Mo Oxidation State of Cd, Fe, and Ag Catalysts Under Propane Mild Oxidation Reaction Conditions

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Activity and selectivity of molybdenum phosphates, $Cd_{1-x}Fe_x$-$MoPO_6$ ($x = 0 \rightarrow 1$) and $AgMo_3P_2O_{14}$, were compared for the propane mild oxidation reaction ($C_3H_8/O_2/N_2 = 60/20/20$, $W/F = 3.5$ g h L^{-1}). Despite different initial molybdenum oxidation states in the $CdMoPO_6$ and $AgMo_3P_2O_{14}$ compounds, both catalysts exhibited almost the same performance. At 733 K, propane conversion reached 6.5% and mild oxidation product selectivity (propylene + acrolein) was 75%. On the other hand, $Cd_{1-x}Fe_xMoPO_6$ ($x \neq 0$) compounds were completely inactive. X-Ray diffraction and absorption wera performed before and after catalytic tests and even during the reaction in the case of $AgMo_3P_2O_{14}$. It was shown that both active catalytic systems were modified under reactive flow; depending on their initial oxidation state, molybdenum species were either partially reduced or partially oxidized. This modification resulted in equilibration of the proportions of Mo^V and Mo^{VI} reaching the $Mo^{5.25}$ average oxidation state in both equilibrated catalysts. The intrinsic ability of the two frameworks to allow establishment of convenient Mo^V/Mo^{VI} balances of $2/3$ and $1/3$ was a determinant factor toward activity. EXAFS studies allowed us to provide evidence of the corresponding structural relaxation phenomena. In contrast, in the case of the iron-containing compounds $Cd_{1-x}Fe_xMoPO_6$, molybdenum remained pentavalent and catalytic activity was thus inhibited. The easier competitive oxidation of divalent iron into trivalent iron may be responsible for the inhibition of the Mo^V/Mo^{VI} redox couple. © 2001 Academic Press

Key Words: oxidation; propane; molybdenum phosphates; X-ray absorption.

INTRODUCTION

The mild oxidation reaction of propane represents a very important challenge, from both the economic and scientific points of view. The performance of the various catalytic formulations tested up to now has remained quite low, partly due to the difficulty of activating the propane molecule at a low enough temperature to avoid overoxidation. Moreover, as this reaction is structure sensitive, many structural

characteristics of the catalyst, such as composition, metal transition oxidation state, and organization of the atoms in the structure, have great influence over catalytic performance. Precise analysis of such parameters over a large amount of transition metal phosphate model catalysts has recently been published (1). It was concluded that one of the most important points is to get the MO_6 octahedra into polynuclear units to enhance electronic exchange but the number of MO_6 octahedra in such clusters should be limited to avoid overoxidation. Another, more surprising result was that the initial oxidation state of the transition metal in the fresh catalysts, i.e., simple valency as Mo^V, Mo^{VI}, or mixed valency Mo^V/Mo^{VI}, did not really influence catalytic performance. Actually, it was shown that, in case of the $AgMo_3P_2O_{14}$ compound, despite the preexisting mixed valency (corresponding to an average oxidation state of 5.66 for Mo), the molybdenum oxidation state was modified by the reactive flow (2). In the present study we report the catalytic performance of two new catalysts, $CdMoPO_6$ and $FeMoPO_6$, which are isostructural compounds, and compare it with that of $AgMo_3P_2O_{14}$. The initial molybdenum oxidation states of the two series of solids are different, respectively Mo^V and $Mo^{5.66}$. Characterizations performed over fresh and equilibrated catalysts under *ex situ* or even *in situ* conditions allow us to define the state of the equilibrated molybdenum phosphate catalyst under propane mild oxidation reaction conditions.

EXPERIMENTAL

Preparation of the Catalysts

To obtain well-defined model catalysts, i.e., single-phase and well-crystallized samples, polycrystalline samples were prepared according to the solid reaction method described elsewhere (3–5). First, MoO_3, $(NH_4)_2HPO_4$, and, according to the formulation $Cd(CH_3COO)_2$, Fe_2O_3 or Ag_2CO_3 were mixed in an agate mortar in the appropriate ratio. To eliminate NH_3, CO_2, and H_2O, the mixture was heated at about 673 K in air for 3 h in a platinum crucible. In a second step, the finely ground product was added to an appropriate

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ratio of metallic molybdenum Mo^0 (and Fe^0 in case of synthesis of $FeMoPO_6$), introduced in a silica tube and heated under vacuum for 12 h at 873 and 963 K, respectively, for $AgMo_3P_2O_{14}$ and $AMoPO_6$ (A = Cd, Fe). Various compositions of the solid solution $Cd_{1-x}Fe_xMoPO_6$ were prepared following the same procedure.

