

# CATALYTIC PERFORMANCE AND STABILITY OF ISOMORPHIC MOLYBDATES USED FOR THE OXIDATIVE DEHYDROGENATION OF PROPANE

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## Abstract

Co and Mn molybdates were used for this reaction. After use, their structure remained the same. However, only the Co molybdate maintained the surface area and the catalytic properties after 48 hours on stream.

*Key words:* Oxidative dehydrogenation, propane, metal molybdates

## INTRODUCTION

The increasing global demand for alkenes and their consequent shortage have brought about a renewed interest in producing them from alkanes. An alternative process to commercial dehydrogenation is the oxidative dehydrogenation of alkanes. In this case, a selective catalyst is needed to control the consecutive oxidation to carbon oxides.

Oxidative dehydrogenation has been studied for C<sub>2</sub>-C<sub>5</sub> alkanes. Most publications mention the use of catalysts based on transition metal oxides such as vanadates, molybdates and chromates. Different catalysts have been tried based on molybdenum combined with other transition metals. Some of them are supported oxides [1-3] and some others are massive oxides [4-7]. The best results have been reported in a patent using nickel molybdate, NiMo<sub>1.5</sub>O<sub>5.5</sub> [8], 29% propane conversion at 600°C with a selectivity to propene of 62.5%, and in two articles: i) (K/Mo)SiO<sub>2</sub>-TiO<sub>2</sub> with 21% yield [3], ii) Cr<sub>2</sub>O<sub>3</sub>/SBA-15 with 20% yield [9]. Ion et al [10] reported that the best catalyst was a cobalt molybdate (no structural information was given). Manganese oxide impregnated with Mo (3 – 20% by weight) has

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also been tried [5]. The best one of this series with a 3% load exhibited a 9% yield at 550°C ( $C_3H_8/O_2 = 1$ ).

Among the eighty papers reporting data for this system that were analyzed in this work, only four of them provided stability data. Cadus and Ferretti [5] reported data concerning a 12-hour run of an active, stable formulation. The authors of the other three papers either performed a six-hour run with good stability but only 2.7% yield [11], reported catalyst decay in six hours [12], or made a 48-hour run and reported decreasing conversion with increasing selectivity [13].

The goal of this work was to investigate the applicability and stability of novel molybdates synthesized and well characterized in our lab [14, 15] for the oxidative dehydrogenation of propane. XRD and Laser Raman Spectroscopy (LRS) were the main tools used for catalyst characterization before and after the reaction.

## EXPERIMENTAL

### Catalysts Preparation

In the hydrothermal method two previously prepared solutions were mixed together. One of them contained the molybdate and the other the transition metal. The gels obtained were kept at the given temperatures for 21-48 hours (Table 1). The solids obtained were heated in flowing air at  $2\text{ }^\circ\text{C}\cdot\text{min}^{-1}$  up to 600° C and held there for 3 hours.

Table 1. Catalysts synthesis

Sample	Preparation method	Gel molar composition	T (°C)	t (h)
CoMo $\phi$ x <sup>a</sup>	Hydrothermal	H <sub>2</sub> N(CH <sub>2</sub> ) <sub>2</sub> NH <sub>2</sub> : Na <sub>2</sub> MoO <sub>4</sub> : Co(NO <sub>3</sub> ) <sub>2</sub> : 175 H <sub>2</sub> O	200	48
MnMo10 <sup>a</sup>	Hydrothermal	MoO <sub>3</sub> : MnCl <sub>2</sub> : 2 NH <sub>4</sub> OH : 184 H <sub>2</sub> O	25	21

<sup>a</sup> Reported as new materials by our laboratory [13,14]

### Characterization

The X-ray diffraction patterns were obtained in a Rigaku Miniflex instrument operated at 40 kV and 30 mA with a Cu source ( $\lambda=1.5418\text{ \AA}$ ). The diffraction PDF (Powder Diffraction File) and crystallographic ICSD (Inorganic Crystal Structure Databank) databases were used.

A Unicam Solaar atomic absorption instrument was used to determine the concentrations of Mo, Na, Co and Mn in the solids. The specific areas were obtained with an ASAP 2010 Micromeritics sorptometer. The Raman spectra were recorded with a Jasco model TRS 600 SZ-P instrument. The excitation source was the 514.5 nm line of an Ar<sup>+</sup> laser. To check homogeneity, spectra in different places of the pellets were always taken.

