

NIOBIUM-DOPED PHOSPHOMOLYBDIC ACID CATALYST INCLUDED IN SILICA MATRIX: STUDY OF STABILITY AND REACTIVITY USING DIFFERENT LOADS

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Abstract— Heteropolyacids are used as catalysts in numerous reactions because they are inexpensive, nontoxic, have high acid strength and excellent redox properties. They have been used as acid catalyst in different ways, and numerous studies indicate that the incorporation of Nb into the structure of a solid generates an increase in the acidity of the sample, both at Lewis and Brønsted acid sites. Heteropolyacids have low surface area, which makes it necessary to include them in a support to increase the surface area and allow their use as heterogeneous catalysts in liquid phase reactions because they are very soluble in polar solvents. In this work, the synthesis of catalysts containing a niobium-doped heteropolyacid (PMoNb) included in silica at different concentrations is reported. The catalysts were characterized by ICP-MS, FT-IR, XRD, potentiometric titration, and their catalytic activity was tested in the selective oxidation of diphenyl sulfide to diphenyl sulfoxide, showing excellent results.

Keywords— Keggin Heteropolyacid, Heterogeneous Catalysis, Oxidation, Diphenyl Sulfide, Green Conditions.

I. INTRODUCTION

Catalysis is a powerful tool in Green Chemistry, and new methodologies for materials production using catalysts are in continuous development. Their use instead of strong oxidants and toxic solvents results in a cheaper, more efficient, and ecofriendly process.

Keggin heteropolyacids (HPAs), such as phosphomolybdic acid (PMo, $H_3PMo_{12}O_{40} \cdot 12H_2O$), are inorganic compounds constituted by twelve MoO_6 octahedra surrounding a central tetrahedron PO_4 (Jeannin, 1998; Ruiz, 2014). HPAs present strong acidity and multielectron properties, which allow their use instead of organic and inorganic acid in many reactions in liquid phase (Palermo *et al.*, 2011).

To improve the catalytic performance of HPAs, one or more addenda atoms should be replaced by different metallic ions. In particular, in this work Nb is used as doping element in PMo. Numerous articles indicate that the incorporation of Nb in the structure of a solid increases the acidity in both Lewis and Brønsted sites

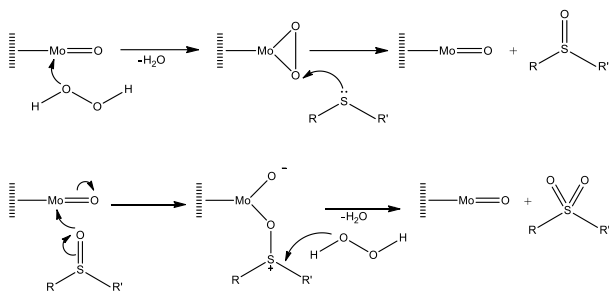
(Datka *et al.*, 1992; Park *et al.* 2011; Méndez *et al.* 2020; Zhang *et al.*, 2021). Moreover, Nb has been used as acid catalyst in different ways (Tanabe and Okazaki, 1995; Tanabe 2003; Mahendran *et al.*, 2021; Ferreira David *et al.* 2021).

Due to the high solubility of HPAs in polar solvents and their low specific surface area, they are supported on different frameworks such as silica, alumina, and titania in order to enhance their performance as heterogeneous catalysts and make the isolation and reuse easier (Rocchiccioli-Deltcheff *et al.*, 1990; Popa *et al.*, 2011; Micek-Ilnicka *et al.*, 2012; Trueba and Trasatti, 2005).

In this article, silica is used as support of the HPA. The porosity of siliceous catalysts, compared with bulk HPAs, enhances the performance since the reactants are spread into the catalyst, which favors their meeting, and consequently, the reaction occurs easily (Atkins *et al.*, 2010; Weber *et al.*, 2010; Deutschmann *et al.*, 2009). Besides, the interaction between the active phase (HPA) and the silanols generates new electron motions in the heterogeneous catalysts, which are not present in the pure silica or in bulk HPA. This could improve the oxidative capacity of the HPA-silica catalysts. For this work, the new materials were prepared by sol-gel method (Palermo *et al.*, 2015).

