Aerobic hydrocarbon oxidation catalyzed by the vanadomolybdophosphate polyoxometalate, $H_5PV_2Mo_{10}O_{40}$, supported on mesoporous MCM-41

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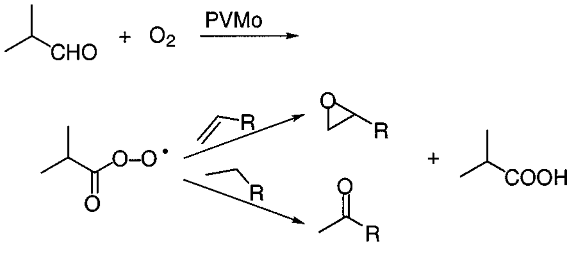
The impregnation of $H_5PV_2Mo_{10}O_{40}$ polyoxometalate onto MCM-41 and amino-modified MCM-41 materials provided mesoporous active catalysts with large surface areas for aerobic hydrocarbon oxidation using isobutyraldehyde as a reducing agent. The results of the oxidation of alkenes and alkanes gave product selectivities similar to those observed in the corresponding homogeneous reaction although catalytic activity was somewhat reduced. Under appropriate experimental conditions there was no leaching and the solid catalyst could be recovered and reused without loss in activity.

Keywords: polyoxometalates, hydrocarbon oxidation, mesoporous silica

1. Introduction

Polyoxometalates are well known as oxidation and acid catalysts in which the redox and acid–base properties can be tuned by variation of the structure type and the heteroatom, addenda and or transtion-metal-substituted atoms [1]. One quite intensively studied polyoxometalate is the vanadomolybdophosphate of the Keggin structure, $H_5PV_2Mo_{10}O_{40}$, known for its redox type catalytic activity in oxydehydrogenation using molecular oxygen as terminal oxidant [2]. More recently, we have studied, in homogeneous reaction media, the use of $H_5PV_2Mo_{10}O_{40}$ as a highly effective catalyst for aerobic hydrocarbon oxidation using isobutyraldehyde as a cooxidant [3]:



(1)

An interesting modification of the above described catalytic system would be the heterogenization of the $H_5PV_2Mo_{10}O_{40}$ heteropoly acid onto a mesoporous molecular sieve, such as MCM-41. In one method for heterogenization, the heteropoly acid is adsorbed as it is onto the support. In this way, the isostructural phosphotungstate, $H_3PW_{12}O_{40}$, supported on MCM-41 demonstrated high activity in acid-catalyzed reactions [4]. Alternatively, polyoxometalates may be bound electrostatically to silica surfaces. In this manner, silicas modified with basic amino groups were reacted with heteropoly acids. The resulting partially neutralized polyoxometalates showed no decrease in activity [5].

In the present letter, we report on the $H_5PV_2Mo_{10}O_{40}$ polyoxometalate (PVMo) supported onto a mesoporous molecular sieve both by adsorption to MCM-41 and by electrostatic binding to MCM-41 modified with amino groups (MCM-41-NH_2). These new solid-phase oxidation catalysts are active in the aerobic oxidation of alkenes and alkanes in the presence of isobutyraldehyde according to equation (1).

2. Experimental

All chemicals used were of reagent grade. $H_5PV_2Mo_{10}O_{40}$ and MCM-41 were prepared according to the known literature procedures [6,7]. MCM-41-NH_2 was prepared by modification of MCM-41 as follows: 3-aminopropyltriethoxysilane (0.52 ml, 2.22 mmol) was added to a suspension of 4.46 g activated (200 °C, vacuum, 22 h) MCM-41 in 40 ml dry m-xylene. The mixture was heated under reflux under an inert argon atmosphere for 15 h. The MCM-41-NH_2 material was collected by filtration, washed with acetone and dried overnight at 80 °C under vacuum. Reactions were carried out in a thermostated glass reactor of 50 ml volume equipped with magnetic stirrer. In a standard experiment, the reaction vessel was loaded with 30 mg catalyst and a solution of 0.8 mmol substrate and 1.1 mmol of isobutyraldehyde in 1 ml of 1,2-dichloroethane. Molecular oxygen was added and the reactor pressurized to 1 atm. The progress of the reaction was monitored by gas chromatography. Oxidation reaction products were characterized and quantified using reference compounds by use of GLC (HP 5890) equipped with a flame ionization detector

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and a 15 m × 0.32 mm 5% phenylmethylsilicone (0.25 μm coating) capillary column. Products whose initial identity was questionable were identified using a gas chromatograph equipped with a mass selective detector (HP-GCD) and the same column. Solid-state MAS NMR spectra were acquired on a Bruker DSX 400 spectrometer operating at 161.9 MHz (^{31}P NMR). Chemical shifts are referenced to 85% H_3PO_4. The BET surface areas and pore size distributions of the catalyst samples were calculated from N_2 isotherms at 77 K using a home-made automated Catasorb apparatus. The samples were degassed under vacuum at 100 °C (PVMo/MCM and PVMo/MCM-N) or 150 °C (MCM-41 and MCM-41-NH_2) for 8 h. UV-vis spectra were taken on a diode array spectrometer (HP 8452) equipped with in integrating sphere. ATR-IR measurements were carried out on a Nicolet 510 M FTIR spectrometer.

