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Niobium-doped heteropolyacid included in silica--titania support as catalyst for selective sulfoxidation

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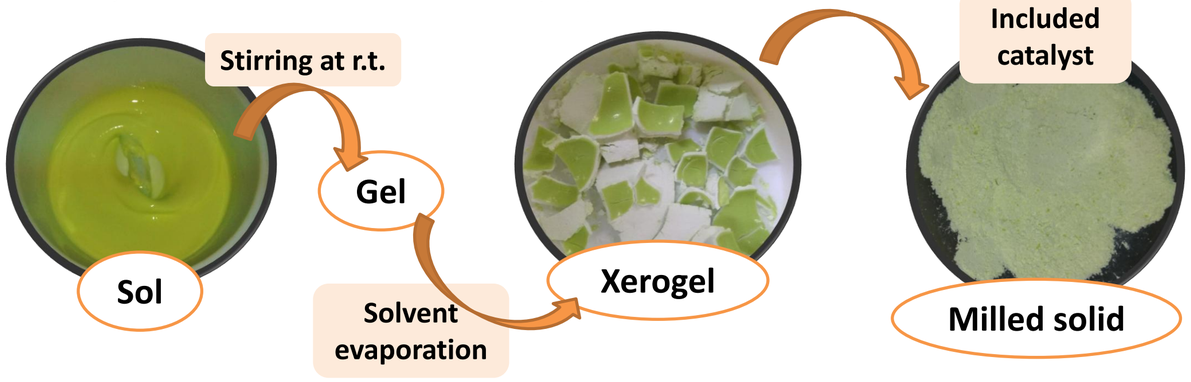
INTRODUCTION & AIM

In the field of catalysis, the use of heteropolyacids is widespread since they operate under mild conditions, favoring selectivity in reactions and reducing environmental pollution by not producing large volumes of waste. Heterogeneous catalysis is preferred because allows the easy recovery and re-use. This work shows the preparation of mixed silica--titania materials to immobilize a Keggin-type heteropolyacid doped with niobium and to use as a heterogeneous catalysts in sulfoxidation reactions under eco-friendly conditions.

METHOD

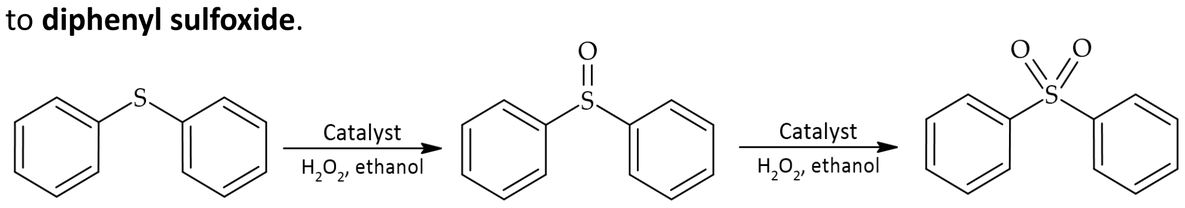
Niobium-doped heteropolyacid (PMoNb) was synthesized by a hydrothermal synthesis method from orthophosphoric acid, molybdenum trioxide, and niobium pentoxide.

Phosphomolybdic acid (PMo) and niobium-doped PMo were included in different silica and titania supports using the sol--gel method from the precursors, i.e., tetraethyl orthosilicate and titanium isopropoxide.