As expected from this solid preparation method which involved high-temperature treatments, the specific areas of the catalyst samples measured by the BET method with N_2 adsorption were found to be very low (about 1 m^2 g^{-1}).

Catalytic Tests: Reaction Procedure

The solids were tested toward the propane mild oxidation reaction under similar conditions: $W/F = 3.5$ g h L^{-1}, $C_3H_8/O_2/N_2 = 60/20/20$, reaction temperature between 573 and 733 K. It was checked that, in that temperature range, propane was not activated in the gas phase. Descriptions of apparatus, procedure, and analysis have been detailed elsewhere (6).

Characterization Methods

XRD. X-Ray diffractometry (XRD) powder diffractograms were recorded with a Philips diffractometer. The instrument was equipped with a copper anode generating Cu$K\alpha$ radiation (λ = 1.5418 Å). Diffractograms were recorded in the 2θ range 10° to 60°.

X-Ray absorption measurements. X-ray absorption measurements were carried out at the French Synchrotron Laboratory LURE, using the DCI storage ring and EXAFS IV beamline equipped with a two-crystal Si (311) monochromator. During the experiments, the storage ring used 1.85-GeV positrons with an average intensity of 250 mA. Data were collected in transmission mode chambers at the Mo K edge (19999 eV). Threshold spectra were recorded with steps of 1 eV and a measuring time of 2 s per data point, in the energy range 19,950–20,100 eV for the Mo K edge. Samples were pressed into pellets of absorbancy close to 1. The Mo K edge of molybdenum metal was regularly registered, and allowed us to use the references Mo(V), Mo(5.33), and Mo(VI) valency states recorded in a previous run (7–9). In the case of the $CdMoPO_6$ and $Cd_{0.9}Fe_{0.1}MoPO_6$ catalysts, data were collected at room temperature on the fresh samples (before any contact with the reactive flow) and on the used catalysts. Used catalysts corresponded to samples that had reacted for few hours at 733 K, the temperature being then quenched under nitrogen flow. The $AgMo_3P_2O_{14}$ threshold data were collected under *in situ* conditions, i.e., from room temperature (RT) to 733 K under reactive flow, using a special reactor cell (10). EXAFS Mo K-edge spectra of the $CdMoPO_6$ catalyst were registered under *ex situ* conditions (on fresh and used samples) with 2-eV steps in the energy range 19,900–20,700 eV.

XANES data processing. The normalization procedure used throughout this work was a standard one: After subtraction of the same diffusion background on the XANES and EXAFS spectra, recorded under the same experimental conditions, a point at high energy, where no more EXAFS oscillations were still observable, was set at unity. Then the intensity of a point with energy between 50 and 100 eV from the edge was recorded on the EXAFS spectrum and was reported on the XANES to set the normalized height.

EXAFS data processing. EXAFS analysis was performed using Michalowicz's chain of programs (11). The procedure was the same as in a previous work (2). The atomic absorption coefficient was approximated by a fourth-degree polynomial expression from 20,036 to 20,690 eV.

RESULTS

Reactivity Results

The catalytic performance of the isostructural compounds $AMoPO_6$ was compared with that of $AgMo_3P_2O_{14}$ (2). Conversion variations were achieved by varying the inlet temperature between 573 and 733 K. For all the samples, conversion remained very low (<1%) until the reaction temperature reaches 683 K. According to Table 1, the $CdMoPO_6$ performance was very close to that of $AgMo_3P_2O_{14}$. The major organic product was propene; acrolein, propanal, and acetic acid were formed in smaller amounts. Maximum propene selectivity was reached at 683 K, then decreased at the benefit of acrolein and mostly of carbon dioxide, the formation of which was enhanced

TABLE 1

Catalytic Results on $AgMo_3P_2O_{14}$ and $CdMoPO_6$ Samples for Propane Mild Oxidation Reaction between 623 and 733 K