3. Results and discussion

3.1. Synthesis and characterization of $H_5PV_2Mo_{10}O_{40}$ supported on mesoporous MCM-41 and MCM-41-NH_2

The mesoporous molecular sieve MCM-41 has pores, whose diameters range from 20 to 40 Å. Since heteropoly acids of the Keggin structure have molecular diameters of ~12 Å, it is feasible to insert polyoxometalates such as $H_5PV_2Mo_{10}O_{40}$ (PVMo) into MCM-41. The (20 wt%) PVMo/MCM catalyst was prepared by addition of 0.1 g $H_5PV_2Mo_{10}O_{40}$ dissolved in 10 ml distilled water to pure silica MCM-41 (0.4 g). The mixture was gently stirred under ambient conditions for 16 h. The PVMo/MCM was isolated by evaporation of the water and was dried at 60 °C under vacuum. The color of the material was initially orange (oxidized), but tended to turn slightly green (partially reduced). Similarly, PVMo/MCM-N was prepared by stirring modified MCM-41-NH_2 (0.4 g) with PVMo (0.1 g in 10 ml of water) at room temperature for 5 h (molar ratio $NH_2 : \mathrm{PVMo} = 5$). The solid was then filtered off and dried under vacuum at 60 °C. Comparative UV-vis measurements of water solution before and after impregnation showed that more than 99% of PVMo was supported on the mesoporous material. The spectrum of PVMo on the support was blue-shifted by by 23 nm vs. the spectrum in solution indicating satisfactory heterogenization within the pores.

All the solid materials were characterized by N_2 physisorption and ^{31}P MAS NMR spectroscopy. Table 1 presents the BET surface areas and the mean pore diameters of the initial MCM-41 and MCM-41-NH_2, and the samples loaded with PVMo, 20% PVMo/MCM and 20% PVMo/MCM-N. Surface areas and pore diameters decreased when the mesoporous silicas were loaded with PVMo, but nevertheless the materials still had large surface areas and retained the uniformity of their mesopores. A good method for examining the structure of polyoxometalates is by ^{31}P NMR. The spectrum of bulk PVMo consists of a singlet at -2.47 ppm and is in agreement with literature data [1]. Due to line broadening in the solid-state NMR, there is no differentiation of the five isomeric forms for $H_5PV_2Mo_{10}O_{40}$ which are observable in certain solutions. Similarly, the ^{31}P NMR shifts for PVMo/MCM and PVMo/MCM-N, figure 1, were slightly shifted and observed at -1.24 and -1.66 ppm, respectively. These results would seem to indicate that the structure of the polyoxometalate is retained upon impregnation. This was supported by the observation of the typical unchanged IR spectrum for PVMo. The slight shifts are attributed to changes in the polyoxometalate hydration state as was found previously for supported phosphotungstic heteropoly acid [4]. Interestingly, the peak width for PVMo/MCM, $\Delta\nu_{1/2} = 400$ Hz,

Table 1
Surface and porosity of mesoporous materials.

Sample	$T_{\max}$[a] (°C)	S (m^2/g)	d (Å)
MCM-41	500	860	39.5
PMo/MCM	100	569	35.2
MCM-41-NH_2	150	698	35.9
PMo/MCM-N	100	583	35.7

[a] Pretreatment temperature.