Wu *et al.* (1996) explained that the plausible mechanisms of interaction between the HPA and the support could be by the formation of an outer-sphere surface complex. Due to the great difference in the acid strength of HPA and the support, many active intermediates could be formed, with their own acid strength and support interaction.

These two aspects lead to a low activation energy for the transfer of electrons and for the creation of anionic vacancies, which can be used by the substrate to interact with the catalyst. Then, in oxidations catalyzed by Mo oxides, the substrate reacts with oxo ions of the catalytic network instead of reacting with the oxygen of the reaction medium directly. Therefore, the structure of the network is regenerated when the catalyst reacts with the oxygen of the medium. Consequently, the metallic ions of the catalyst are involved in oxide-reduction reactions that lead to oxygen transfer (Mitchell, 1974). In relation to the use of this type of compound as catalysts in oxidation re-



Scheme 1: Possible sulfur oxidation mechanism using H_2O_2 as an oxidizing agent and HPA as catalyst

actions, there are two aspects of the Mo chemistry that are relevant: Mo is easily converted between its oxidation states +5 and +6, and the change in the coordination number for Mo^{6+} is easy to achieve, Mo complexes with 4, 5, and 6 ligands being very common.

The general oxidation mechanism using HPA as a catalyst (reversible oxidant) is of the electron transfer type. Hydrogen peroxide in the presence of HPA generates an electrophilic intermediate that suffers a nucleophilic attack by the S atom of the sulfide, giving rise to sulfoxide. Subsequently, sulfoxide is associated with HPA, through oxygen, and the S of the sulfoxide (now with electrophilic characteristics) suffers a nucleophilic attack by a new H_2O_2 molecule (Scheme 1) (Maciucă *et al.* 2008; Smith *et al.* 2006). By incorporating a less electronegative element than Mo (Nb in this case) into the structure of PMo, the catalytic activity is expected to increase.

II. METHODS

A. Synthesis of niobium-doped phosphomolybdic acid (PMoNb)

PMoNb ($\text{H}_3\text{PMo}_{12-x}\text{Nb}_x\text{O}_{40} \cdot 13\text{H}_2\text{O}$) was prepared from a mixture of MoO_3 (14.40 g), Nb_2O_5 (1.33 g), and H_3PO_4 85% w/v (0.58 mL) in distilled water (150 mL) by hydrothermal synthesis at 75 °C (Colombo Migliorero *et al.*, 2021).

B. Synthesis of silica (SiO_2)

The bare support was prepared by sol-gel method. First, in a nitrogen atmosphere, tetraethyl orthosilicate (TEOS, 34 mL) and absolute ethanol (43.5 mL) were mixed at room temperature. Then, acetic acid (10 mL) and distilled water (10 mL) were added under atmospheric conditions and stirred for 2 h (Palermo *et al.*, 2013).

C. Synthesis of PMoNb included in silica (PMoNb-Si-7.5, PMoNb-Si-15, and PMoNb-Si-30)

Under nitrogen atmosphere TEOS (34 mL) and absolute ethanol (30 mL) were mixed. Then, in atmospheric conditions, PMoNb (0.75, 1.5, or 3 g) dissolved in absolute ethanol (13.5 mL) and distilled water (10 mL) were added and stirred for 2 h, and finally dried at room temperature and milled.

D. Synthesis of PMo included in silica (PMo-Si-15)

TEOS (34 mL) and absolute ethanol (30 mL) were mixed under nitrogen atmosphere. Then, under atmospheric conditions and magnetic stirring, PMo (1.5 g) dissolved

in absolute ethanol (13.5 mL) and distilled water (10 mL) were added and stirred for 2 h, and finally dried at room temperature and milled.

