ }^\circ\text{C}$ for 3 h. Specific surface area (S_{BET}) was calculated using the Brunauer Emmett–Teller (BET) method based on adsorption data in the partial pressure of 0.1 b $p/p_0 < 0.35$. Total pore volume (V_{tot}) and average pore diameter (Φ) were determined by the amount of nitrogen adsorbed at $p/p_0 = 0.99$.

Fourier transform infrared (FTIR) spectra were recorded by an Agilent Technologies Cary 600 series FTIR spectrometer using an attenuated reflection accessory (ATR), under atmospheric conditions. The FTIR spectra were obtained in the range of $400\text{--}4000\text{ cm}^{-1}$, and all spectra were collected at room temperature with a resolution of 4 cm^{-1} .

C. Cyclohexene oxidation

Catalytic cyclohexene oxidation was performed in a round bottom flask, under magnetic stirring. Unless otherwise specified, all oxidation reactions were carried out at atmospheric pressure under reflux with 30 mmol of cyclohexene, H_2O_2 (30 mmol) was used as oxidant, 10 mL of acetonitrile as solvent, 1 mL of 1,2 dimethoxy ethane as internal standard for product quantification, and 25 mg of catalyst. The reaction mixture was stirred at $70\text{ }^\circ\text{C}$. The catalytic reactions were monitored using gas chromatography (Agilent Technologies 6500 GC System) equipped with a Agile HP-FFAP (30 m x

0.25mm 0.25 μm) column; a flame ionization detector (FID) was also used.

III. Results and Discussions

A. Catalysts Characterization

The surface area and pore volume of HMont and PVMo loaded HMont were measured. It appeared that, in general, the surface area and pore volume of HMont decreased considerably upon loading with PVMo. The results of a typical example, i.e. PVMo/HMont catalysts, are given in Table 1. The surface area (195 m² g⁻¹) and the total pore volume of HMont decreased as the amount of PVMo loading increased. Thus, for 20% PVMo loading, the surface area fell to 141 m² g⁻¹ and the total pore

volume to 0.17 cm³ g⁻¹ only. The high surface area of acid activated clay was due to the removal of aluminum from the octahedral sites in the clay sheet. The reduction in surface area and pore volume upon PVMo loading might be due to the blockage of pores by PVMo molecules.

Table 1. Textural properties of various samples

	S _{BET} (m ² g ⁻¹)	V _{tot} (cm ³ g ⁻¹)	D _{p(moy)} (Å)
H-mont	101	1,22	18,94
10 % PVMo/H-mont	49	0,77	18,87
20 % PVMo/H-mont	51	0,87	18,89
30 % PVMo/H-mont	54	0,80	18,85
40 % PVMo/H-mont	23	0,36	18,99

S_{BET} : surface area, V_{tot} : total pore volume, D_{p(moy)} : average pore diameter

