TETRABUTYL AMMONIUM SALTS OF KEGGIN-TYPE POLYOXOMETALATE CATALYSTS FOR SELECTIVE OXIDATION OF BENZYL ALCOHOL TOWARDS LIGNIN VALORIZATION

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Abstract - A series of Mo tetrabutyl ammonium (TBA) salts with V-included Keggin-type polyoxoanions ($TBA_4PMo_{11}V_1O_{40}$ and $TBA_5PMo_{10}V_2O_{40}$) as addenda atoms were prepared using a hydrothermal method. These synthesized materials were characterized by X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV-Vis diffuse reflectance (DRS UV-Vis), thermogravimetric analysis (TGA), CHN elemental analysis (EA), inductively coupled plasma spectrometry (ICP-MS) and N_2 physisorption techniques to assess their physicochemical/textural properties and correlate them with their catalytic performances. According to FT-IR and DRS UV-Vis, $(PV_xMo_{12-x}O_{40})^{(3+x)-}$ anions are the main species present in the TBA salts. Additionally,CHN-EA and ICP-MS revealed that the desired stoichiometry was obtained.

Their catalytic activities in the liquid-phase and aerobic oxidation of benzyl alcohol to benzaldehyde were studied at 5 bar of O_2 and 170°C. Independently of the addenda atom nature the catalytic activity increased with the number of V in Keggin anion structure. For both series of catalysts, TBA salts of polyoxometalates with the highest V-substitution degree ($TBA_5PMo_{10}V_2O_{40}$ and $TBA_5PW_{10}V_2O_{40}$) showed the higher activity. The maximum benzyl alcohol conversion obtained was 93% and 97% using $(TBA)_5$ $PMo_{10}V_2O_{40}$ and $(TBA)_5$ $PW_{10}V_2O_{40}$ as catalysts, respectively. In all the cases, the selectivity toward benzaldehyde was higher than 99%. Finally, the catalysts were used in a operational conditions optimization by an RSM study by using phenethoxybenzene molecule, which is representative of the lignin B-O-4 bond.. This study offers the opportunity to investigate the effect of V-inclusion polyoxotugsto- and polyoxomolybdovanadates with Keggin structures in the catalytic oxidation of benzyl alcohol will help to a better understanding of the mechanisms involved in this reaction. This information will be useful for a next study in the catalytic oxidation of lignin.

Keywords - Kegginphosphomolybdovanadate; Kegginphosphotungstovanadate; Lignin model compounds; Selective oxidation; Catalyst; Green oxidant

I. INTRODUCTION

Lignin is a complex macromolecule with a large variability in bond types, thus, the design of a specific catalyst to transform it is a complex task, and it is necessary to use model compounds of the lignin structure to be studied. Recent research has established that the development of robust and selective catalytic processes specifically designed for efficient lignin conversion will be key and should be a central effort in a lignin valorization program, as they are currently in the petrochemical refinery. Among the technologies needed to overcome the technological barriers, selective oxidative catalysis is proposed to obtain oxidized lignin monomers such as syringaldehyde, vanillin and vanillic acid. In view of the above background, it is necessary to overcome the technological barriers presented by the valorization of lignin to low molecular weight aromatic compounds or high value-added monomers, which are an alternative (short-medium term) or substitution (long term) of chemical industry precursors from the fossil fuel industry. In recent years, many catalysts have been studied, and among them polyoxometalates (POMs) have attracted attention and revealed to be very active for alcohol oxidation. POMs are inorganic nanosized anionic transition metal oxide anions with different types of structural architectures. These aggregates consist of d^0 metal addenda atoms (usually Mo, W, Nb, etc.) and oxygen arranged in octahedral units MO_6. POMs with Keggin structures have been intensively studied as green oxidation catalysts for both homogeneous and heterogeneous systems because this catalyst shows both acid and redox properties. The most important characteristic is that their thermal stability and both the acidic and redox properties can be tuned by modifying their molecular compositions. Several studies have demonstrated that the catalytic redox activity in Keggin-type polyoxometalates can be enhanced via the substitution of V in place of the Mo or W addenda atom in their primary structure. This effect can be explained by considering that M^{+6} substitution via V^{+5} increases the POM oxidation potential due to the higher reducibility of vanadium. Frenzel et al., studied the oxidation of sulfides to sulfones using Keggin-type silicopolyoxotungsto compounds ($K_5(SiVXW_{11}O_{40})$ with a variable (1,2) vanadium

content and reported that vanadium incorporation improves the catalytic activity under mild reaction conditions. This will provide background information on the role of the vanadium content in the oxidation properties and the catalytic activity of tetraalkylammonium salts of phosphomolybdates and phosphotungstates catalytic systemsincreases the oxidation potential of POM, due to the higher reducibility of vanadium. Among the techniques used to characterize POMs structurally and texturally are X-ray diffraction (XRD), Fourier transform infrared spectroscopy (FT-IR), UV-Vis diffuse reflectance (DRS UV-Vis), thermogravimetric analysis (TGA), CHN elemental analysis (EA), inductively coupled plasma spectrometry (ICP-MS) and N_2 adsorption desorption isotherms.