E. Catalyst characterization

For inductively coupled plasma mass spectrometry (ICP-MS) Perkin Elmer NexION 300X equipment was used. Fourier transform infrared spectra (FT-IR) were measured in Bruker Vertex 70v equipment. X-ray diffraction (XRD) patterns were acquired in PANalytical X'Pert Pro 333/00 equipment using $\text{CuK}\alpha$ radiation and Ni filter. Potentiometric titration was used to obtain the total acidity using *n*-butylamine in acetonitrile (0.025 N) and 794 Basic Titrimetric device. SEM micrographs were obtained in Philips 505 equipment using a voltage of 25 eV supporting the samples on graphite and metallizing them with gold. The samples for obtaining TEM micrographs were prepared by suspending the material in water and subjecting it to an ultrasonic bath for 15 min to promote dispersion; subsequently, drops of this suspension were placed on a grid provided with a Formvar® film and allowed to dry for 30 min. TEM micrographs were obtained using JEOL equipment, model 100 CX, operated at 100 kV, and model 1200 EX II.

F. Catalytic test

The catalyst (0.266 g), diphenyl sulfide (DPS, 0.167 mL), ethanol (8 mL), and aqueous H_2O_2 35% (w/v) (0.15 mL) were mixed in a glass tube and magnetically stirred at room temperature. A sample (0.1 mL) was taken every hour from the reaction mixture and treated with 1 mL of dichloromethane:distilled water (1:1). The organic layer was removed and dried on anhydrous Na_2SO_4 , filtered off, and analyzed by gas chromatography (Shimadzu 2014 with a Supelco column and a flame ionization detector).

III. RESULTS AND DISCUSSION

The most relevant periodic properties of Nb are similar to Mo properties (Table 1), and the incorporation of Nb as doping element does not cause steric or electronic modifications. Keggin heteropolyanions are able to accept a huge number of electrons, without structural changes. This is possible due to the d^0 configuration, which means that in the higher oxidation level, the orbital is empty and available to accept electrons (Buckley and Clark, 1985).

Niobium catalysts PMoNb-Si-7.5, PMoNb-Si-15, and PMoNb-Si-30 present a green color, with an intensity that enhances with the HPA loading. The amount of PMoNb incorporated into the silica matrix was corroborated with ICP-MS assays (Table 2).

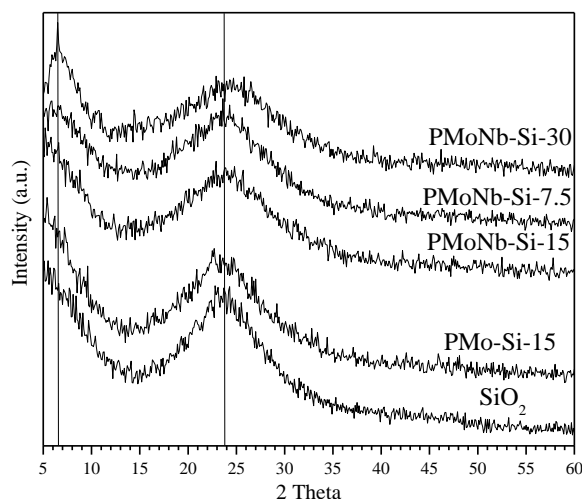
The FT-IR spectra (not shown) of all samples, SiO_2 and included HPA, present the characteristic bands of amorphous silica structure. The strongest band, at 1078 cm^{-1} , is associated with O-Si-O stretching, and the shoulder at 1178 cm^{-1} appears for the stretching and bending modes. Additional signals of O-Si-O are at 798 and 453 cm^{-1} . The signal at 957 cm^{-1} is associated with Si-OH stretching, while the band at 1643 cm^{-1} corresponds to SiO-H stretching, and the broad band at 3500 cm^{-1} to

Table 1. Periodic properties of Mo and Nb

Property	Mo	Nb
Atomic mass	95.94	92.91
Atomic radius (Å)	1.39	1.46
Pauling atomic radius (Å)	0.62	0.70
Covalent radius (Å)	1.45	1.37
Electronegativity	1.8	1.6

