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Oxidation of Cyclohexene with H_2O_2 Catalyzed by Vanadium Based Polyoxometalates Doped Modified Clays as Green Catalysts

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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 the Keggin structure $H_4[PVMo_{11}O_{40}]\cdot 13H_2O$ (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 employed ultrasonication as a means of the dispersion homogenization, followed by freeze-drying. The catalysts were characterized by the Brunauer–Emmett–Teller, the Fourier transform infrared, and ^{31}P solid-state magic angle spinning-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 H_2O_2, for 3 h.

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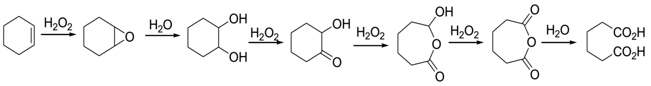
PACS/topics: heteropolyacids, bentonite, acid catalyst, cyclohexene oxidation, hydrogen peroxide

1. Introduction

Cyclohexene oxidation has been the subject of extensive studies as the products obtained are important synthetic intermediates for the production of fine chemicals and can also be utilized in polyether polymers synthesis. However, cyclohexene (CyH) oxidation to cyclohexene oxide followed by epoxide ring opening and subsequent oxidation of *trans*-cyclohexane-1,2-diol rates as a possible route to adipic acid [1–3].

Thus the heterogeneous oxidation of cyclohexene in the presence of hydroperoxides has much more advantages in the field of synthetic chemistry [4]. The development of green practical procedures for the oxidation of six-carbon feedstock is highly desirable — particularly for the medium and large-scale synthesis of various intermediates and fine chemicals [5].



Heteropolyacids with the Keggin-type structure have been extensively studied for the use as acid and redox catalysts. They 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 [6–10]. 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 [11]. Montmorillonite was also used in different fields [12–15].

In this perspective, a series of the catalysts containing Keggin-type heteropolyacids 11-molybdo-vanadophosphoric acid $H_4[PVMo_{11}O_{40}].13H_2O$ (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.

2. Experimental

2.1. Catalysts preparation

The synthesis of vanadium substituted polyphosphomolybdate with Keggin structure (PVMo) and acid activated clay (Hmont) is reported in the literature [3].

Modified impregnation involved the preparation of dispersion by mixing 1 g of montmorillonite powder

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(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 $-70\,^{\circ}$C, in a vacuum 4×10^{-3} Torr). Dried sample was ground using an agate mortar.

2.2. Characterization

Nitrogen sorption analysis was carried out at $-196\,^{\circ}$C using Quantachrome Instruments (Nova 1000^e). Prior to analysis, the samples were degassed at 150 °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 $0.1 < p/p_0 < 0.35$. Total pore volume (V_{tot}) and average pore diameter (Φ) were determined by the amount of nitrogen adsorbed at $p/p_0 = 0.99$.

The 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 400–4000 cm^{-1}, and all spectra were collected at room temperature with a resolution of 4 cm^{-1}.

2.3. Oxidation of cyclohexene

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-dimethoxyethane as internal standard for product quantification, and 25 mg of catalyst. The reaction mixture was stirred at 70 °C. The catalytic reactions were monitored using gas chromatography (Agilent Technologies 6500 GC System) equipped with a Agile HP-FFAP (30 m × 0.25 mm × 0.25 m) column; a flame ionization detector (FID) was also used.

3. Results and discussions

3.1. 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 I. The surface area (195 m^2/g) 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 m^2/g and the total pore volume to 0.17 cm^3/g 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.

The complete adsorption–desorption isotherms of calcined samples, are presented in Fig. 1A. 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 N_2 adsorption isotherm using the Barrett–Joyner– Halenda (BJH) method (Fig. 2), shows that the average pore sizes of different weight percents of PVMo on HMont are in the microporous region.

TABLE I

Textural properties of various samples

	S_{BET} [m^2/g]	V_{tot} [cm^3/g]	$D_{p(moy)}$ [Å]
Hmont	101	1.22	18.94
10 % PVMo/Hmont	49	0.77	18.87
20 % PVMo/Hmont	51	0.87	18.89
30 % PVMo/Hmont	54	0.80	18.85
40 % PVMo/Hmont	23	0.36	18.99

S_{BET} — surface area. V_{tot} — total pore volume. $D_{p(moy)}$ — average pore diameter.