	Temperature (°K)	$CdMoPO_6$	$AgMo_3P_2O_{14}$
Propane conversion (%)	623	0.5	1
	683	2	3
	733	6.5	7
Oxygen conversion (%)	623	2	4
	683	8	10
	733	32	33
Propene selectivity (%)	623	83	80
	683	78	82
	733	71	70
Acrolein selectivity (%)	623	1	2
	683	3	4
	733	4	6
CO_x selectivity (%)	623	14	15
	683	15	7
	733	19	18

by secondary oxidation reactions. At 733 K, propane was selectively activated by the $CdMoPO_6$ and $AgMo_3P_2O_{14}$ samples, leading respectively to 6.5 and 7% propane conversion, 71 and 70% propylene selectivity, and finally, 4 and 6% acrolein selectivity. Carbon balance corresponds to propanal and acetic acid, the amounts of which remained quite small. In contrast, under the same conditions, $FeMoPO_6$ remained completely inactive toward propane activation, whatever the temperature (propane conversion <1% at 733 K). Actually, the presence of iron, even in very low proportions, in the solid solution compounds $Cd_{1-x}Fe_xMoPO_6$, inhibited catalytic activity. Taking into account the analysis precision (limited by the use of three chromatograph detectors), the very low level of conversion does not allow us to check whether there is a linear dependence of conversion on iron content.

Characterization Results

XRD Results

X-Ray diffraction patterns of samples were indexed following the crystallographic symmetries and parameters deduced from single-crystal studies (3–5) and allowed us to check that the polycrystalline powders were well-crystallized and single-phased. In particular, in the case of characterizations of $Cd_{1-x}Fe_xMoPO_6$ samples, no splitting of the diffraction line was observed, indicating that the samples correspond to a true solid solution and not to a mixture of $CdMoPO_6$ and $FeMoPO_6$ phases.

$AgMo_3P_2O_{14}$ was described earlier (2, 3). It exhibits a layer structure involving three-center molybdenum clusters (Fig. 1a) surrounded by phosphate tetrahedra.

The structure of $CdMoPO_6$ had previously been determined from a single-crystal diffraction study. The $FeMoPO_6$ structure was shown to be isotypic of the latter one. This structure can be described as a MoPO three-dimensionnal framework (Fig. 2) in which cadmium or iron divalent cations are inserted. Molybdenum atoms are in classic Mo^V coordination (12) with one short Mo=O bond at 1.693 Å. Actually, octahedra are linked by one edge (Fig. 1b), resulting in a Mo–Mo distance of 2.61 Å and a buildup of Mo_2O_{10} units. The two molybdenyl ions of this pair are in *trans* configuration toward the equatorial plane of the unit. In both compounds, the divalent countercation (Cd^{2+} or Fe^{2+}) involves octahedral coordination, building up also bioctahedral A_2O_{10} units.

No modification of the XRD spectra was detectable after the catalytic test.

XANES Results

A previous study performed at RT under *ex situ* conditions (2) allowed us to measure the edge energies of molybdenum for several reference compounds on the derivative
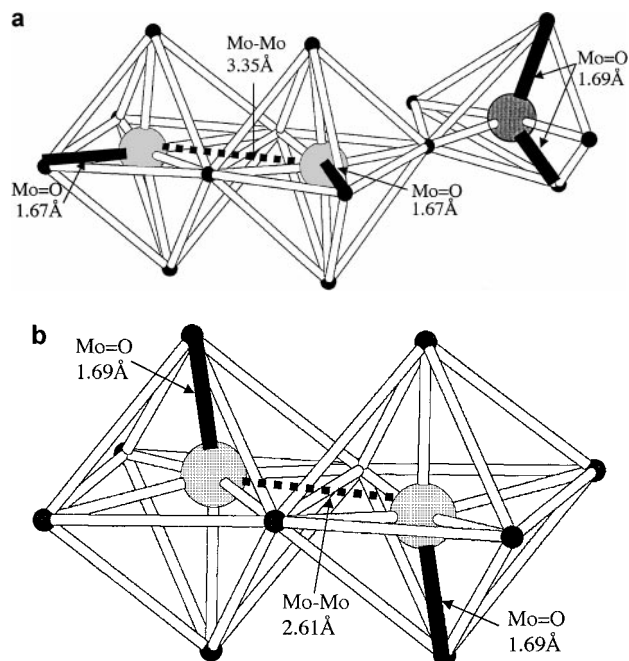

FIG. 1. (a) Mo_3O_{15} structural unit in $AgMo_3P_2O_{14}$. (b) Mo_2O_{10} structural unit in $CdMoPO_6$.

spectra. These energies correspond to the midheight of the main absorption jump. This first series of experiments allowed us to check that the Mo average oxidation in fresh $AgMo_3P_2O_{14}$ catalyst is 5.66, as expected from the crystallographic data. The same sample was submitted to reactive flow at 733 K and reacted as described above; after reaching the equilibrated state (no modification of performance for few hours), it was rapidly cooled to RT under inert gas. The treshold was then registered on this used catalyst. It was shown that the Mo average oxidation state was modified in a reductive way. Assuming a linear dependence of the edge energies on the mean formal valency state of molybdenum cations between, on one hand, the ζ-$NaMo_3P_2O_{13}$ sample which was used as the Mo^V reference (7), and, on the other hand, $AgMo_3P_2O_{14}$ fresh sample ($Mo^{5.66}$), the Mo valency was estimated to be 5.25 in the used catalyst (Table 2). This edge result was in full agreement with XPS measurements (2); it suggests a bulk phenomenon with an influence on surface properties.

