

Catalytic behavior of Zn(II) and Co(II) molybdates

Luz Amparo Palacio*, Carlos Saldarriaga** and Eduardo A. Lombardo***

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Abstract

Isotopic molybdates of Zn(II) and Co(II) were hydro thermally prepared and the solid products characterized by XRD, TGA, AA, SEM, CHN analysis and N₂ adsorption. The materials are layered type and exhibit structures formed by Zn and Co octahedrons and molybdenum tetrahedrons with one vertex unconnected which protrudes into the interlayer space. The catalytic behavior was tested by means of the reaction of cyclohexene hydroxylation with hydrogen peroxide. ZnMo shows high selectivity to 2-cyclohexene-1-ol while CoMo shows lower activity than the blank.

----- *Key words:* transition metal molybdates, hydrothermal synthesis, cyclohexene hydroxylation.

Comportamiento catalítico de molibdatos de Zn(II) y Co(II)

Resumen

Se prepararon dos molibdatos de Zn(II) y Co(II) isotópicos, por medios hidrotérmicos y los productos sólidos fueron caracterizados por XRD, TGA, AA, SEM, CHN y adsorción de nitrógeno. Los materiales son laminares y exhiben estructuras formadas por octaedros metálicos y tetraedros de molibdeno, de los cuales uno de los vértices está desconectado y se extiende dentro del espacio interlaminar. El comportamiento catalítico se examinó por medio de la reacción de hidroxilación de ciclohexeno con peróxido de hidrógeno. El ZnMo muestra alta selectividad a 2-ciclohexen-1-ol mientras que el CoMo muestra actividad menor que el blanco.

----- *Palabras clave:* molibdatos de metales de transición, síntesis hidrotérmica, hidroxilación de ciclohexeno.

* To whom correspondence should be addressed (lpalacio@jaibana.udea.edu.co).

** Department of Chemical Engineering. University of Antioquia. A.A. 1226. Medellín, Colombia.

*** Instituto de Investigaciones en Catálisis y Petroquímica —Incape— Santiago del Estero 2829, 3000 Santa Fe, Argentina.

Introduction

Molybdenum containing solids are the basis of many catalytic formulations used in selective oxidations. It has been reported that they are particularly good for olefin oxidation [1], hydrocarbon ammoxidation [2], and partial oxidation of methane [3]. In the process of propylene ammoxidation, several catalysts (Fe-Mo, Co-Mo, Mn-Mo, Bi-Mo, Ca-Mo, Tl-Mo, Pb-Mo, and MoO₃) have been tested as well as the activity associated to metal-oxygen double bonds has been studied [2].

On the other hand, the catalytic hydroxylation of unsaturated compounds is a reaction currently used to determine the activity of inorganic catalysts [4-6]. Apparently, this reaction generates the release of a free hydroxyl radical involving metallic ions according to the equation:



then producing just one radical species per each H₂O₂ molecule. Since the H₂O₂ molecule shows no tendency to react in the completely polarized form (HO⁺...OH), it needs the solid catalyst in order to bond to an ethylenic linkage [4]. The cyclohexene and hydrogen peroxide hydroxylation reaction, in particular, is commonly used as a probe reaction. Zhang *et al.* [5, 6] used W-MCM-41 to catalyze the mentioned reaction and concluded that the tungsten sites are the *loci* of activity in these materials. Thus, molybdenum containing solids might also catalyze hydroxylation reactions.

This paper reports the results of synthesis, characterization and catalytic performance for the cyclohexene hydroxylation of two isotopic molybdates compounds, namely (NaOH)Zn₂(MoO₄)₂·2(H₂O) and (NaOH)Co₂(MoO₄)₂·(H₂O).

Experimental

Synthesis

A solution, containing 4,84 g of Na₂MoO₄·2H₂O in 30 ml of distilled water, was added to the metal source specified in table 1, which was also dissolved in 30 ml of water. After stirring the mixture for 1 h the amine was added drop by drop, the gel was further homogenized for two hours and then transferred to a Teflon lined stainless steel autoclave, sealed and heated for the temperatures and times given in table 1.

Characterization

Thermo gravimetric analysis were carried out using a TA Instruments Hi-Res 2950 unit at a heating rate of 5 °C/min, and by flowing 60 ml/min of a mixture of 2/3 oxygen and 1/3 nitrogen. The metal contents in the solid were determined by atomic absorption spectrometry in a Perkin Elmer 2380 equipment. Carbon, hydrogen and nitrogen analysis was performed in a Perkin Elmer 2400 CHN Analyzer. Powder X-ray data were collected on a STOE STADIP diffractometer at the Haute Alsace University (France), fitted with a graphite monochromator. For this purpose CuKα radiation was used from a source operating at 35 kV and 55 mA; λ= 1,54060. Zinc molybdate micrographs were obtained using a Hitachi S-510 scanning electron microscope. Surface area measurements were carried out with N₂ in a Micromeritics ASAP 2010 equipment, after degassing the sample 24 hours at 150 °C.