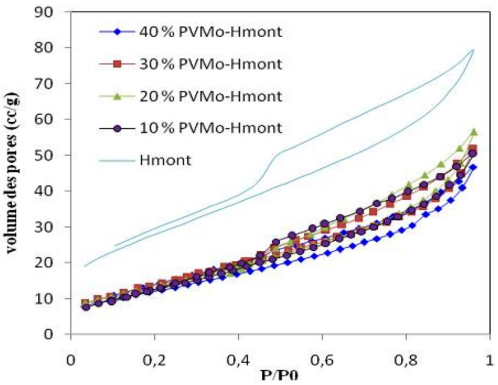

Fig. 1. N_2 adsorption-desorption isotherms of catalysts.

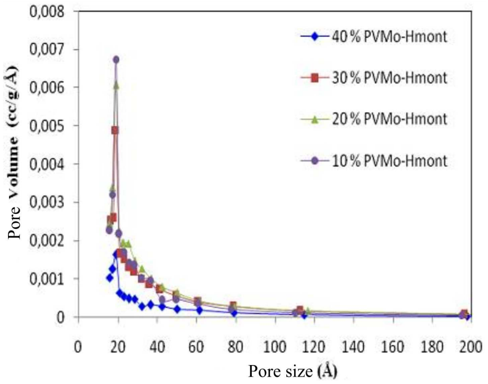

Fig. 2. Pore size distribution curves of catalysts.

The IR spectra for bulk PVMo (Fig. 3) shown at 1054, 954, 878, 752, and 541 cm^{-1} can be attributed to the stretching vibrations of υ_{as} (P-O_a), υ_{as} (Mo-O_d), υ_{as} (Mo-O_b – Mo), υ_{as} (Mo-O_c – Mo) et and υ (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 [16, 17]. On Hmont supported catalysts (Fig. 4), 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.

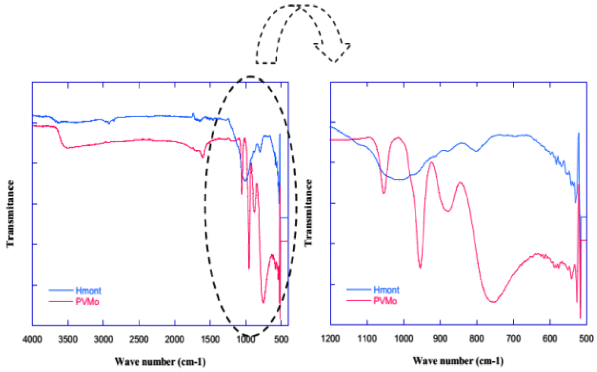

Fig. 3. FTIR analysis of PVMo and Hmont.

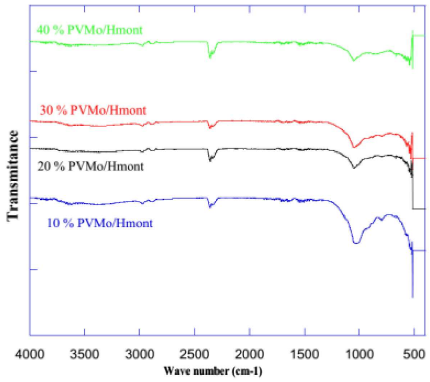

Fig. 4. FTIR analysis of catalysts.

The solid state ^{31}P (MAS) NMR of PVMo is shown in Fig. 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 [8].

3.2. *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. Generally, the cyclohexene oxidation reaction leads mainly to the formation of cyclohexene oxide (epoxide) and cyclohexane diols (diol), besides cyclohexenol (Enol), cyclohexenone (Enone), cyclohexanol (Ol) and cyclohexanone (One) (Fig. 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 Table II.

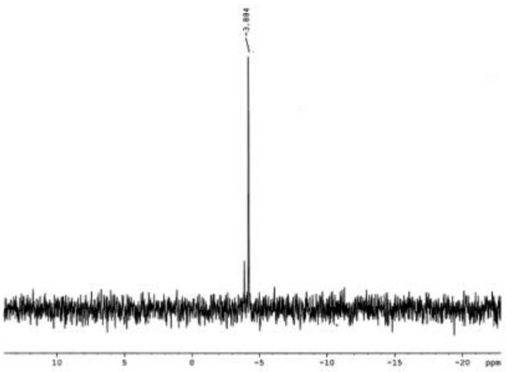

Fig. 5. ^{31}P NMR spectra in D_2O (room temperature) of PVMo.

TABLE II

Activity of various catalysts with given PVMo content towards the oxidation of cyclohexene. All data in [%].

PVMo	Conv.	Sel.					
		epoxide	C6-diol	C6-ol	C6enol	C6-enone	C6-one
10	77.4	94.3	–	1.9	–	3.8	–
20	84.2	82.8	–	3.1	–	–	14.1
30	98.8	64.8	–	–	–	32.8	3.4
40	97.9	88.6	–	2.5	2.5	6.4	–

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 peroxo species are generated by the reaction of polyoxometalates with hydrogen peroxide, and the peroxo species are supposed to be the active species for epoxidation of olefins within a POM/H_2O_2 system [18–20]. Best yields and selectivity are reached with 40% PVMo/Hmont (conversion 98% and 89% of cyclohexene epoxide).