$AgMo_3P_2O_{14}$ in situ conditions. To check whether these previous results obtained under *ex situ* conditions are really representative of the working catalyst, threshold data were collected under *in situ* conditions, i.e., from RT to 733 K under reactive flow, using a special reactor cell (10). Analysis of the products of the occurring reaction by chromatography allowed us to check that the cell indeed behaved as a reactor.

Comparison of the spectra registered at increasing temperatures (Fig. 3) shows that the threshold is not modified
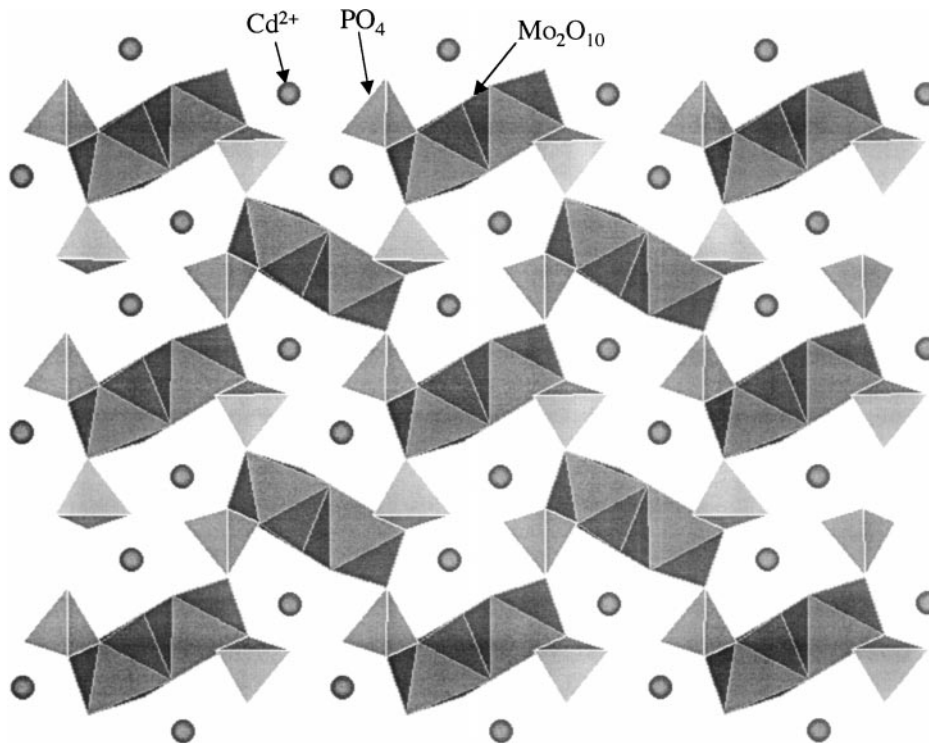
FIG. 2.   Projection of $CdMoPO_6$ along [100].

from RT to 573 K. A slight modification occurs at 683 K, and, finally at 733 K, the molybdenum reduction appears more pronounced. This temperature corresponds to the maximum reaction temperature considered in the catalytic reaction study.

Comparisons with previous results obtained under ex situ conditions.   Periodic registration of XANES spectra of several references, especially the Mo metal compound, allowed comparison of the two series of data and quantification of the edge energy reached in the equilibrated catalyst for molybdenum (Table 2).

First, comparison of the spectrum previously recorded under *ex situ* conditions on a fresh $AgMo_3P_2O_{14}$ sample with the RT *in situ* spectrum indicates that the Mo K edge is not modified at all by the reactive flow at RT (Fig. 3). Moreover, it can be seen that the *ex situ* spectrum registered after catalytic reaction performed at 733 K and the *in situ* registered spectrum at 733 K are almost identical, both leading to a final Mo oxidation state of 5.25.