Table 2. PMoNb load (%) in the silica matrix

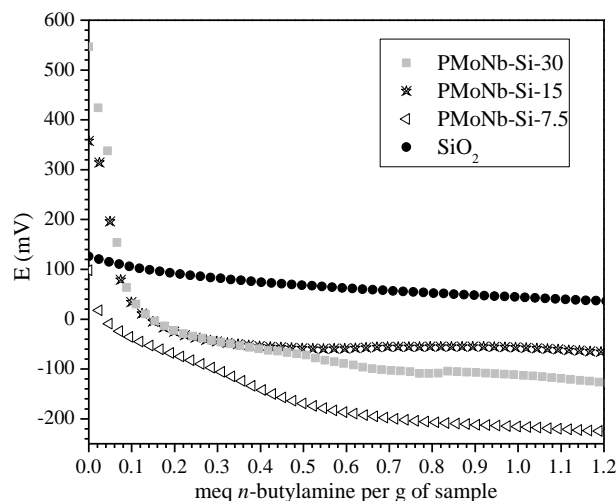
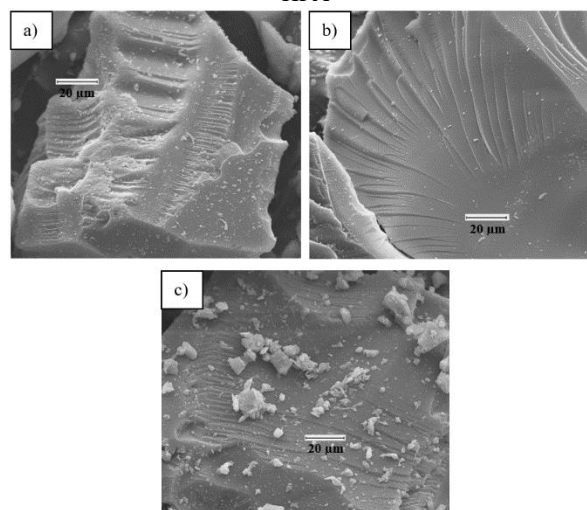
Catalyst	Theoretical load	Obtained load ^a
PMoNb-Si-7.5	7.5	10.1
PMoNb-Si-15	15	18.1
PMoNb-Si-30	30	31.9

^a by ICP-MSFigure 1: XRD patterns of SiO₂ and included HPA

O-H stretching (Martinez and Ruiz, 2002). The band located between 570 and 630 cm⁻¹ can be attributed to cyclotetrasiloxane ring deformation (Araujo-Andrade *et al.*, 2000). On the other hand, the characteristic bands associated with the Keggin structure of HPA (1064 cm⁻¹ (P–O_a), 962 cm⁻¹ (Mo–O_d), 871 cm⁻¹ (Mo–O_b–Mo), and 780 cm⁻¹ (Mo–O_c–Mo)) are overlapped with silica bands, which is an indication of the good dispersion of active phase into the support (Palermo *et al.*, 2015).

The XRD patterns of SiO₂ and included HPA (Fig. 1) show the typical broad band of amorphous silica (marked in the figure with vertical lines) at 15–35 2 θ and the thinner one at 5–10 2 θ (Popa *et al.*, 2010). In the FT-IR spectra, the signals of HPA cannot be observed since they are masked by silica bands. However, in PMoNb-Si-30 patterns, a peak at 7 2 θ is observed, which is assigned to HPA clusters.

The acidity of solids was analyzed by potentiometric titration (Fig. 2). It was found that the catalysts with the highest amount of active phase, PMoNb-Si-30, present the highest acid strength (547 mV), followed by PMo-Si-15 (377 mV) and PMoNb-Si-15 (358 mV). Finally, PMoNb-Si-7.5 has an acid strength slightly lower than pure silica (98 and 126 mV, respectively). The fact that PMoNb-Si-30 has a strong acidity is another indication of an HPA agglomeration in the support framework.

Figure 2: Potentiometric titration curves of SiO₂ and included HPAFigure 3: SEM micrographs obtained for: a) SiO₂, b) PMo-Si-15, c) PMoNb-Si-15

The results obtained by SEM on the morphology of the synthesized siliceous compounds are shown below. Fig. 3 shows the SEM micrographs of the pure silica and of the HPAs included in silica, where the sheet morphology that is characteristic of this support can be seen.

Figure 4 shows the TEM micrographs obtained for the materials in which PMoNb was included at different concentrations. It is observed that these particles have an irregular shape where the small nanoparticles agglomerate on the surface of another larger particle and straight sections, giving rise to an agglomerate with a size that varies from 0.6 μ m for PMoNb-Si-7.5, which contains the lowest percentage of active phase, to 1.2 μ m for the PMoNb-Si-30 catalyst, which has the highest percentage of active phase.