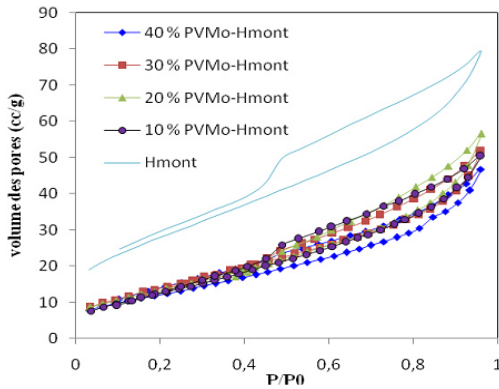


Figure 1. N₂ adsorption-desorption isotherms of catalysts

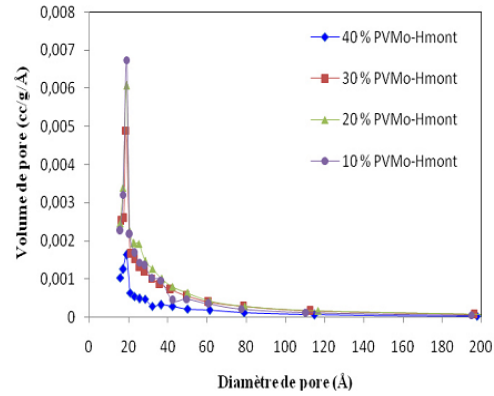


Figure 2. Pore size distribution curves of catalysts

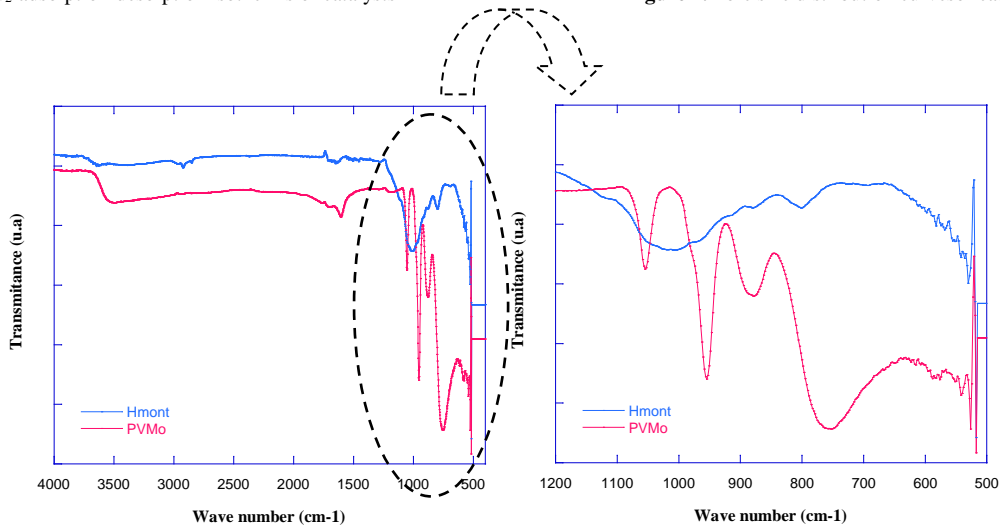


Figure 3. FTIR analysis of PVMo and H-mont.

The complete adsorption–desorption isotherms of calcined samples, are presented in Figure. 1. All the curves are nearly similar and can be included in type IV in the IUPAC classification. The pore size distribution, determined from the desorption branch

of the N₂ adsorption isotherm using the Barrett–Joyner– Halenda (BJH) method (Figure 2), shows that the average pore sizes of different weight percents of PVMo on HMont are in the microporous region.

The IR spectra for bulk PVMo shown at 1054, 954, 878, 752 and 541 cm^{-1} that can be attributed to the stretching vibrations of $\nu_{\text{as}}(\text{P-O}_a)$, $\nu_{\text{as}}(\text{Mo-O}_d)$, $\nu_{\text{as}}(\text{Mo-O}_b - \text{Mo})$, $\nu_{\text{as}}(\text{Mo-O}_c - \text{Mo})$ et and $\nu(\text{P-O})$ vibrations, respectively. In a Keggin-type unit, O_a refers to the oxygen atom common to PO_4 tetrahedron and one trimetallic group Mo_3O_{13} , O_b connects two trimetallic groups, O_c binds two octahedral MoO_6 units inside a trimetallic group and O_d is the terminal oxygen atom [30, 31]. On Hmont supported catalysts, some of the characteristic Keggin bands are seen at 982 and 893 cm^{-1} and other bands are exhibited as in case of Hmont clay. The spectra show a band around 3600 cm^{-1} for all the samples, which is due to asymmetric stretching of OH group. The adsorption band at 1620–1640 cm^{-1} is due to H–O–H bending vibration in water. A decrease in the intensities of these bands was noted as the loading increased.

The solid state ^{31}P (MAS) NMR of PVMo is shown in Figure 5. The ^{31}P chemical shift provides important information about the structure, composition and electronic states of these materials. The ^{31}P NMR spectra of PVMo (Fig. 5) show a chemical shift at 3.884 ppm, this is in good agreement with the reported one [21].

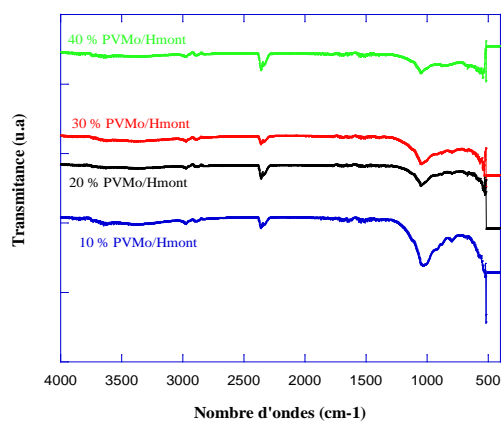


Figure 4. FTIR analysis of catalysts.

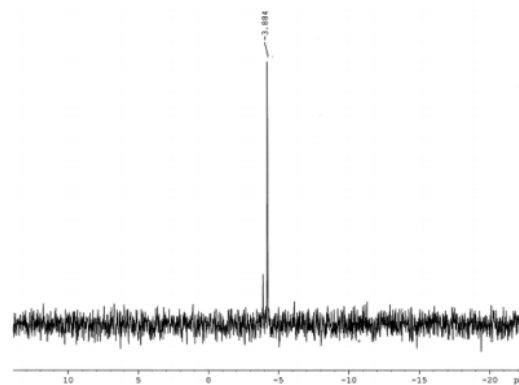


Figure 5. ^{31}P NMR spectra in D_2O (room temperature) of PVMo.