### Catalytic measurements

A quartz flow through reactor (i.d. 5 mm, length 400 mm) was used. The catalytic tests were carried out at atmospheric pressure in the 400-600°C temperature range. Propane 98% and dry air were used to feed the reactor. Most of the experiments were run with a feed containing 29% of propane and 71% of air, corresponding to a molar ratio of propane/oxygen = 2.

## RESULTS AND DISCUSSION

### Characterization

The crystalline phases of the calcined solids were identified by X-ray diffraction. They were both monophasic (Table 2). The diffractograms (not shown) revealed that the catalysts were isomorphous.

Table 2. Identification of crystalline phases

Catalysts	Crystalline phases	PDF <sup>a</sup>	ICSD <sup>a</sup>	Amorphous phase <sup>b</sup>
MnMo10	MnMoO <sub>4</sub>	27-1280	15615	none
CoMoφx	CoMoO <sub>4</sub>	21-868	15615	Na <sub>2</sub> O

<sup>a</sup> PDF: Powder Diffraction File, ICSD: Inorganic Crystal Structure Databank.

<sup>b</sup> It arises from the mass balance taking into account the chemical analysis and the crystalline phase

Figure 1 shows the Raman spectra of the catalysts in the range where the characteristic vibration bands of the molybdenum polyhedrons appear. In each case, different sample regions were analyzed and they always showed the same bands, indicating that the solids were homogeneous. Note that the CoMoφx spectrum is very noisy. This is consistent with the lower crystallinity of this solid seen in the XRD patterns (not shown)

With the bond distances in each of the structures and the correlation of Wachs and coworkers [16] the molybdenum-oxygen stretching frequencies were calculated in the Raman spectrum for each of the catalysts. Starting from the crystallographic data, it was detected that they possessed different types of tetrahedrons in the structure. It was then verified that each band that appears in the spectra of Figure 1 corresponds to Mo-O stretching frequencies of the polyhedrons that compose the catalysts.

### Catalytic tests

A blank test showed that no reaction occurred in the absence of catalyst till 600° C. Besides, the catalysts shown here, two zinc, two iron, two copper and one cobalt molybdate catalyst were tested without much success. In all cases, propene was the main reaction product together with CO, CO<sub>2</sub> and water. Ethylene was also formed in some cases and methane only appeared at 600°C. Figure 2 shows the propane conversion and the propene selectivity for the two catalysts. Each point shows the average of three data values.

The X-ray diffraction patterns and Raman spectra of the used catalysts did not reveal any structural changes after reaction. However, the manganese molybdate showed a significant decrease of the surface area possibly due to textural changes. The surface areas and the olefin yields obtained at 600°C are reported in Table 3.

Experiments were made with the two catalysts at different space velocities. The results are presented in Figures 3 and 4. The highest yields were obtained with MnMo10. At 600°C and at 3000 mL/g.h the yield was 7.3% and at 6000 mL/g.h 10.1%.

Table 3. Surface area of the catalysts before and after reaction (m<sup>2</sup>/g) and olefin yields (%) at 600°C and 6000 mL/g.h.

Catalyst	Area BET before	Area BET after	Yield to propene	Yield to ethylene
MnMo10	4.0	1.1	10.1	3.6
CoMoφx	6.2	6.3	5.8	0.9

*Catalysts stability.* To test stability, the reaction was run by increasing and decreasing the temperature twice between 400 and 600°C. When this was done, only the CoMoφx catalyst maintained the conversion and yield values (Table 4). To further confirm the stability of this

formulation, it was kept on stream during 48 hours at 600°C. Again, no variation in either conversion or propene selectivity was observed. So, despite the fact that this is the second best catalyst when fresh, it rapidly becomes the best one due to its good stability.