The catalytic activity of the synthesized solids was evaluated in the selective oxidation of DPS to diphenyl sulfoxide (DPSO) (Scheme 2). When pure SiO₂ was used as catalyst, the DPS conversion was null after 24 h, indicating that the support does not catalyze the reaction. PMoNb-Si-15 gave a conversion of 92.0% and a DPSO selectivity of 93.9% after 4 h of reaction. Compared to

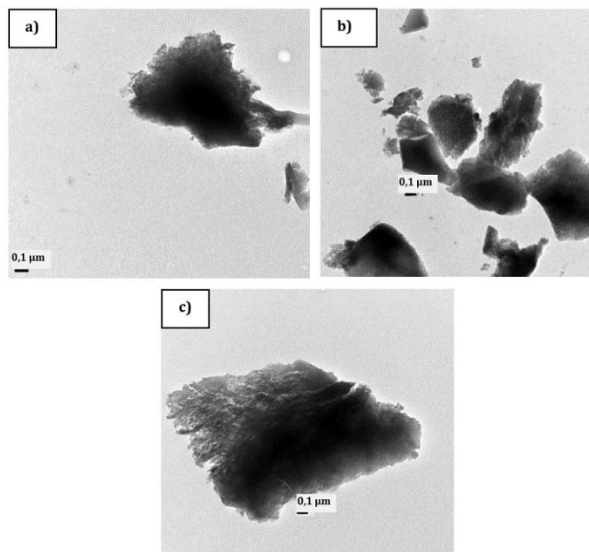
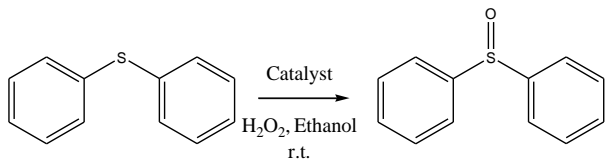


Figure 4: TEM micrographs obtained for: a) PMoNb-Si-7.5, b) PMoNb-Si-15, c) PMoNb-Si-30



Scheme 2: Sulfoxidation of diphenyl sulfide

PMo-Si-15 (40.6% DPS conversion), the presence of Nb as doping element enhances the catalytic activity.

With respect to the different HPA loads (Fig. 5), it was found that when 7.5% of PMoNb was included, the conversion achieved was only 10% after 7 h. Meanwhile, using 15% and 30% of active phase, a DPS conversion of 92.0% was reached with both catalysts after 4 h. Also, it can be noticed that when PMoNb-Si-7.5 is used as catalyst, after 24 h the conversion was high (90%) and this value was close to those obtained when PMoNb-Si-15 or PMoNb-Si-30 was used (100%). This behavior was in accordance to the low amount of active phase that is present in PMoNb-Si-7.5, so the same quantity of the reagent takes longer to convert, however, high conversion was achieved in a longer reaction time.

The DPSO selectivity after 4 h was 93.9% and 96.1% for PMoNb-Si-15 and PMo-Si-30, respectively. At longer reaction times, the selectivity toward DPSO decreases due the further oxidation to diphenyl sulfone (Fig. 6).

In order to compare the catalytic stability of PMoNb-Si-15 and PMoNb-Si-30, the reuse of these catalysts was evaluated. For this, the catalysts were separated from the reaction media, washed with fresh ethanol, dried and used in a new reaction cycle. Figures 7 and 8 show the DPS conversion in successive cycles for PMoNb-Si-15 and PMoNb-Si-30, respectively. There was an important loss of catalytic activity with the catalyst with higher HPA load, while PMoNb-Si-15 maintained its performance at least in four reaction cycles, indicating that the latter is the catalyst with the optimal concentration of active phase.