B. Cyclohexene Oxidation

Cyclohexene oxidation with H_2O_2 30 % was chosen as a model reaction to compare the behaviours of different catalysts. This reaction is widely used as a road for the production of the adipic acid, which is a key intermediary for the synthesis of nylon 6,6. To estimate the activity of our catalysts PVMo/Hmont, we synthesized according to the % in active phase, four catalysts results of which obtained according to the analysis chromatography are recapitulated in the table 2. According to the results, the reaction was selective to cyclohexene oxide (Epoxide) and the conversion increases with the increase of the active phase. Monomeric, dimeric, and tetrameric peroxy species are generated by the reaction of polyoxometalates with hydrogen peroxide, and the peroxy species are supposed to be the active species for epoxidation of olefins within a POM/ H_2O_2 system [32–34]. Best yields and selectivity's are reached with 40 % PVMo/Hmont (Conversion 98 % and 89 % of cyclohexene epoxide).

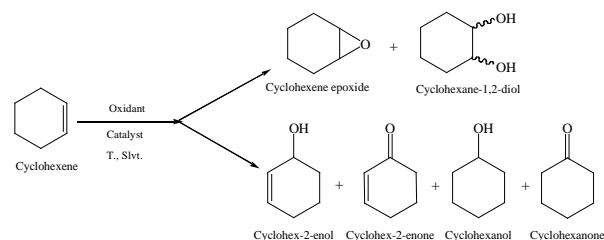


Figure 6. Cyclohexene epoxidation reaction products

To check if our reaction is done in homogeneous or heterogeneous phase, we studied the leaching of

catalyst. For that, it is necessary initially to filter it reactional mixture at the end of the reaction then to start again the reaction by adding that the desired load. In our case, one A chooses to test the leaching of the catalyst which gave us the best results in term of conversion and selectivity. The catalyst selected is 40 % PVMo/H-mont. Analysis CPG indicated a conversion into unknown products to us.

FTIR analysis of the filtered reactional mixture (figure 7), showed the presence of the band V=O which appears to 920 cm^{-1} . Thus, an orange color referring to vanadium was observed.

Table 2. Cyclohexene epoxidation with different catalysts

Catalyseurs	Conversion (%)	Sélectivité (%)					
		Epoxyde	C ₆ -ol	C ₆ -énol	C ₆ -énone	C ₆ -diol	C ₆ -one
10 %PVMo/H-mont	77,39	94,24	1,93	/	3,81	/	/
20 %PVMo/H-mont	84,22	82,82	3,01	/	/	/	14,15
30 %PVMo/H-mont	98,75	64,77	/	/	32,84	/	3,55
40 %PVMo/H-mont	97,90	88,57	2,5	2,5	6,42	/	/

Reaction conditions: 25 mg of catalyst: x% PVMo/Hmont, 30 mmol cyclohexene, 30 mmol 30 % H₂O₂, 10 mL CH₃CN, 6 h, 70 °C

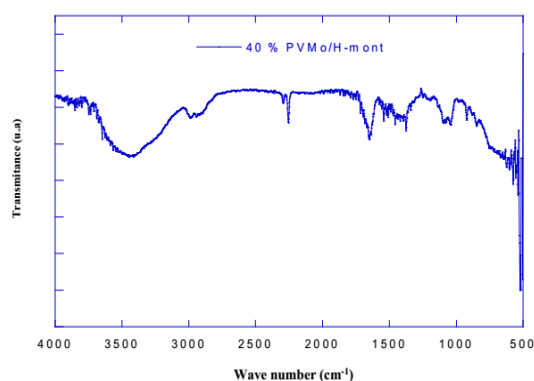


Figure 7. FTIR analysis of medium relational after filtration.

IV. Conclusion

Four catalysts of various percentages were synthesized (10%, 20%, 30% et 40 % PVMo/H-mont). The analysis IR showed that the structure Keggin was protected after impregnation on the acid activated clay according to the appearance of the characteristic bands of vibration of the anion Keggin $\text{PM}_{12}\text{O}_{40}]^{3-}(\text{M}=\text{V})$. The prepared catalysts show a good activity in cyclohexene epoxidation with a conversion of cyclohexene 98% and a selectivity of 89% of cyclohexene epoxide. The increase of the conversion at the same time with the increase of the percentage in active phase expresses the contribution of the vanadophosphomolybdic acid (PVMo).

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