Table 4. Stability of catalysts<sup>a</sup>

Temperature (°C)	MnMo10				CoMoφx			
	First cycle		Second cycle		First cycle		Second cycle	
	c <sup>b</sup>	s <sup>c</sup>	c <sup>b</sup>	s <sup>c</sup>	c <sup>b</sup>	s <sup>c</sup>	c <sup>b</sup>	s <sup>c</sup>
400	1.1	61.4	0.9	52.8	0.1	-	0.5	-
450	3.1	49.9	1.6	53.8	0.8	50.6	0.8	49.8
500	7.7	41.2	1.7	52.7	1.9	45.7	1.4	43.9
550	8.6	44.3	3.5	56.8	7.9	35.8	5.6	39.4
600	20.1	50.4	10.7	52.5	15.5	35.6	15.5	34.2

<sup>a</sup>Space velocity 6000 mL/g.h, reactant mixture composition 29% C<sub>3</sub>H<sub>8</sub>, 71% air, C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub> = 2

<sup>b</sup> c: conversion

<sup>c</sup> s: selectivity

*Effect of operating conditions upon CoMoφx performance.* In an attempt to improve the propene yield, space velocities between 1500 and 12000 were explored (Figure 4). The propane/oxygen ratio was also modified within the safety and equipment capability constraints. In both cases, the best yields were obtained at 600°C. They are reported in Table 5.

Table 5. Propene yields given by the CoMoφx catalyst at 600°C and varying conditions

Ve = 6000 C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> = 2	Ve = 3000 C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> = 2	Ve = 12000 C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> = 2	Ve = 6000 C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> = 1	Ve = 1500 C <sub>3</sub> H <sub>8</sub> /O <sub>2</sub> = 2
5.8	7.7	6.0	8.1	7.6

Probably, by combining a space velocity of 1500 mL/g.h with propane/oxygen = 1 the conversion would increase a great deal more. Note however that this molar ratio is located in the inflammability region of the mixture propane-oxygen and, moreover, the design of our reaction equipment does not allow this operation. The best operating conditions found here

for CoMo $\phi$ x are then: 600°C, space velocity of 6000 mL/g.h and propane/oxygen ratio equal to 1.

The data published in the open literature show a cluster of good catalysts with yields between 7 and 10% [17, 18] and a few exceptional cases with values between 15 and 20% [19, 3, 9]. Our catalysts enter in the first category but the key feature of the cobalt molybdate is its stability. This behavior may be a consequence of its structural stability for its X-ray pattern, Raman spectrum, and surface area were not modified after use. Note that the structures of MnMo10 and CoMo $\phi$ x are the same. This might be related to the good yield obtained with these catalysts. The difference in stability between both formulations could be due to the sharp decrease in surface area of the MnMo10 after use.

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## Figure Legends

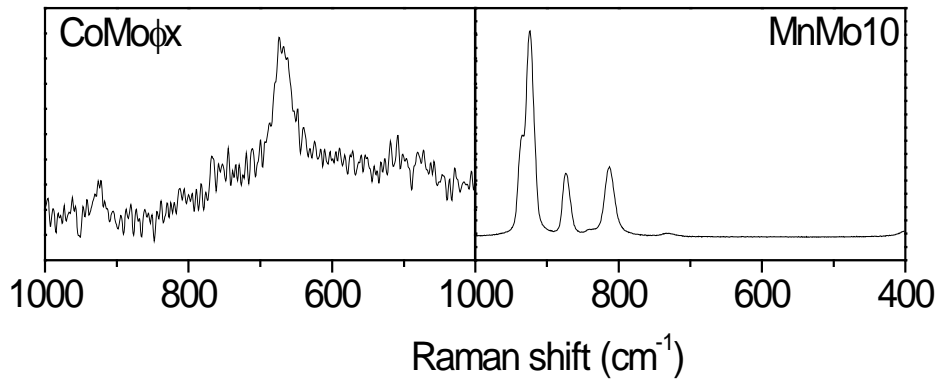
**Figure 1.** Raman spectra of the fresh catalysts.

**Figure 2.** Catalytic behavior of metallic molybdates. Space velocity 6000 mL/g.h., reactant mixture composition 29% C<sub>3</sub>H<sub>8</sub>, 71% air, C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub> = 2 ratio. ★CoMoϕx, ☆MnMo10.