It can thus be concluded that transformations of the catalyst occurring during reaction are irreversible, even after cooling. The threshold study performed under post-catalytic reaction conditions on a previously equilibrated sample is representative of the state of the equilibrated catalyst during the reaction. XANES characterizations of $Cd_{1-x}Fe_xMoPO_6$ samples were therefore performed under *ex situ* conditions and the eventual modification occurring

after reaction should be considered as representative of the state of the working catalysts.

CdMoPO_6.   XANES spectra of the $CdMoPO_6$ samples before and after the catalytic test are shown in Fig. 4; the Mo K edge of the fresh $CdMoPO_6$ sample fits the spectrum corresponding to the Mo(V) reference (Table 2) and

TABLE 2

Mo Valencies Estimated from Mo K-Edge Energies

| Compound	Mo formal valency state	Energy (eV) at mid height of the main jump	Estimated formal valency state
Mo metal	Mo(0)	11.1 ± 0.3	
$NaMo_3P_2O_{13}$	Mo(5)	15.4 ± 0.3	
$NaMo_3P_3O_{16}$	Mo(5.33)	17.2 ± 0.3	5.45 ± 0.3
$BaMo_2P_2O_{12}$	Mo(6)	18.6 ± 0.3	5.80 ± 0.3
$AgMo_3P_2O_{14}$ (B)	Mo(5.66)	18.1 ± 0.3	
$AgMo_3P_2O_{14}$ (A)		16.4 ± 0.3	5.25 ± 0.3
$AgMo_3P_2O_{14}$ (*in situ* 450°C)		16.3 ± 0.3	5.25 ± 0.3
$AgMo_3P_2O_{14}$ (*in situ* 300°C)		18.2 ± 0.3	5.70 ± 0.3
$AgMo_3P_2O_{14}$ (*in situ* 300°C)		18.2 ± 0.3	5.70 ± 0.3
$CdMoPO_6$ (B)[a]		15.3 ± 0.3	5.00 ± 0.3
$CdMoPO_6$ (A)		16.5 ± 0.3	5.25 ± 0.3
$Cd_{0.9}Fe_{0.1}MoPO_6$ (B)		15.3 ± 0.3	5.00 ± 0.3
$Cd_{0.9}Fe_{0.1}MoPO_6$ (A)		15.4 ± 0.3	5.00 ± 0.3

[a] (B) Before catalytic test. (A) After catalytic test.
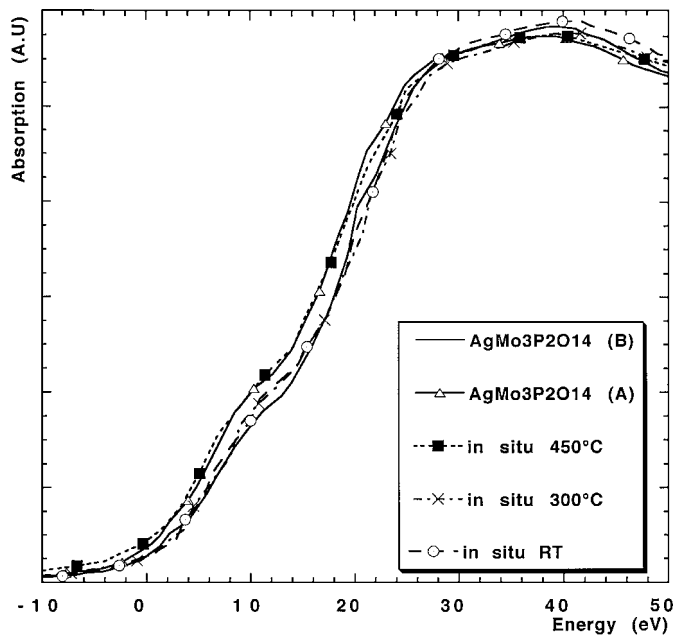
FIG. 3. XANES, Mo K edge of $AgMo_3P_2O_{14}$ catalysts registered before (B) and after (A) reaction and under *in situ* conditions at several temperatures.

thus confirms the initial Mo^V oxidation state. After the catalytic reaction, the Mo K edge is modified in such a way that molybdenum is partially oxidized. The molybdenum average oxidation state was estimated to be 5.25 from a linear interpolation between the Mo(V) reference and the $AgMo_3P_2O_{14}$ fresh sample ($Mo^{5.66}$).