The aim of this work is the synthesis and characterization of two series of Keggin-type phosphomolybdovanadates (PMoV)with two different V replacement degrees (X= 1 and 2) of tetrabutylammonium (TBA) salts to be used as bulk catalysts in the heterogeneous liquid phase aerobic oxidation of benzyl alcohol to benzaldehyde. This reaction was used as a model reaction for further lignin valorization

II. DETAILS EXPERIMENTAL

2.1. Materials and Procedures

The TBA salts of the Keggin-type phosphomolybdovanadates $[PMo_{11}VO_{40}]^{4-}$ (PMoV) and $[PMo_{10}V_2O_{40}]^{5-}$ ($PMoV_2$) were prepared using a hydrothermal process. In a typical synthesis for V mono-substituted, a stoichiometric mixture of 0.01 mol H_3PO_4 (85%, Merck, Germany), 0.005 mol V_2O_5 (99%, Merck, Germany), and 0.11 mol MoO_3 (99,5%, Merck, Germany) was suspended in 150 mL of distilled water. The mixture was then heated and stirred at 80°C and 800 rpm on a hotplate for 4 h. After cooling to room temperature and removing the insoluble molybdates and vanadates via vacuum filtration, the heteropolyacid solution was again heated to 60°C, and tetrabutylammonium bromide (0.012 mol) was added. Precipitation of the organic salt was observed immediately (at 60°C). The obtained organic salt was filtered at room temperature and dried under a vacuum to a constant weight (± 0.002 g). For the V di-substituted, 0.01 mol of V_2O_5 was used in the synthesis.

Catalyst			$(TBA)_3PMo$	$(TBA)_4PMoV$	$(TBA)_5PMoV_2$
M[a]	(wt%) exp.[b]		43.7	39.1	35.1
V	(wt%) exp.		-	1.9	3.9
M[a]	(wt%) calc.[c]		45.1	38.4	32.6
V	(wt%) calc.		-	1.8	3.5
M[a] mmol	exp.		4.6	4.1	3.7
V	mmol	exp.	-	0.4	0.8
M[a]/V	ratio	exp.	-	10.9	4.8
M[a]/V	ratio	calc.	-	11.0	5.0

Table1: Metal analysis of pure and substituted Mo catalysts determined by ICP-MS.

Catalyst	$(TBA)_3PMo$	$(TBA)_4PMoV$	$(TBA)_5PMoV_2$
C (wt%)	23.1	25.2	29.1
H (wt%)	4.4	4.7	5.3
N (wt%)	1.6	1.8	2.0
cation (mmol x10^3)[a]	3.0	2.0	2.0
anion (mmol x10^3)[b]	1.0	0.5	0.4
cation/anion exp.[c]	3.1	3.9	4.9
cation/anion theory[d]	3	4	5

Table 2: CHN analysis of the pure and substituted Mo catalysts by elemental analysis

2.2. Characterization

The XRD patterns were recorded at room temperature in a D8 ADVANCE Bruker diffractometer with a Bragg-Brentano geometry using a LYNXEYE XE-T detector and copper Kα radiation (λ =1.5406 Å) in a 2θ range of 5–80° (step =0.015°, time per step =0.15 s). The X-ray source was operated with a tension of 40 kV and a current of 30 mA. The FT-IR spectra were recorded using a Nicolet Nexus 470 spectrometer in the 400-4000 cm^{-1} wavenumber range at room temperature, and KBr tablets were used. The DRS UV-visible spectra were recorded on a Shimadzu UV-3600 Plus UV–Vis–NIR Spectrophotometer with a Harrick single-beam Praying Mantis Diffuse Reflectance collection system. The spectra were then recorded at room temperature in the 190–1000 nm range. A Spectralon® Diffuse Reflectance Standard was used to measure the background spectra. The DRS UV-visible spectra were background corrected and normalized by the most intense absorption band, and the Kubelka-Munk function was used to display the data. A TGA analysis was performed on a NETZSCH TG 209F1 Iris thermogravimetric analyzer under an N_2 atmosphere in the temperature range of 25-550°C using 10-25 mg of the solid and a heating rate of 10°C min^{-1}. The CHN elemental analysis was performed on an EA 2400 series II (Perkin Elmer, USA), measurements were carried out with weighted samples 10-25 mg. Inductively coupled plasma mass spectrometry (ICP-MS) measurements for Mo, W and V determination in the materials were performed using an iCAP Q series ICP-MS (Thermo Scientific, USA) spectrometer. Specific areas, the pore volume and the pore diameter were evaluated via the Brunauer-Emmet-Teller (BET) method using the nitrogen adsorption isotherms obtained on a Micromeritics ASAP 2010 apparatus at -196°C in the relative pressure range of 0.01-0.99 (P/P_0). The Samples were previously pre-treated at 150°C for 3 h. The specific surface area (SSA) was calculated from the adsorption isotherm branch using the BET method.