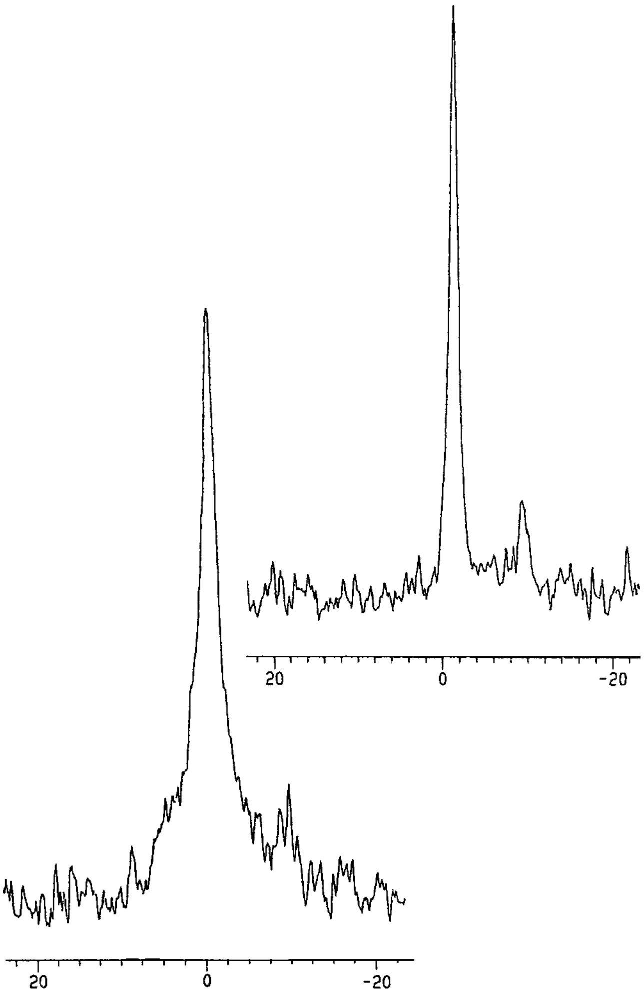

Figure 1. ^{31}P NMR of PVMo/MCM (bottom left) and PVMo/MCM-N (top right).

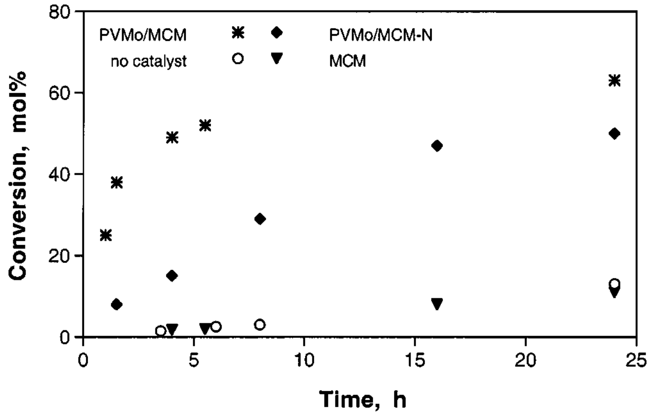

Figure 2. Reaction profiles for cyclooctene epoxidation. Reaction conditions: 30 mg supported catalyst containing 1.7 μmol PVMo, 0.8 mmol cyclooctene, 1.1 mmol isobutyraldehyde (IBA) in 1 ml of 1,2-dichloroethane, $T = 25\,^{\circ}$C. Cyclooctene oxide was the only product. The homogeneous reaction was about twice as fast as the PVMo/MCM heterogeneous catalyzed reaction [3].

is significantly broader than the peak width of PVMo/MCM-N, $\Delta\nu_{1/2} = 200$ Hz. The probable explanation for this finding is that for PVMo/MCM-N the polyoxometalate is attached to the molecular sieve via a propylamino group which allows more movement and, therefore, narrower linewidths than observed for PVMo/MCM, which is directly adsorbed on the molecular sieve surface.

3.2. Catalytic oxidation

The PVMo polyoxometalate was found in homogeneous solution to be an active catalyst for hydrocarbon oxidation using the molecular oxygen–aldehyde system, equation (1) [3]. It was therefore of interest to use this catalyst in a heterogeneous mode in such a way that catalytic activity would not be lost. The solid catalysts prepared herein showed high catalytic activity without leaching of catalyst into solution. The catalytic performance was first demonstrated in the epoxidation of cyclooctene, figure 2. Reaction conditions were optimized using PVMo/MCM as catalyst and dichloroethane, which does not dissolve PVMo, as solvent. At an isobutyraldehyde concentration of 1.1 M no leaching into the solution at the reaction temperature was observed by UV-vis or AAS. In addition, after recovery of the solid catalyst by filtration, full catalytic activity was retained in further reaction cycles, whereas the filtrate showed no catalytic activity in the oxidation of cyclooctene above the level of the control reaction. It is valuable to note that at a higher isobutyraldehyde concentration of 2 M, slight leaching of PVMo was observed, as indicated by UV-vis of the solution and kinetic profiles of recovered catalysts. Noticebly, the PV2-MCM-N catalyst is less active than PV2-MCM, presumably due to a decrease in the redox potential of PVMo upon partial neutralization of the protons of the heteropoly acid. The reduction in redox potential upon neutralization has been documented by cyclic voltammetry measurements of protic and quaternary ammonium forms of PVMo dissolved in acetonitrile [8].