Reaction conditions

The catalytic behavior of the metal molybdates was tested using the as-synthesized solids without any further treatment.

Table 1 Synthesis conditions for the metal molybdates

| System | Metal source | Amine | T, °C | t, hr |
|--------|---|---------------------------|-------|-------|
| ZnMo | 4,39 g of (CH ₃ COO) ₂ Zn·2H ₂ O | 2,4 ml of Triethanolamine | 100 | 2 |
| CoMo | 5,56 g of Co(NO ₃) ₂ ·6H ₂ O | 1,3 ml of Ethylenediamine | 200 | 72 |

Hydrogen peroxide (30%) was the hydroxylation agent and pure acetic acid the diluent to improve the miscibility between the organic phase and the peroxide. Since hydrogen peroxide in acetic acid is known to be a hydroxylation agent by itself [4], parallel experiments were carried out without the solid catalyst. The reagent volume ratio was 100:7:5 (acetic acid, hydrogen peroxide, cyclohexene) and the cyclohexene to catalyst ratio was 25 ml/g. The reagent composition was the same as used by Zhang *et al.* [5, 6]. The reaction was carried out in a glass reactor fitted with a reflux condenser, at a controlled temperature of 70 °C. The mixture composition was monitored every fifteen minutes, up to complete conversion of the cyclohexene. These measurements were done by means of a gas chromatograph coupled to a mass spectrometer Perkin Elmer Autosystem Gas Chromatograph-QMass910 Mass Spectrometer, with a Carbowax capillary column.

Results and Discussion

Structural and compositional aspects

Figure 1 shows a scheme of the structure of molybdates compounds. This crystal structure scheme was obtained employing POVray [7] and POWDERCELL [8] software and the coordinates of the zinc molybdate [9, 10]. Both software packages are specialized in crystallographic studies. The material is composed by parallel chains of edge-sharing zinc-oxygen octahedrons connected through tetrahedral molybdate groups. Two of the tetrahedron vertices connect consecutive octahedrons in one chain and extend the third vertex to an adjacent chain; the fourth vertex protrudes into the interlayer space. The result is a laminar structure with layers held together by sodium ions.

The X-ray diffractograms (figure 2) indicate that the two solids are isotypic. The morphology of the zinc molybdate crystals is shown in figure 3 where the largest average dimension observed is approximately 25 μm . Table 2 gives chemical

composition data and the BET surface area of the catalysts.

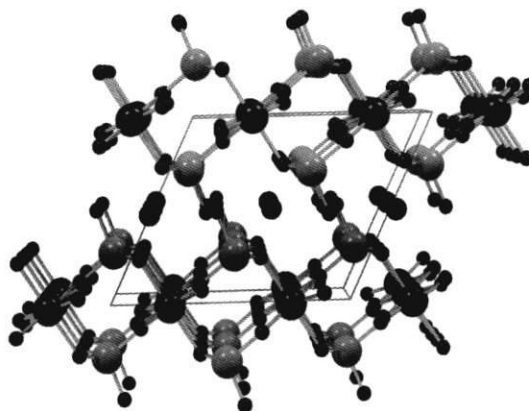


Figure 1 View along the b-axis of the crystal structure of the molybdates. (Mo: large clear, Zn: large dark, Na: medium dark, O: small dark spheres)

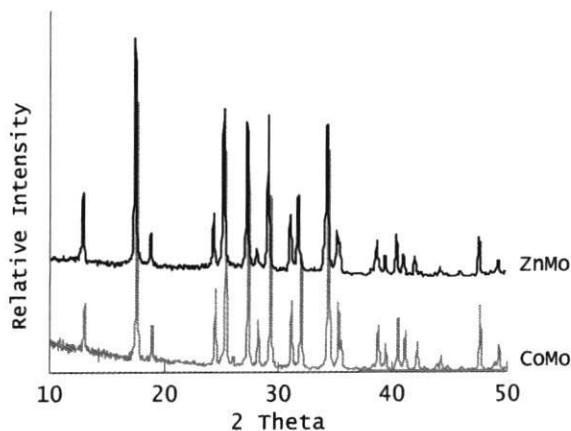


Figure 2 Diffractograms of the as-synthesized catalysts

Figure 4 shows thermo gravimetric curves before and after reaction. CoMo releases the equivalent of one water molecule at a unusually high temperature of *ca* 450 °C, both before and after being used in the reaction. Synthesized ZnMo