2.3. Catalytic benzyl alcohol oxidation.

The catalytic activity of the obtained solids was examined using benzyl alcohol as the reaction substrate. The tests were performed in an O_2 atmosphere in a semi-batch Parr-type reactor with methanol:water (90:10 v/v) as the solvent at 170°C for 4 h. In a typical reaction, 1 g (0.01 mol) of benzyl alcohol, 100 mg of the catalyst, and 20 ml of the solvent were added to the reactor. Subsequently, in order to avoid contamination with other gases, after the reactor was sealed it was purged three times with O_2 (99.5%, Linde, Chile) and pressurized with 5 bar of the same gas. Finally, the pressurized reactor was heated to 170°C (10°C min^{-1} heating ramp), and the O_2 pressure was adjusted to 5 bar. The selected agitation speed was 600 rpm to avoid undesirable diffusion control during the catalytic performance evaluation. The study was then conducted for all the catalysts by taking samples at different reaction times for 4 h. All the reaction products were followed based on the commercial standards. The reaction products were identified and quantified by using an HLPC-DAD (Perkin Elmer, Flexar) with a mobile phase composition of 0.1% glacial acetic acid (A) and acetonitrile (B) with a flow rate of 1.0 ml minute $^{-1}$. The column used was an Inertsil C18 ODS-3 (250 mm × 4.6 mm, 5 µm), and the HPLC-DAD detection wavelength was 254 nm. Finally, the reaction products were confirmated by GC-MS using a model 7890A GC system (Agilent, USA) interfaced to a single quadrupole mass selective detector 5975C (triple-axis detector).

The conversion for benzyl alcohol (X_{BzOH}) and the selectivity toward the products ($S_{product}$) were calculated by using calibration curves as follows:

$$X_{BzOH}\ (\%) = \frac{[BzOH]_i - [BzOH]_t}{[BzOH]_i} \cdot 100$$

$$S_{product}\ (\%) = \frac{[product]_t}{[BzOH]_i - [BzOH]_t} \cdot 100$$

The control experiment was performed the same as the typical reaction mentioned above but without any catalyst addition.

III. RESULTS AND DISCUSSION

3.1. Characterization

The results of elemental analysis of the materials synthesized in the present study and determined by ICP-MS are shown in Table1. The results obtained show that such anions have been successfully synthesized following the procedure described above. The ICP-MS values are in good agreement with the calculated theoretical ones, and this fact confirmed the desired Mo/V ratio. The results of the CHN elemental analysis of the synthesized materials are summarized in Table2. The elemental analysis allows confirming that for the $(TBA)_3PMo$, $(TBA)_4PMoV$ and $(TBA)_5PMoV_2$ materials the expected cation/anion ratio (3, 4, and 5 respectively) was successfully obtained. Infrared spectra of the $(TBA)_3PMo$, $(TBA)_4PMoV$, $(TBA)_5PMoV_2$organic salts are shown in Figure 2. These spectra show their main absorption bands in the 800-1100 cm^{-1} region, which is characteristic of the Keggin structure, and they agree with those previously reported in the literature for substituted structures.The Keggin-type heteropolyanions and their salts display a characteristic XRD diffraction peaks group at the 2θ values between 5° and 10°. These characteristic peaks related to the $H_3PMo_{12}O_{40}$ (H_3PMo) Keggin structure appears at 6.5(111), 8.2(200), and 10.7(220) of 2θ (hkl) [JCPDS File 01-070-0059] (Figure 1)

3.2. Catalytic benzyl alcohol oxidation.

In all the liquid-phase aerobic catalytic oxidation of benzyl alcohol reactions the selectivity was >99%. The $(TBA)_3PMo$ catalyst shows a total conversion of 52% and increases up to 67% for $(TBA)_4PMoV$, achieving a total conversion of 93% for the largest substituted material $(TBA)_5PMoV_2$. (Figure 3)