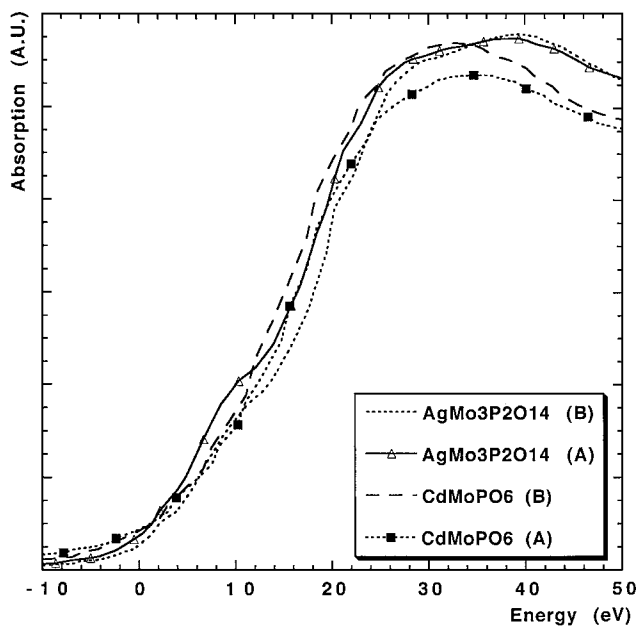**FIG. 4.** XANES, Mo K edge of $AgMo_3P_2O_{14}$ and $CdMoPO_6$ catalysts registered before (B) and after (A) reaction.
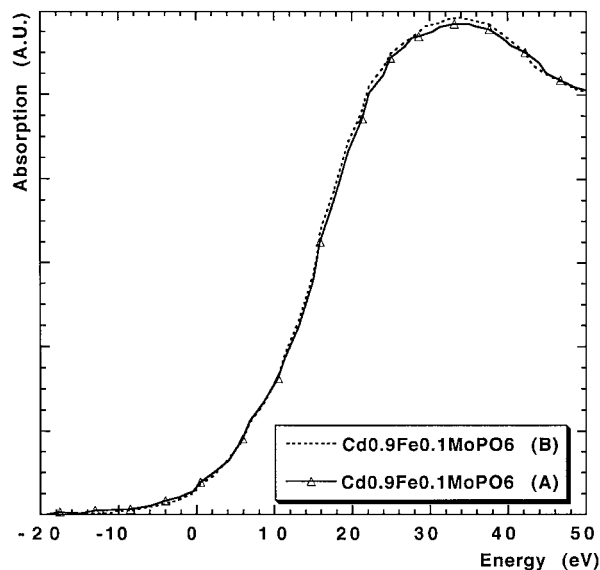

FIG. 5. XANES, Mo K edge of $Cd_{0.9}Fe_{0.1}MoPO_6$ before (B) and after (A) reaction.

$Cd_{1-x}Fe_xMoPO_6$.   A Mo K edge study has also been carried out on a sample that contained very little iron ($x = 0.1$). The edge energy of molybdenum for the fresh catalyst confirms the Mo^V valency, but, contrary to the $CdMoPO_6$ compound, the spectrum of the used catalyst shows no modification compared with the fresh sample (Fig. 5).

EXAFS Results

Previously, an EXAFS study was performed on the $AgMo_3$-P_2O_{14} catalyst. Structural modifications of the first sphere of coordination of molybdenum species induced by the catalytic reaction were analyzed. The slight modifications observed were consistent with the transformation of a few Mo^{VI} species into Mo^V species. Indeed, in the phosphate network, the coordination number of molybdenum and the number of molybdenyl groups, as well as their length, are very well defined in relation to the molybdenum valency (12). Moreover, the transformation of a molybdenyl group into a Mo–OH group was proposed and is also consistent with the partial reduction that is observed with no decrease in the number of oxygen neighbors.