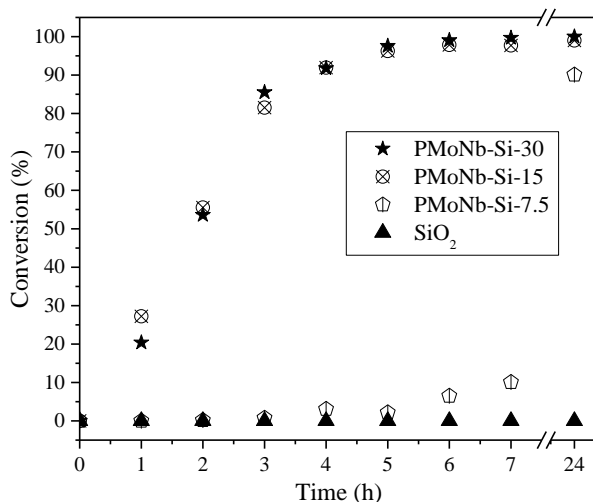


Figure 5: DPS conversion using SiO₂ and included HPA

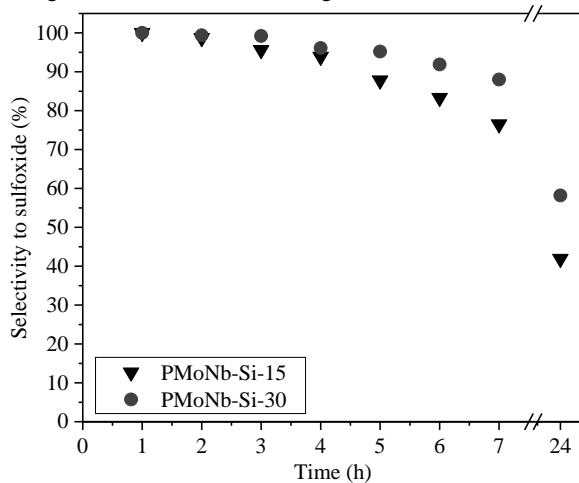


Figure 6: DPSO selectivity using PMoNb-Si-15 and PMoNb-Si-30

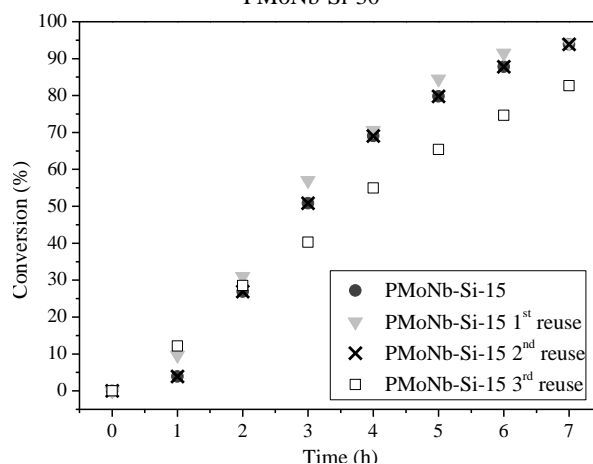


Figure 7: DPS conversion in PMoNb-Si-15 reuses

IV. CONCLUSIONS

According to the results obtained with the different characterization techniques of the synthesized solids and their evaluation as catalysts in the sulfoxidation of DPS, we can conclude that 15% of active phase is the optimal load, since a lower concentration reduces the catalytic activity. However, if a huge amount of HPA is incorporated, clusters of HPA are formed within the silica structure, favor-

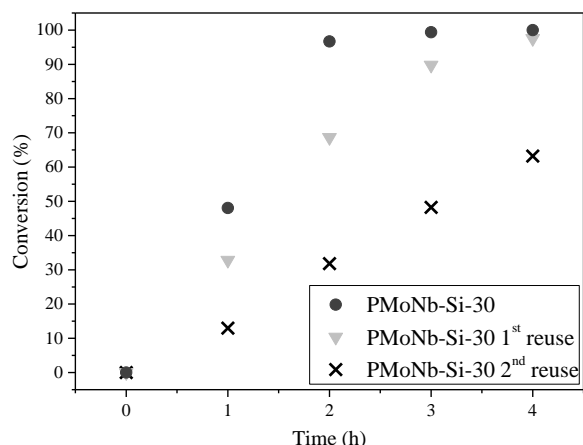


Figure 8: DPS conversion in PMoNb-Si-30 reuses

ing the leaching of active phase into the reaction medium, and the performance in the reuse decreases.

The synthesized material PMoNb-Si-15 showed high catalytic activity in the studied reaction, both in conversion and selectivity toward the desired product. The reaction conditions used in the synthesis of the catalyst and in the oxidation of sulfide are in accordance with the principles of Green Chemistry.