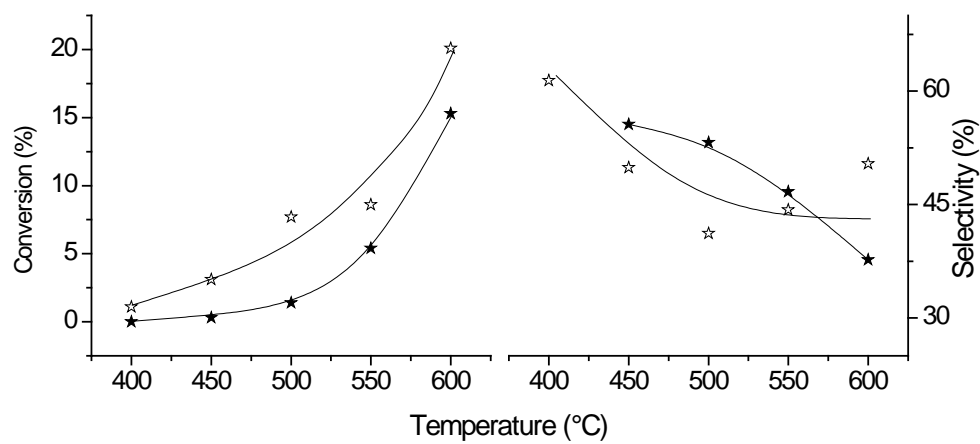
**Figure 3.** Influence of space velocity on the MnMo10 activity. Reactant mixture composition 29% C<sub>3</sub>H<sub>8</sub>, 71% air. C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub> ratio = 2. □3000 mL/g.h, ☆6000 mL/g.h, ○12000 mL/g.h.

**Figure 4.** Influence of the space velocity in the CoMoϕx activity. Reactant mixture composition 29% C<sub>3</sub>H<sub>8</sub>, 71% air. C<sub>3</sub>H<sub>8</sub>/O<sub>2</sub> ratio = 2. □3000 mL/g.h, ☆6000 mL/g.h, ○12000 mL/g.h.

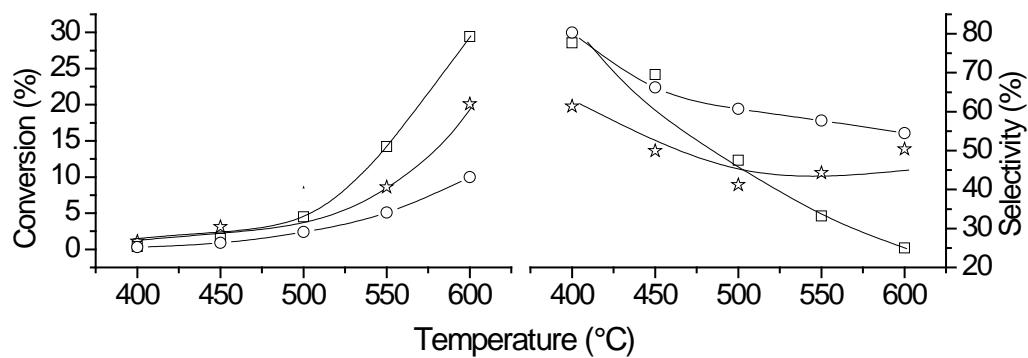




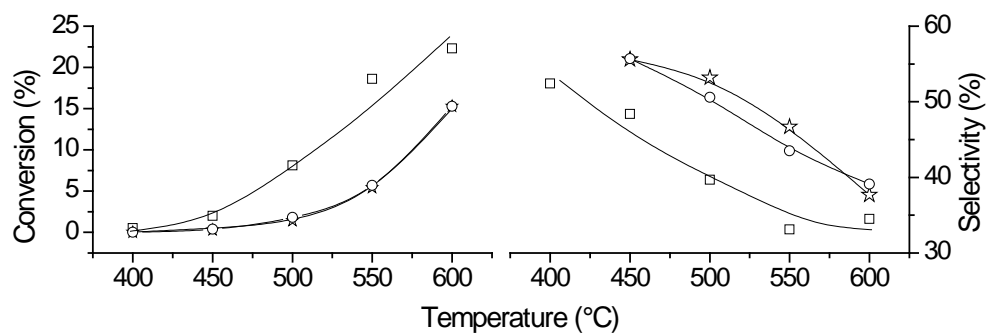
**Figure 1**



**Figure 2**



**Figure 3**



**Figure 4**