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Preparation and characterisation of diatomaceous earth/$MnMo_9O_{32}$ system and its potential application in clean oxidation

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INTRODUCTION & AIM

Heteropolyanions containing molybdenum and/or tungsten are an important class of compounds with properties such as high reactivity, selectivity, and structural diversity.

The heteropolymolybdate Waugh type containing Mn(II) as a heteroatom,
$(NH_4)_6MnMo_9O_{32}$ ($MnMo_9$), was studied as a supported catalyst, using diatomaceous earth as support from northwestern Argentina.

The diatomaceous earths are highly adsorbent porous materials. Also, they are inexpensive and widely available in the pre-Cordillera region of Argentina.

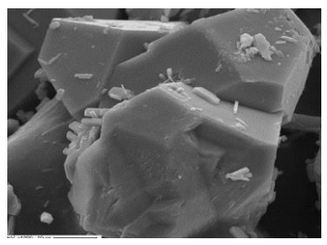
The clean oxidation of diphenyl sulfide (DPS) was chosen as the catalytic reaction for system evaluation. The reaction products, are of great interest as intermediates in the fine chemical and pharmaceutical industries. Diphenyl sulphide also acts as a test molecule for the study of processes to obtain ultra-low-sulphur fuels.

METHOD

NH_4OH

$Mn(II) + H_2O_2 \rightarrow Mn(IV)$

$9\ (NH_4)_6Mo_7O_{24}$



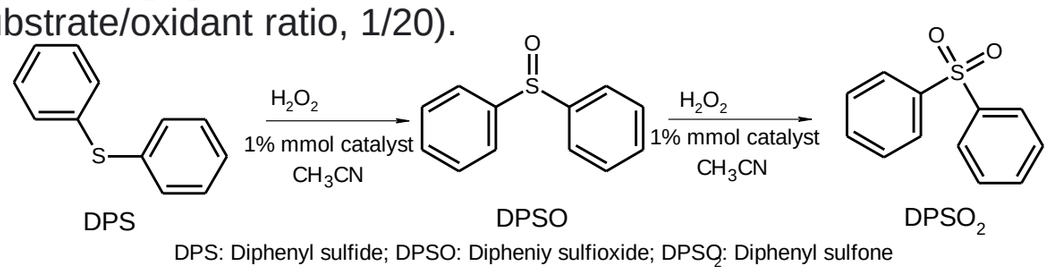
$(NH_4)_6MnMo_9O_{32}$

Yellow Micro-crystals (Orange micro-crystals as impurities)

The catalyst was supported on diatomaceous earth by equilibrium impregnation method.

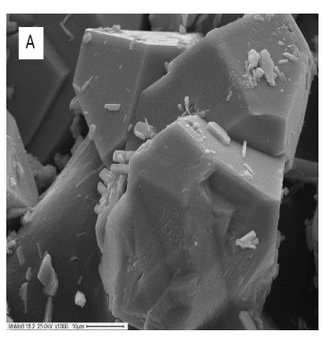
The HPOM and supported systems were characterised by XRD, FTIR, SEM-EDS, and RTP

The $MnMo_9$ system was evaluated as bulk and supported in the oxidation of DPS with H_2O_2, as clean oxidant. The oxidation reaction was carried out in batch at acetonitrile reflux, using 1% mmol of catalyst, H_2O_2 as excess oxidant, and 1 mmol of DPS or DBT (substrate/oxidant ratio, 1/20).



DPS: Diphenyl sulfide; DPSO: Diphenyiy sulfioxide; $DPSO_2$: Diphenyl sulfone

RESULTS & DISCUSSION



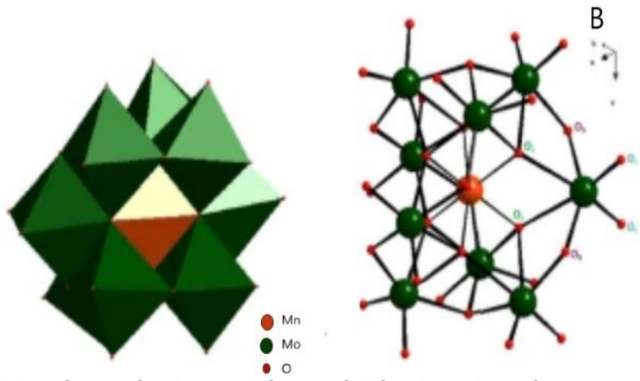


Figure 1: A) SEM microphotograph and B) structural representation of the Waugh-type phase, $(NH_4)_6MnMo_9O_{32}$.

Element	Weight (%)
O	66.05
Al	1.62
Si	25.47
K	0.74
Na	0.45
Fe	0.74
Cu	0.34
Mo	3.37
Ca	0.17
Ti	0.14
Mn	0.14
Mg	0.25
S	0.53

Waugh-type phase supported on natural aluminosilicate: diatomaceous earth achieving a Mo content of 3%..