Currently, we are testing the use of the catalyst for the selective oxidation of sulfides with different structures.

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REFERENCES

- Araujo-Andrade, C., Ortega-Zarzosa, G., Ponce-Castañeda, S., Martínez, J.R., Villegas-Aguirre, F. and Ruiz, F. (2000) Análisis de las reacciones de hidrólisis y condensación en muestras de sílica xerogeles usando espectroscopía infrarroja. *Rev. Mex. Fis.* **46**, 593-597.
- Atkins, P., Overton, T., Rourke, J., Weller, M. and Armstrong, F. (2010) *Shriver & Atkins' Inorganic Chemistry*. Oxford University Press, 5th ed., Oxford.
- Buckley, R. I., Clark, R.J.H. (1985) Structural and electronic properties of some polymolybdates reducible to molybdenum blues, *Coord. Chem. Rev.* **65**, 167-218.
- Colombo Migliorero, M.B., Palermo, V., Romanelli, G.P. and Vázquez, P.G. (2021) New niobium heteropolyacid included in a silica/alumina matrix: Application in selective sulfoxidation, *Catal. Today* **372**, 89-97.
- Datka, J., Turek, A., Jehng, J. and Wachs, I. (1992) Acidic properties of supported niobium oxide catalysts: An infrared spectroscopy investigation. *J. Catal.* **135**, 186-199.
- Deutschmann, O., Knözinger, H., Kochloefl, K. and Turek, T. (2009) *Heterogeneous catalysis and solid catalysts*, in *Ullmann's Encyclopedia of Industrial Chemistry*, (Ed.), Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.
- Ferreira David, G., de Paiva Silva Pereira, S., Fernandes, S. A., Cubides-Roman, D. C., Siqueira, R. K., Perez, V. H. and Lacerda, V. J. (2021) Fast pyrolysis as a tool for obtaining levoglucosan after pretreatment of biomass with niobium catalysts. *Waste Manage.* **126**, 274-282.
- Jeannin, Y.P. (1998) The nomenclature of polyoxometalates: How to connect a name and a structure, *Chem. Rev.* **98**, 51-76.
- Maciucă, A. L., Ciocan, C. E., Dumitriu, E., Fajula, F. and Huela, V. (2008) V-, Mo- and W-containing layered double hydroxides as effective catalysts for mild oxidation of thioethers and thiophenes with H₂O₂. *Catal. Today.* **138**, 33-37.
- Martínez, J.R. and Ruiz, F. (2002) Mapeo estructural de sílica xerogel utilizando espectroscopía infrarroja. *Rev. Mex. Fis.* **48**, 142-149.
- Mahendran, S., Srinivasan, V.V., Karthikeyan, G. and Pachamuthu, M.P. (2021) Selective oxidation of 5-hydroxymethylfurfural to 2,5-diformylfuran over niobium incorporated MCM-41 catalyst. *Mol. Catal.* **510**, 111682.
- Méndez, F.J., Franco-López, O.E., Díaz, G. Gómez-Cortés, A., Bokhimi, X. and Klimova, T.E. (2020) On the role of niobium in nanostructured Mo/Nb-MCM-41 and NiMo/NbMCM-41 catalysts for hydrodesulfurization of dibenzothiophene. *Fuel.* **280**, 118550.
- Mícek-Ilnicka, A., Bielańska, E., Lityńska-Dobrzyńska, L. and Bielański, A. (2012) Carbon nanotubes, silica and titania supported heteropolyacid H₃PW₁₂O₄₀ as the catalyst for ethanol conversion, *Appl. Catal. A Gen.* **421-422**, 91-98.
- Mitchell, P.C.H. (1974) The chemistry and uses of molybdenum: Introductory lecture. *J. Less-Common Met.* **36**, 3-11.
- Palermo, V., Sathicq, A., Vázquez, P., Thomas, H. and Romanelli, G. (2011) Doped Keggin heteropolyacids as catalysts in sulfide oxidation. *Reac. Kinet. Mech. Cat.* **104**, 181-195.
- Palermo, V., Romanelli, G. and Vázquez, P. (2013) Mo based Keggin heteropolyacids as catalysts in the green and selective oxidation of diphenyl sulfide. *J. Mol. Catal. A: Chem.* **373**, 142-150.
- Palermo, V., Sathicq, Á., Constantieux, T., Rodríguez, J., Vázquez, P. and Romanelli, G. (2015) New vanadium Keggin heteropolyacids encapsulated in a silica framework: Recyclable catalysts for the synthesis of highly substituted hexahydropyrimidines under suitable conditions. *Catal. Lett.* **145**, 1022-1032.
- Park, D.R., Choi, J.H., Park, S. and Song, I.K. (2011) Reduction potential, UV-visible absorption edge energy, and oxidation catalysis of niobium-containing H_{3+x}PW_{12-x}Nb_xO₄₀ Keggin and H_{6+x}P₂W_{18-x}Nb_xO₆₂ Wells-Dawson heteropolyacid catalysts. *Appl. Catal. A: Gen.* **394**, 201-208.
- Popa, A., Sasca, V., Kiss, E. E., Marinkovic-Neducin, R., Bokorov, M. and Holclajtner-Antunović, I. (2010)