$CdMoPO_6$.   An EXAFS study was carried out on $CdMoPO_6$ samples before and after the catalytic test. The moduli of the Fourier transforms of the experimental EXAFS spectra of $CdMoPO_6$ before and after the catalytic test are shown in Fig. 6a. All peaks shifted to radii shortened by 0.35 Å owing to the presence of a backscattering phase shift. Simulations taking into account both the first and second coordination spheres around molybdenum atom centers (respectively Mo–O and Mo–Mo bonds) were performed. Introduction of theoretical backscattering
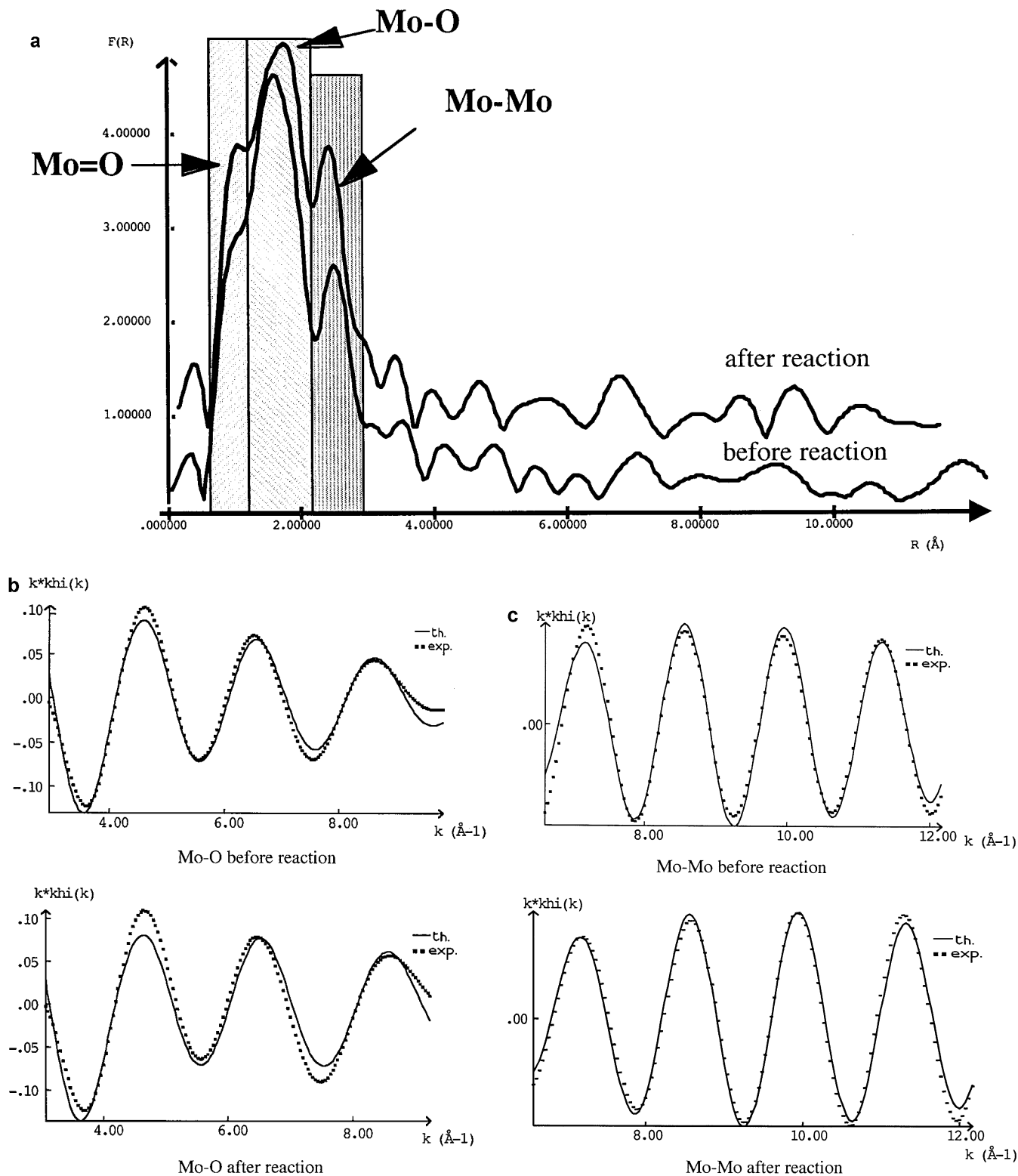
FIG. 6. (a) Fourier transform EXAFS of CdMoPO$_6$ samples before and after reaction. (b) Simulated and experimental EXAFS spectra of the Mo–O shell of CdMoPO$_6$ compound before and after catalytic testing. (c) Simulated and experimental EXAFS spectra of the Mo–Mo shell of CdMoPO$_6$ compound before and after the catalytic test.

phase shifts and amplitude into the calculation brought the positions of experimental Mo–O and Mo–Mo peaks in Fourier transforms into agreement with the model structure. It should be noted that the fits of EXAFS spectra were greatly facilitated by knowledge of the exact geometric data of the corresponding structure, which were issued from previous studies on single-crystal X ray diffraction (4).