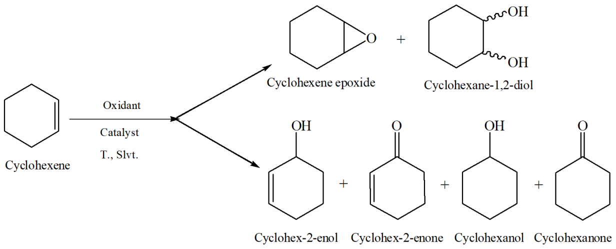

Fig. 6. Cyclohexene oxidation reaction products.

4. Conclusion

Four catalysts of various percentages were synthesized (10%, 20%, 30% and 40% PVMo/Hmont). The IR analysis showed that the Keggin structure was protected after impregnation on the acid activated clay according to the appearance of the characteristic bands of vibration of the Keggin anion $[PM_{12}O_{40}]^{3-}$ (M=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).

References

[1] S. El-Korso, I. Khaldi, S. Bedrane, A. Choukchou-Braham, F. Thibault-Starzyk, R. Bachir, *J. Mol. Catal. A Chem.* **394**, 89 (2014).

[2] J.M. Fraile, J.I. García, J.A. Mayoral, L. Salvatella, E. Vispe, D.R. Brown, G. Fuller, *J. Phys. Chem. B* **107**, 519 (2003).

[3] S. Boudjema, E. Vispe, A. Choukchou-Braham, J.A. Mayoral, R. Bachir, J.M. Fraile, *RSC Adv.* **5**, 6853 (2015).

[4] G. Lapisardi, F. Chiker, F. Launay, J. Nogier, J. Bonardet, *Micro. Meso. Mater.* **78**, 289 (2005).

[5] C.-Y. Cheng, K.-J. Lin, M.R. Prasad, S.-J. Fu, S.-Y. Chang, S.-G. Shyu, H.-S. Sheu, C.-H. Chen, C.-H. Chuang, M.-T. Lin, *Catal. Commun.* **8**, 1060 (2007).

[6] P.A. Shringarpure, A. Patel, *Chem. Eng. J.* **173**, 612 (2011).

[7] M.E. Chimienti, L.R. Pizzio, C.V. Caceres, M.N. Blanco, *Appl. Catal. A* **208**, 7 (2001).

[8] P. Sharma, A. Patel, *Appl. Surf. Sci.* **255**, 7635 (2009).

[9] S. Tangestaninejad, V. Mirkhani, M. Moghadam, I. Mohammadpoor-Baltork, E. Shams, H. Salavati, *Ultrason. Sonchem.* **15**, 438 (2008).

[10] T. Ressler, U. Dorn, A. Walter, S. Schwarz, A.H.P. Hahn, *J. Catal.* **275**, 1 (2010).

[11] H. Salavati, N. Rasouli, *Mater. Res. Bull.* **46**, 1853 (2011).

[12] B. Otsukarci, Y. Kalpakli, *Acta Phys. Pol. A* **130**, 198 (2016).

[13] F. Akti, F. Boran, *Acta Phys. Pol. A* **130**, 147 (2016).

[14] A. Evcin, N. Bezir, R. Kayalı, M. Kaşıkçı, A. Oktay, *Acta Phys. Pol. A* **128**, B-303 (2015).

[15] B. Tuğrul, S. Erentürk, S. Haciyakupoğlu, N. Karatepe, N. Altinsoy, N. Baydoğan, F. Baytaş, B. Büyük, E. Demir, S. Gedik, *Acta Phys. Pol. A* **128**, B-180 (2015).

[16] S. Benadji, P. Eloy, A. Leonard, B.L. Su, K. Bachari, C. Rabia, E.M. Gaigneaux, *Micro. Meso. Mater.* **130**, 103 (2010).

[17] H. Salavati, N. Rasouli, *Appl. Surf. Sci.* **257**, 4532 (2011).

[18] Z. Weng, J. Wang, S. Zhang, C. Yan, X. Jian, *Appl. Catal. A* **339**, 145 (2008).

[19] N.K.K. Raj, A.V. Ramaswamy, P. Manikandan, *J. Mol. Catal. A Chem.* **227**, 37 (2005).

[20] C. Swalus, B. Farin, F. Gillard, M. Devillers, E.M. Gaigneaux, *Catal. Commun.* **37**, 80 (2013).