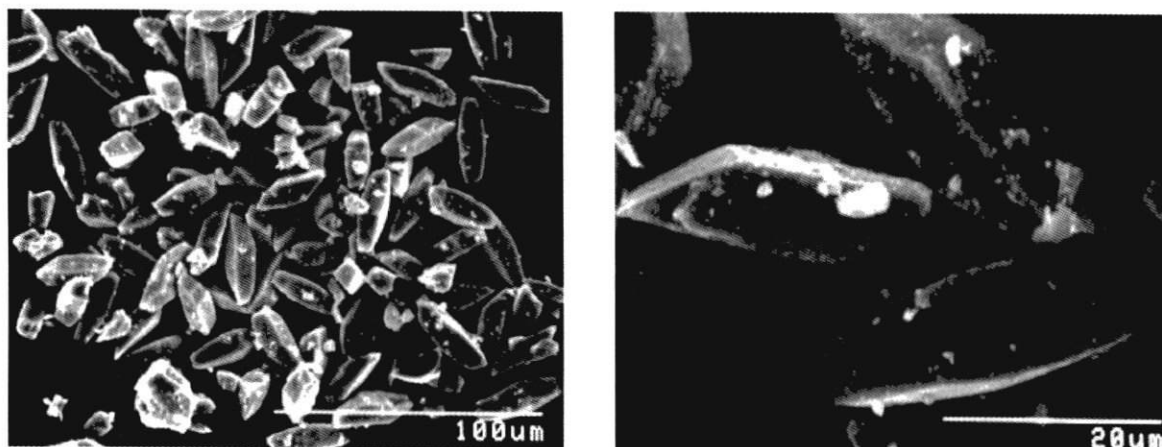


Figure 3 SEM of the zinc molybdate crystals

Table 2 Analytical data and surface area of the catalysts

| Catalyst | Formula | Source | %Na | %M | %Mo | %H ₂ O | (m ² /g) |
|----------|---|--------|-----|------|------|-------------------|---------------------|
| ZnMo | (NaOH)Zn ₂ (MoO ₄) ₂ ·2(H ₂ O) | Ideal | 4,4 | 24,8 | 36,4 | 9,3 | 10,80 |
| | | Found | 4,6 | 25,1 | 36,2 | 10,0 | |
| CoMo | (NaOH)Co ₂ (MoO ₄) ₂ ·(H ₂ O) | Ideal | 4,6 | 23,8 | 38,7 | 5,5 | 5,04 |
| | | Found | 4,6 | 23,7 | 37,1 | 5,4 | |

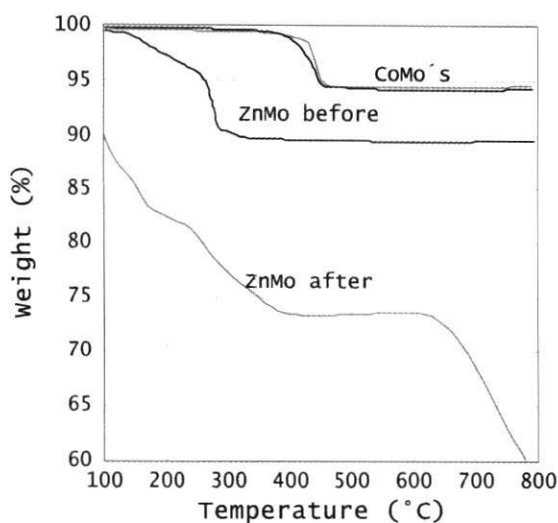


Figure 4 Thermo gravimetric curves for the catalysts

losses about 10% weight before 280 °C. After reaction, ZnMo was recovered by filtration and dried in air stream. It shows a 10% weight loss before 100 °C, and two additional weight loss events of about 7,0% up to 180 °C and about 9,5% up to 400 °C. These changes obey to water and organic material evolution, as confirmed by the CHN analysis (see table 3), and they also suggest that the reaction mixture (cyclohexene and its derivatives, and acetic acid) has penetrated to the interior of the solid. The weight loss observed beyond 640 °C is probably an indicative of partial molybdenum oxide sublimation. This sublimation phenomenon was confirmed in ammonium molybdate containing 84,57% MoO₃, by running a TGA in reagent grade molybdic acid (Fisher Scientific), where the weight drop begins at 670 °C. After reaction,

ZnMo shows the x-ray pattern of an unknown partially crystalline phase of larger unit cell, while CoMo retains its original structure.