Table 2
Oxidation of hydrocarbons by PVMo-MCM/IBA/O_2.[a]

Substrate	Product(s) (selectivity, mol%)	Conversion (mol%)	TON[b]
Cyclooctene	Cyclooctene oxide (100)	63	300
Oct-1-ene	Octene oxide (50) Oct-1-en-3-one (50)	6.3	30
Styrene	Benzaldehyde (65) Phenylacetaldehyde (28) Styrene oxide (7)	49	233
Cyclooctane	Cyclooctanone (100)	2.8	14
Adamantane	Adamantan-1-ol (75) Adamantan-2-ol (12) Adamantan-2-one (13)	8.5	40
Ethylbenzene	Acetophenone (100)	3.7	8
Diphenylmethane	Benzophenone (100)	4.0	20

[a] Reaction conditions: 30 mg catalyst, 1.7 μmol PVMo, 0.8 mmol substrate, 1.1 mmol isobutyraldehyde (IBA) in 1 ml of 1,2-dichloroethane, $T = 25\,^{\circ}$C, $t = 24$ h. Conversion of IBA was quantitative. Analysis by GLC.

[b] TON is defined as mole substrate reacted per mole catalyst.

In homogeneous systems, the oxidation proceeds via catalytic initiation of reaction by PVMo with formation of acylperoxo radical which propagates the alkane oxidation according to equation (1). In order to check whether this mechanism is valid for the analogous heterogeneous catalytic system, the oxidation of different alkenes, alkanes and alkylaromatics as probe substrates was studied, table 2. In a typical series of reactions using a catalyst : substrate : isobutyraldehyde ratio of 1 : 470 : 650 under 1 atm O_2 at room temperature moderate catalytic activities were observed. Oxidation of cyclooctene with deactivated allylic positions yielded epoxide as the sole product. Oxidation of 1-octene was less efficient and gave both allylic ketone and epoxide. Benzaldehyde was the main product in the oxidation of styrene. These latter product distributions, parallel to the results observed in homogeneous reactions, confirm that acylperoxo radical is the more likely active species. Similar reactions with adamantane, cyclooctane, ethylbenzene and diphenylmethane yielded ketone as a major product upon reaction at the secondary carbon atom and alcohol at the tertiary carbon atom. We surmise that the acyl/acylperoxo radicals are generated inside the mesopores at the PVMo sites. The subsequent oxidation of the hydrocarbon can occur both within the pores or in the bulk liquid solution. Comparison of the activity of this catalyst in the oxidation of adamantane with that of homogeneous PVMo [3] and an another heterogeneous catalyst, the vanadium-substituted MCM-41, V-MCM-41 [9], showed that the present catalyst, PVMo/MCM was more active than V-MCM-41, but both heterogeneous catalytic systems were inferior to the homogeneous reaction. The reduced reactivity in the heterogeneous vs. homogeneous reaction is probably related to the more limited autocatalytic propagation cycles in the former case due to the constrained mesopore environment which limits contact and/or diffusion of the reacting species.

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References

[1] (a) N. Mizuno and M. Misono, J. Mol. Catal. 86 (1994) 311;
(b) C.L. Hill and C.M. Prosser-McCartha, Coord. Chem. Rev. 143 (1995) 407;
(c) R. Neumann, Prog. Inorg. Chem. 47 (1998) 317.
[2] (a) R. Neumann and M. Levin, J. Am. Chem. Soc. 114 (1992) 7278;
(b) I.V. Kozhevnikov, J. Mol. Catal. 117 (1997) 151.
[3] A.M. Khenkin, A. Rosenberger and R. Neumann, J. Catal. 182 (1999) 82.
[4] I.V. Kozhevnikov, A. Sinnema, R.J.J. Jansen, K. Pamin and H. van Bekkum, Catal. Lett. 30 (1995) 241.
[5] Y. Hanada, M. Kamada, K. Umemoto, H. Kominami and Y. Kera, Catal. Lett. 37 (1996) 229.
[6] G.A. Tsigdinos and C.H. Hallada, Inorg. Chem. 7 (1968) 437.
[7] A. Tuel and S. Gontier, Chem. Mater. 8 (1996) 114.
[8] S.P. Harmalker and M.T. Pope, J. Inorg. Biochem. 28 (1986) 85.
[9] R. Neumann and A.M. Khenkin, J. Chem. Soc. Chem. Commun. (1996) 2643.