Based on the results presented above, we can determine that the catalytic activity in the oxidation of benzyl alcohol was significantly improved by introducing V in the $(TBA)_3PMo$structure. The conversions of $(TBA)_4PMV$ and $(TBA)_5PMV_2$ were much higher than those obtained for the V-free phosphomolybdates, which implies that V atoms play an important role in the studied reaction. Likewise, the conversions obtained for the inclusion of two V atoms were higher than those obtained for a single V atomIn summary, shortening the induction time and incrementing the maximum conversion upon the addition of V in the Keggin structure were observed for $(TBA)_3PMo$. This effect could be attributed to the higher the number of vanadium atoms, the higher the concentration and the faster the formation of these species.Therefore, for the synthesized pure and substituted Mocatalysts, the obtained results reveal that they are very selective in benzyl alcohol oxidation toward benzaldehyde, without forming overoxidized products

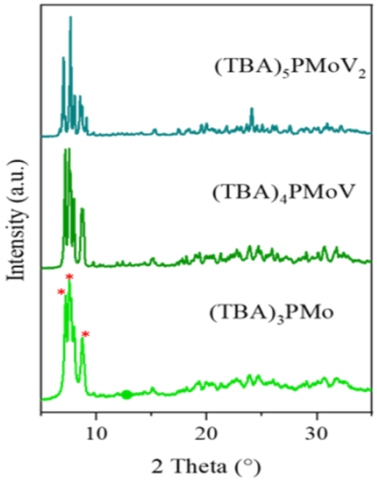


Fig.1. XRD patterns of pure and V-substituted Mo- Keggin-type polyoxometalates. The red symbol represents the comparison between equivalent diffractograms with JCPDS cards.

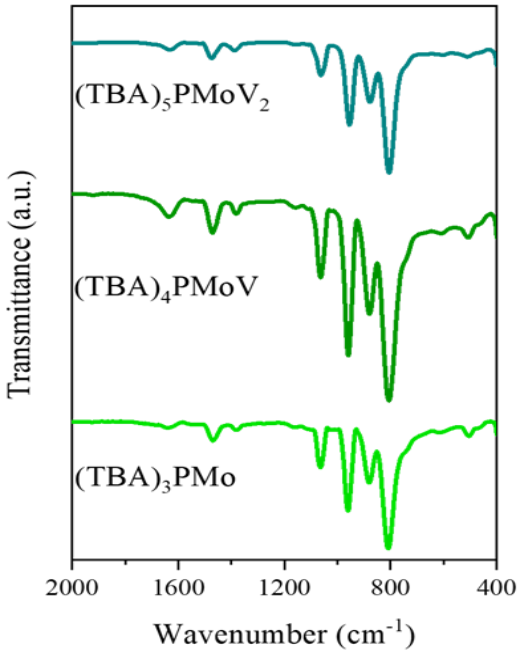


Fig.2. FT-IR spectra of pure and V-substituted Mo- Keggin-type polyoxometalates TBA salts.

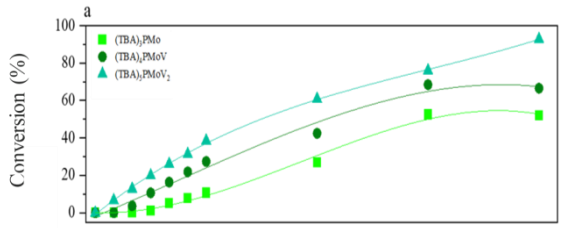


Fig.3. Total conversion (%) of the liquid phase aerobic oxidation of benzyl alcohol upon time for the pure and substituted Mo- catalysts.

IV. CONCLUSIONS

In this work, series of tetrabutyl ammonium (TBA) salts of V-included Keggin-type polyoxoanions with Mo ($TBA_4PMo_{11}V_1O_{40}$ and $TBA_5PMo_{10}V_2O_{40}$) as addenda atoms were prepared and characterized by XRD, FT-IR and DRS UV-Vis techniques.

The catalytic performance in the selective liquid phase aerobic oxidation of benzyl alcohol, using O_2 as a green oxidant agent indicates that in Mo series, the replacement of addenda atoms by V enhances the catalytic activity with respect to non-substituted atoms. At the reaction conditions, the di-substituted $(TBA)_5PMoV_2$ exhibits the higher catalytic activity for the benzyl alcohol oxidation with a total conversion of 93% and a selectivity towards benzaldehyde > 99%. These catalysts also proved to be reusable in the reaction conditions. This study offers the opportunity to investigate the effect of V-inclusion in polyoxomolybdovanadates with Keggin structures in the catalytic oxidation of benzyl alcohol will help to a better understanding of the mechanisms involved in this reaction.

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