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Modifications of the $\text{AgMo}_3\text{P}_2\text{O}_{14}$ Catalyst in the Oxidation of Propane

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Abstract: The catalytic performances in the oxidation of propane of the $\text{AgMo}_3\text{P}_2\text{O}_{14}$ catalyst are quite good, leading to 70% of propene selectivity at 7% of propane conversion. We have checked that, before reaction, results of XANES and EXAFS obtained at the Mo K-edge (19999 eV) confirm those obtained by X-ray spectroscopy (oxidation state and Mo number of oxygen neighbour of 5.66, Mo=O bond length=1.72Å). After reaction, we have shown that the catalyst is partially reduced (5.66→5.2), the number of oxygen atoms increases to 6 and the mean molybdenyl bond length decreases (1.68Å) which is in agreement with the variation of this bond length with the oxidation state of the molybdenum in molybdenum phosphates. XPS measurements also confirmed a partial reduction of molybdenum species and showed a migration of the silver cation to the surface, certainly participating to the surface stabilization. Moreover, a correlation between the catalytic activity and the modification of the catalyst is made showing that an equilibrium between Mo^{V} and Mo^{VI} species in the catalyst leading to the average oxidation state of molybdenum of 5.2 seems to be very important.

I) INTRODUCTION

It has been shown that the catalysts performances of several systems in the mild oxidation of propane in acrolein are really increased by adding molybdenum atoms in their formulation (for example, in the $\text{V}_2\text{O}_5+\text{MgO}$ system [1]). Moreover, adding silver in the catalyst synthesis seems to enhance the selectivity in acrolein in the oxidation reaction of propane. The $\text{AgMo}_3\text{P}_2\text{O}_{14}$ [2] compound is effectively a quite efficient catalyst for this reaction and it is also an interesting model system to try to correlate its catalytic performances to its structural properties.

A very fine study of the $\text{AgMo}_3\text{P}_2\text{O}_{14}$ catalyst crystalline structure has been done : the comparison of the catalytic and structural properties of other molybdenum phosphate will allow us to precise the structural parameters which should act positively in the catalytic reaction. X-ray spectroscopy by transmission at the K-edge of molybdenum was performed ex situ on two samples, one corresponding to fresh catalyst and the second one to catalyst after catalytic test. The modification of the catalyst occurring during the reaction could thus be followed.

II) RESULTS AND DISCUSSION

1) STRUCTURE DESCRIPTION

In $[\text{Mo}_3\text{P}_2\text{O}_{14}]_{\infty}$ host lattice, the Mo atoms are located on three independant crystallographic sites resulting in an Mo_3O_{15} unit which is composed of two octahedra linked by one edge and one trigonal bipyramid linked to one of the two octahedra by one corner. The exact geometry of this unit is described on figure 1 in case of $\text{AgMo}_3\text{P}_2\text{O}_{14}$ compound. In this case, the average molybdenum oxidation state is 5.66, the mixed valency being a located one with the following repartition $(\text{Mo}^{\text{V}})_{\text{oct}}(\text{Mo}^{\text{VI}})_{\text{oct}}(\text{Mo}^{\text{VI}})_{\text{bipyrr}}$ in the Mo_3O_{15} unit. When strontium (divalent cation) is substituted to silver (monovalent cation), the average molybdenum oxidation state becomes 5.33 with the new repartition $(\text{Mo}^{\text{V}})_{\text{oct}}(\text{Mo}^{\text{V}})_{\text{oct}}(\text{Mo}^{\text{VI}})_{\text{bipyrr}}$.

2) XANES

Firstly, several molybdenum phosphates, whose structure had been determined by XRD on a single crystal, were used as references. Their XANES spectra showed a difference of above 10 eV between the Mo^{0} and Mo^{VI} edges in those compounds. Then, in a second part, the room temperature absorption spectra of the $\text{AgMo}_3\text{P}_2\text{O}_{14}$ catalyst before and after the catalytic oxidation reaction of propane in acrolein have been recorded. Generally, the Mars and Van Krevelen supposed mechanism implies that the oxidation state of the catalyst keeps constant after the catalytic reaction. We have shown that our catalyst is partially reduced (5.2 instead of 5.66). It is necessary to precise here that we observed a global reduction of the catalyst but the catalytic reaction is only a surface phenomena : it may exist a difference of reduction state between the molybdenum surface species and the bulk species.

3) EXAFS

It is known that in the molybdenum phosphate, the Mo^{V} octahedra contain three kinds of bonds : i) a very short molybdenyl one at 1.65 Å, ii) four bonds at 2 Å, iii) and a long one opposite to the molybdenyl bond at 2.3 Å. The Mo^{VI} exhibit either an octahedral or a trigonal bipyramidal coordination, with in each case two short bonds at 1.7 Å. The oxidation reactions are structure sensitive, so it is very important to follow the eventual changes in the number and length of the bonds (particularly the short bond) of the Mo_3O_{14} unit (figure 1). As far as the oxygen shell is concerned, two kinds of peaks can be considered corresponding respectively to molybdenyl short bonds and to the whole longer Mo-O bonds. Therefore, the fits which were performed between 3 and 13.2 Å⁻¹ on $k\chi(k)$ EXAFS spectra from a back Fourier Transform taken from 1 to 2.2 Å took into account two separate layers corresponding respectively to the oxygen short Mo=O layer and to the Mo-O (≈2Å) layer, which are characterized by to ($N_1 - R_1, N_2 - R_2$) parameters ($N-R$ = number of O atoms and MoO average distance of the layer).