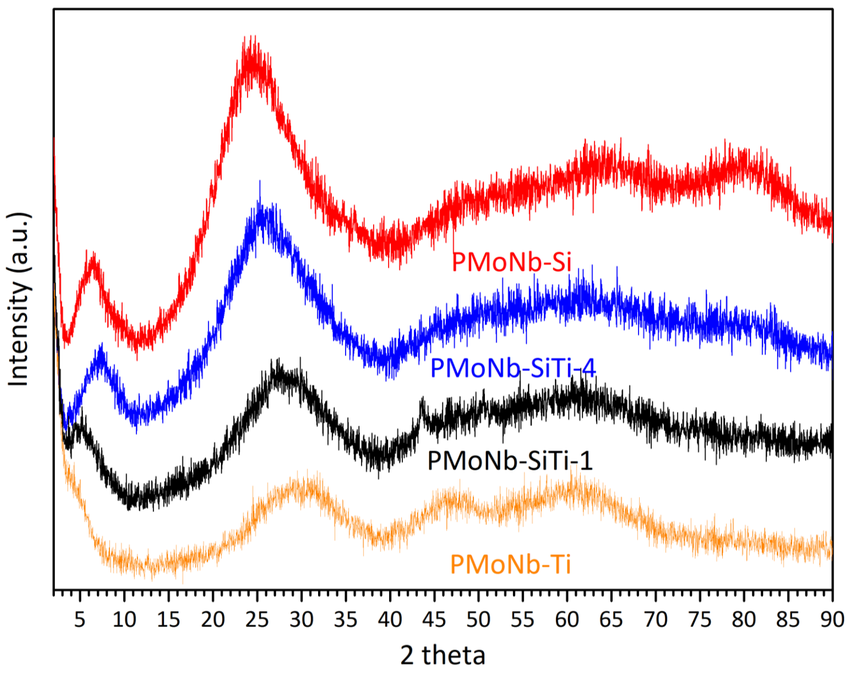
The synthesized catalysts were PMo and PMoNb included in silica (**PMo-Si** & **PMoNb-Si**), titania (**PMo-Ti** & **PMoNb-Ti**), and mixtures in silica:titania ratios of 1:1 (**PMo-SiTi-1** & **PMoNb-SiTi-1**) and 4:1 (**PMo-SiTi-4** & **PMoNb-SiTi-4**).

The prepared catalysts were characterized by XRD, FT-IR, Raman, and potentiometric titration, and tested in the selective oxidation of **diphenyl sulfide** to **diphenyl sulfoxide**.



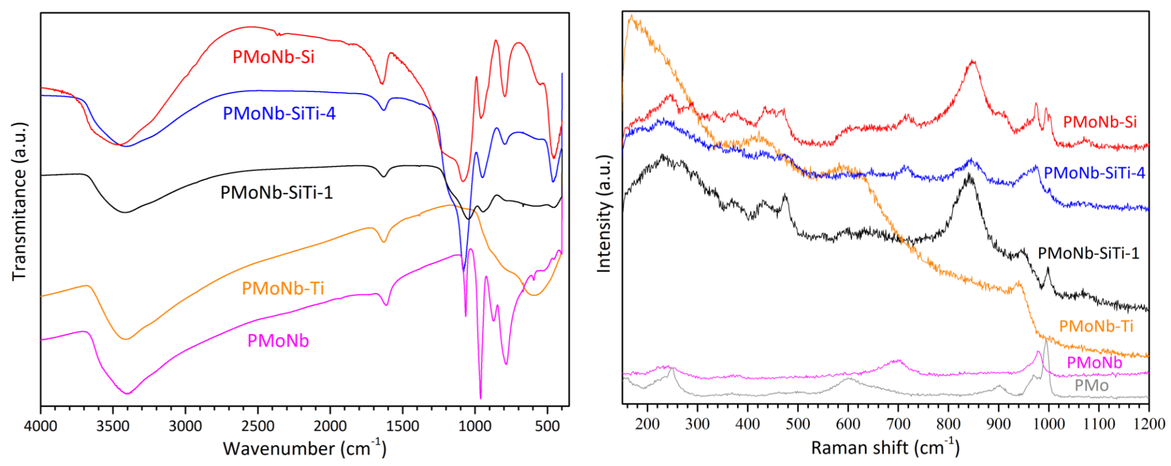
RESULTS & DISCUSSION

In the **X-ray diffractograms** corresponding to the matrices with Titania, it was found that a mostly amorphous structure (PMoNb-Ti) or anatase (for PMo-Ti, not shown) was obtained [1]. With respect to PMo and PMoNb included in Silica and in the mixed supports, the broad bands corresponding to Silica [2] or Titania [1] are found.



The typical diffraction bands of the active phase (Keggin structure) are not visible, since they would be masked by the support bands, which would confirm that a good dispersion of it was achieved in the support.