- Studies in structural characterization of silic-heteropolyacids composites prepared by sol-gel method. *Mater. Chem. Phys.* **119**, 465-470.
- Popa, A., Sasca, V., Kiss, E., Marinkovic-Neducin, R. and Holclajtner-Antunović, I. (2011) Mesoporous silica directly modified by incorporation or impregnation of some heteropolyacids: Synthesis and structural characterization. *Mater. Res. Bull.* **46**, 19-25.
- Rocchiccioli-Deltcheff, C., Amirouche, M., Hervé, G., Fournier, M., Che, M. and Tatibouët, J.M. (1990) Structure and catalytic properties of silica-supported polyoxomolybdates. II. Thermal behavior of unsupported and silica-supported 12-molybdosilicic acid catalysts from IR and catalytic reactivity studies, *J. Catal.* **126**, 591-599.
- Ruiz, J.C. (2014) Química de los Polioxometalatos Estudio termodifracométrico de la deshidratación del compuesto $[\text{Ni}(\text{C}_6\text{H}_5\text{NO}_2)_3]_2[\text{GeW}_{12}\text{O}_{40}] \cdot 18\text{H}_2\text{O}$, 1-43.
- Smith, J.R.L., Gilbert, B.C., Mairata i Payeras, A. Murray, J., Lowdon, T.R., Oakes, J., Pons i Prats, R. and Walton, P.H. (2006) Manganese 1,4,7-trimethyl-1,4,7-triazacyclononane complexes: Versatile catalysts for the oxidation of organic compounds with hydrogen peroxide. *J. Mol. Catal. A: Chem.* **251**, 114-122.
- Tanabe, K. (2003) Catalytic application of niobium compounds, *Catal. Today.* **78**, 65-77.
- Tanabe, K. and Okazak, S. (1995) Various reactions catalyzed by niobium compounds and materials. *Appl. Catal. A, Gen.* **133**, 191-218.
- Trueba, M. and Trasatti, S. P. (2005) γ -alumina as a support for catalysts: A review of fundamental aspects, *Eur. J. Inorg. Chem.* 3393-3403
- Weber, D., Sederman, A., Mantle, M., Mitchell, J. and Gladden, L. (2010) Surface diffusion in porous catalysts. *Chem. Chem. Phys.* **12**, 2619-2624.
- Wu, Y., Ye, X., Yang, X., Wang, X., Chu, W. and Hu, Y. (1996) Heterogenization of heteropolyacids: A general discussion on the preparation of supported acid catalysts. *Ind. Eng. Chem. Res.* **35**, 2546-2560.
- Zhang, Z., Li, Y., Yang, P., Li, Y., Zhao, C., Li, R. and Zhu, Z. (2021) Improved NH_3 -SCR deNO_x activity and tolerance to H_2O & SO_2 at low temperature over the $\text{Nb}_m\text{Cu}_{0.1-m}\text{Ce}_{0.9}\text{O}_x$ catalysts: Role of acidity by niobium doping. *Fuel.* **303**, 121239.

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