Before reaction, as shown in table 1, the results are in good agreement with the XRD model : the total number of oxygen neighbours (N_1+N_2) is very close to 5.66 which correspond the Mo_3O_{14} unit.

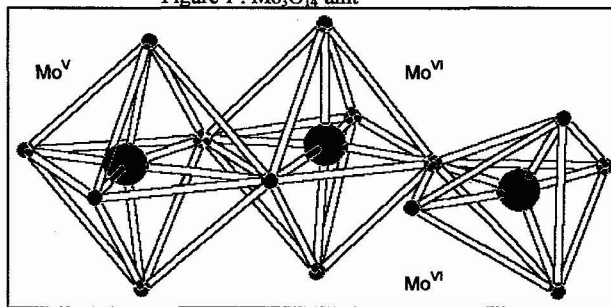
After reaction, it appears that in one hand, the number N_1+N_2 of oxygen neighbours is increased, and in the other hand, the number N_1 and the length R_1 of the molybdenyl bond decreases : this is coherent with the increase of the number of Mo^{V} atoms in relation with its very specific coordination. The reduction of molybdenum species which is accompanied of an increase of its coordination number could be related to an reorganization of molybdenum cluster, involving three octahedra sharing edges.

These results show that the Mo oxidation state has been reduced and moreover, its local surrounding is slightly modified after the catalytic tests. It should be underlined that the structural model available for the structure before reaction is nevertheless still available after reaction because of the flexibility of the Mo_3O_{14} unit which can accept two average oxidation state : 5.66 and 5.33, as confirmed by the existence of the two $\text{AgMo}_3\text{P}_2\text{O}_{14}$ and $\text{SrMo}_3\text{P}_2\text{O}_{14}$ phases respectively.

Table 1 : Crystallographic parameters before and after catalytic test

	1st oxygen layer	2nd oxygen layer
crystallographic model	$N_{1mc} = 1.33$ $R_{1mc} = 1.682\text{Å}$	$N_{2mc} = 4.33$ $R_{2mc} = 2.018\text{Å}$
$\text{AgMo}_3\text{P}_2\text{O}_{14}$ EXAFS parameters before catalytic test	$N_1 = 1.39$ $R_1 = 1.72\text{Å}$ $\sigma_1 = 4.72 \cdot 10^{-2}$ $\tau_1 = 1$ $\Delta E_1 = 6.34 \text{ eV}$	$N_2 = 4.24$ $R_2 = 2.00\text{Å}$ $\sigma_2 = 4.57 \cdot 10^{-2}$ $\tau_2 = 1$ $\Delta E_2 = 3.00 \text{ eV}$
$\text{AgMo}_3\text{P}_2\text{O}_{14}$ EXAFS parameters after catalytic test	$N_1 = 1.12$ $R_1 = 1.68\text{Å}$ $\sigma_1 = 4.57 \cdot 10^{-2}$ $\tau_1 = 1$ $\Delta E_1 = 3.00 \text{ eV}$	$N_2 = 4.90$ $R_2 = 2.02\text{Å}$ $\sigma_2 = 4.57 \cdot 10^{-2}$ $\tau_2 = 1$ $\Delta E_2 = 8.26 \text{ eV}$

Figure 1 : Mo_3O_{14} unit



4) XPS

The XPS measurements showed surface reduction of the catalyst from 5.66 to 5.2 which is the same than global reduction from XANES data. Comparisons of the theoretical concentrations of Mo, Ag and P showed an increase of silver concentration of 15% at the surface of the catalyst after reaction. This cation migration to the surface only happens when the catalyst has reached a good catalytic activity (Table 2). This migration of silver cation could participate to the stabilization of the surface of the catalyst and would make easier the electronic exchanges necessary to the redox mechanism of the catalytic reaction.

Table 2 : Relative concentrations

Compounds	Thermal treatment	Mo/Ag		P/Ag		Mo/P	
		XPS	XRD	XPS	XRD	XPS	XRD
$\text{AgMo}_3\text{P}_2\text{O}_{14}$ before reaction		2.79	3	1.22	1.5	2.27	2
$\text{AgMo}_3\text{P}_2\text{O}_{14}$ after reaction	(1) : 450°C	2.36	3	1.06	1.5	2.22	2
	(2) : 350°C	2.79	3	1.17	1.5	2.38	2

III) CONCLUSION

X-Ray Absorption and XPS characterizations have shown a global reduction of molybdenum species after catalytic reaction, which confirms a global participation of the catalysts in oxidation reactions and the importance of a correct balance between Mo^{V} and Mo^{VI} species for this reaction mechanism.

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