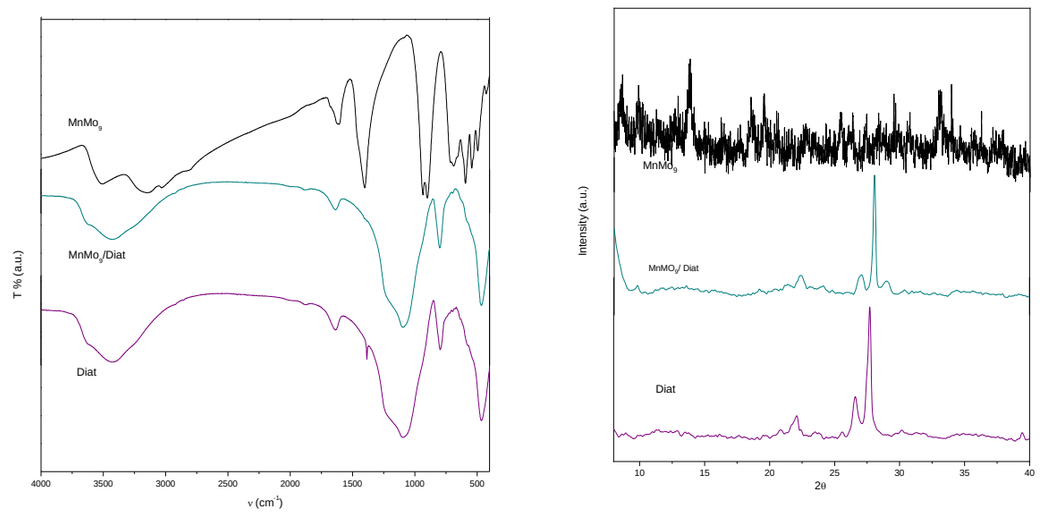


Figure 2: A) Comparative FTIR spectrum of $MnMo_9$, diatomaceous earth and $MnMO_9$ supported on diatomaceous earth and B) DRX comparative

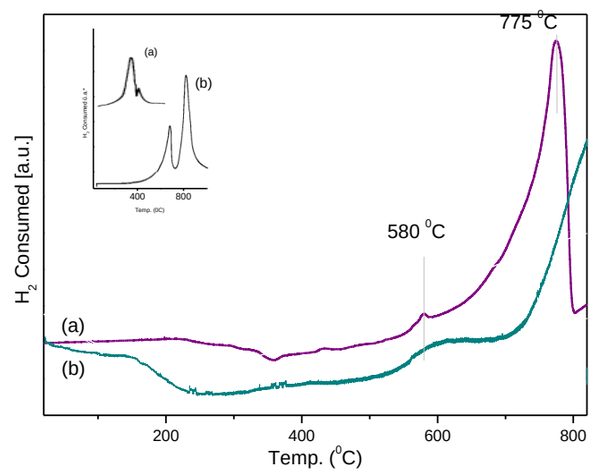
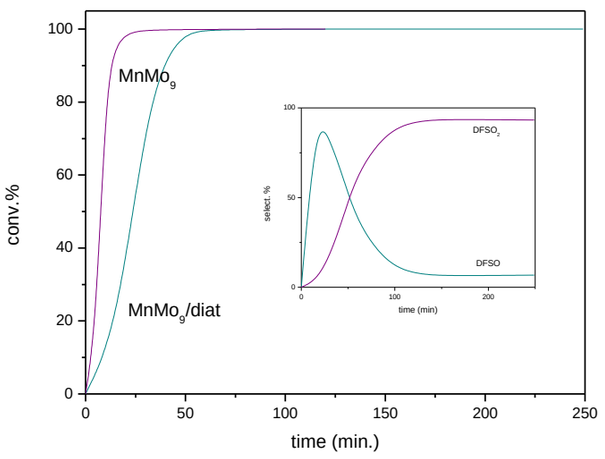


Figure 3: TPR diagram between ambient T and 820 °C for the phases: (a) MnMo9 and (b) MnMo9/Diat.



- the supported phase showed high reactivity
- a conversion of 100% of DPS was achieved at longer reaction times
- good selectivity for diphenyl sulfone at short reaction times.

CONCLUSION

The $(NH_4)_6MnMo_9O_{32}$ phase, Waugh-type, supported diatomaceous earth, was studied. The Mo content was of 3%.

The presence and interaction of the active phase on the support was observed by XRD, SEM-EDS, and RTP.

The systems were evaluated in the clean oxidation of DPS. Conversions of 100% were achieved for both systems in short reaction times, with selectivity to the corresponding diphenyl sulfone.

It is interesting to note that the $MnMo_9$/supported phase achieves excellent conversion with a much lower concentration of active phase.

FUTURE WORK / REFERENCES

The promising results obtained led us to investigate the catalyst on other natural oxidic systems and in other reaction media.

"$(NH_4)_6MnMo_9O_{32}$ como catalizador de oxidesulfurización" Egusquiza, M. Gabriela; Acosta, Jerónimo; Muñoz, Mercedes; Romanelli Gustavo P.; Gazzoli, Delia; Cabello, Carmen I. XXII Congreso Argentino de Catálisis, Actas A-5563 (2022)

"$(NH_4)_6MnMo_9O_{32}$ as Oxydesulfurization Catalyst". María Gabriela Egusquiza, Jerónimo Acosta, Mercedes Muñoz, Gustavo Pablo Romanelli, Delia Gazzoli, Carmen Inés Cabello. Latin American Applied Research, Vol. 53 Nº 1 (2023).