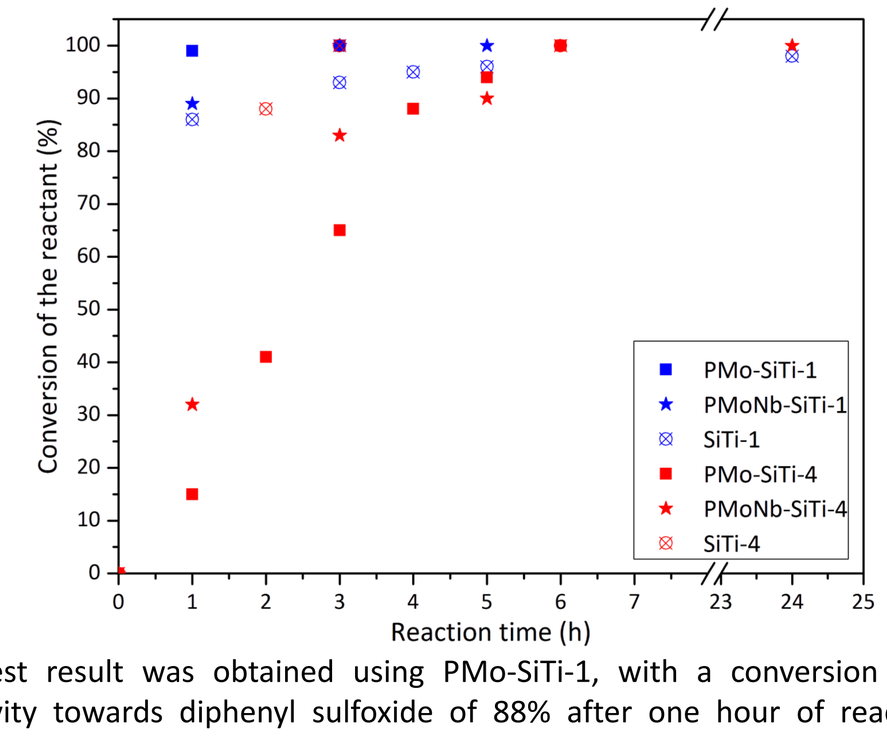
The characteristic bands of both supports were found in the **FT-IR** (left) and **Raman** spectra (right), with no appreciable differences due to the presence of PMo or PMoNb [3,4].



The mixed materials silica--titania show bands related to both supports, with the incorporation of Titania into Silica being evidenced by the existence in the FT-IR spectra of the Ti-O-Si vibration band at 945 cm^{-1} [5] and the 950 cm^{-1} Raman band related to vSi-O-Ti bonds [6].

All the obtained solids present high acidity, measured by **potentiometric titration**, which is attributed to the acidity of both the titania and the active phase: PMoNb-SiTi-4 = 222 mV, PMo-SiTi-4 = 219 mV, PMo-SiTi-1 = 153 mV, PMoNb-SiTi-1 = 133 mV, SiTi-4 = 133 mV, SiTi-1 = 119 mV.

Regarding **catalytic performance**, it was observed that the incorporation of Nb improved the catalytic behavior of the homogeneous catalysts: 94% conversion and 94% selectivity (PMoNb) vs. 36% conversion and 100% selectivity (PMo) after 7 h. Moreover, the activity improved when the heteropolyacids were included in the support. However, the presence of Nb did not enhance the activity of the heterogeneous catalysts.



The best result was obtained using PMo-SiTi-1, with a conversion of 99% and a selectivity towards diphenyl sulfoxide of 88% after one hour of reaction. Also, the catalyst was reused in two further reaction cycles without significant loss of its activity (Conversion = 99, 88, 65% and selectivity = 88, 92, 95% in a 1st, 2nd and 3rd reaction cycle, respectively)

CONCLUSION

According to the results of the characterizations, it can be concluded that mixed supports of silica and titania were synthesized, and the active phase is adequately dispersed in the different supports.

The synthesized catalysts were used in the selective oxidation of diphenyl sulfide to diphenyl sulfoxide, with excellent results in terms of conversion and selectivity, obtaining the best results with PMo-SiTi-1, which was reused in two further reaction cycles without significant loss of its activity.

FUTURE WORK / REFERENCES

We currently continue studying the use of these catalysts for the selective oxidation of diphenyl sulfide to both sulfoxide and sulfone, and seeking to optimize the reaction conditions to subsequently carry out the oxidation of more complex sulfides of biological importance.

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