Catalytic behavior

The catalytic experiments were run up to total conversion of cyclohexene. However, CoMo catalyst only reached a stable conversion of approximately 51%, which did not change even after 360 minutes of contact (figure 5). Since, in addition to the TGA results, the ZnMo sample shows residual carbonaceous matter after reaction (table 3), it is postulated that the reaction takes place inside the catalyst after a partial molecular exchange of water has taken place in the reactant organic substance.

“Inside” means a space between ZnMo lamellae, or cavity, in the new phase formed under the influence of reaction conditions.

Apparently, under the same treatment CoMo is more rigid than ZnMo, retains better its crystallization water, and prevents the formation of the hydroxyl radicals needed to initiate the reaction, thus effectively acting as a poison (table 4). It is known that hydrogen peroxide

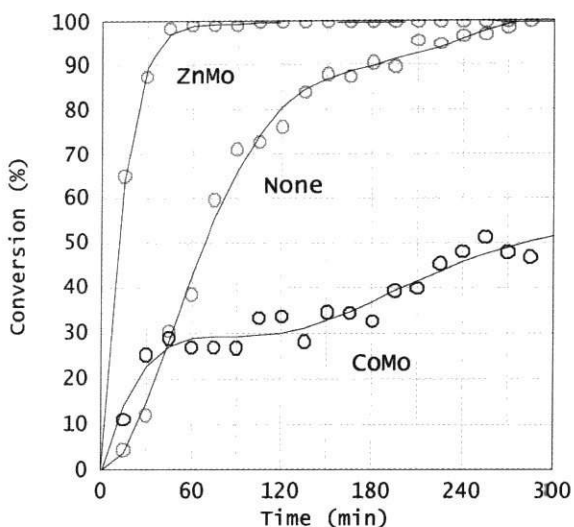


Figure 5 Conversion vs time in the hydroxylation of cyclohexene

Table 3 CHN analysis before and after reaction

| Weight % | Zinc molybdate | | Cobalt molybdate | |
|----------|----------------|-------|------------------|-------|
| | Before | After | Before | After |
| C | 0,14 | 5,99 | 0,12 | 0,04 |
| H | 0,12 | 2,97 | 0,61 | 0,33 |
| N | 0,07 | 0,01 | 0,04 | 0,01 |

Table 4 Yields of glycol and allyl alcohol

| Catalyst | Product | 1,2-cyclohexanediol | 2-cyclohexen-1-ol |
|----------|---------|---------------------|-------------------|
| | | ZnMo | 28,3 |
| CoMo | | 2,7 | 6,9 |
| None | | 2,4 | 22,7 |

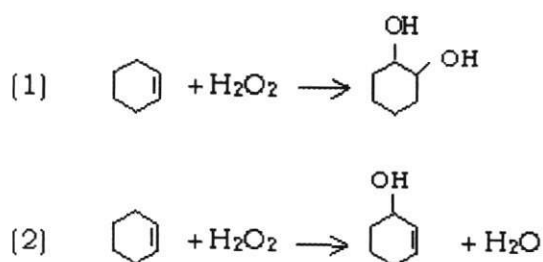
decomposition leading to oxygen formation is catalyzed by iron compounds [11], CoMo could well behave similarly.

Zinc molybdate gave complete conversion in 45 minutes and for the system with no catalyst takes about 270 minutes (figure 5). Tungsten containing catalyst has been reported to give full conversion in 60 minutes at 80 °C [5, 6]. Thus, the ZnMo catalyst appears to show as good or better activity for the same reaction than CoMo.

Finally, table 4 compares the yields of both 1,2-cyclohexenediol and 2-cyclohexene-1-ol, which were formed according to the reactions (1) and (2) of scheme 1, and they correspond to hydroxylation and oxidation reactions, respectively.

Conclusions

1. ZnMo and CoMo are isostructural but show important differences in the amount of water of crystallization and structural stability. The zinc molybdate accommodates more water and losses it more easily.
2. ZnMo during reaction, becomes a different phase, partially crystalline, with a larger unit cell, while CoMo retains its original structure.



Scheme 1

3. ZnMo shows adhered carbonaceous matter after reaction, while CoMo does not.
4. The hydroxylation reaction needs hydroxyl radicals which are formed near MoO groups.
5. The higher activity of ZnMo implies the exposure of a higher number of reaction sites.
6. ZnMo then undergoes penetration of reactants to its interior, as additionally supported by the TGA and CHN analysis.
7. ZnMo shows higher selectivity for 2-cyclohexene-1-ol than for 1,2-cyclohexanediol.
8. CoMo presents a lower activity than the blank which suggests a suppression of hydroxyl radicals.

Acknowledgments

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