Oxygen Shell

The fits were performed between 3 and 13.2 Å^{-1} on the EXAFS spectra from a back Fourier transform taken from 1 to 2.2 Å. As specified in Fig. 6a, the oxygen first shell was considered as resulting from two contributions: a molybdenyl short bond and all the other Mo–O bonds. These two separate shells were respectively characterized by N_1-R_1, N_2-R_2 parameters (N = number of O atoms, R = Mo–O average distance of the corresponding shell). Since the amplitude and phase shifts were taken from theoretical files, Γ and S_0 were respectively fixed at 1 and 0.8. Other parameters were refined. Table 3 summarizes the results and allows comparisons with the initial model structure.

CdMoPO$_6$ before catalytic test. There is very good agreement between the refined parameters and the model structure. This result ensures the purity of the polycrystalline powder. The $N_1 + N_2$ value is consistent with the octahedral coordination of molybdenum. The lone short Mo=O bond (N_1 = 0.85) is clearly seen with R_1 = 1.70 Å. The other peak at R_2 = 2.05 Å is the most intense (N_2 = 5.15): it is consistent with an assignment to the four equatorial bonds and to the *trans*-molybdenyl distance; the average M–O distance was calculated from the single-crystal structural determination is 2.05 Å.

CdMoPO$_6$ after catalytic test. Figure 6b represents the simulated and experimental EXAFS spectra. According to the fitted parameters (Table 3), octahedral coordination is conserved, but the molybdenum–oxygen bond length repartition is modified: the number of the short bond (R_1 = 1.71 Å) is increased to N_1 = 1.15, whereas the second shell's contribution (R_2 = 2.07 Å) decreases to N_2 = 4.85. This evolution is consistent with the appearance of few Mo(VI) species and, thus, with the partial oxidation evidenced by the Mo K-edge study.

Second Shell: Mo–Mo Bond

From Fourier transforms, a second EXAFS contribution can be considered. This contribution corresponds to second backscattering neighbors: Mo atoms situated 2.61 Å from absorbing Mo atoms, according to structural data (Fig. 1b).

The fits were performed between 3 and 13.2 Å^{-1} on EXAFS spectra from a back Fourier transform taken from 2 to 2.9 Å. Once more, Γ and S_0 were respectively fixed at 1 and 0.8 and $N - R$ parameters were refined. The final fit results (Fig. 6c) are collected in Table 3.

CdMoPO$_6$ before catalytic test. Before reaction, there is one (N = 0.95) backscattering molybdenum atom around each absorbing molybdenum at a distance of R = 2.62 Å, which is in good agreement with the model structure (Fig. 1b, 2).

CdMoPO$_6$ after catalytic test. The N value is significantly increased in the case of the post-catalytic reaction sample (N = 1.36), whereas the Mo–Mo distance remains unchanged. The average backscattering of Mo atoms is thus more important, indicating clustering of few molybdenum species.

TABLE 3

Variation of the EXAFS Parameters before and after the Catalytic Test for CdMoPO$_6$: Comparison with the Initial Crystallographic Model Results[a]

	First coordination sphere		Second coordination sphere Mo–Mo
	First oxygen shell	Second oxygen shell	
Crystallographic model	$N_{1\,cm}$ = 1 $R_{1\,cm}$ = 1.693(2) Å	$N_{2\,cm}$ = 5 $R_{2\,cm}$ = 2.0498(2) Å	N_{cm} = 1 R_{cm} = 2.61 Å
CdMoPO$_6$ EXAFS parameters before catalytic test	N_1 = 0.85 R_1 = 1.70(1) Å σ_1 = 1.501 × 10^{-2} ΔE_1 = 3.87 eV	N_2 = 5.15 $R_{2\,cm}$ = 2.05(1) Å σ_2 = 8.52 × 10^{-2} ΔE_2 = 4.14 eV	N = 0.95 R = 2.63(1) Å σ = 4.42 × 10^{-2} ΔE = 4.51 eV
CdMoPO$_6$ EXAFS parameters after catalytic test	N_1 = 1.15 R_1 = 1.71 (1) Å σ_1 = 2.88 × 10^{-2} ΔE_1 = 4.90 eV	N_2 = 4.85 $R_{2\,cm}$ = 2.07(1) Å σ_2 = 7.51 × 10^{-2} ΔE_2 = 5.92 eV	N = 1.36 R = 2.63(1) Å σ = 3.53 × 10^{-2} ΔE = 3.94 eV

[a] σ = Debye–Waller factor, ΔE = energy shift.

DISCUSSION

Among the several molybdenum phosphate compounds tested in the propane mild oxidation reaction (1), most have exhibited quite different behaviors, indicating the sensitivity of this reaction to structural parameters. In particular, those involving isolated molybdenum atoms remain always completely inactive whatever the reaction conditions, whereas the active ones exhibit several transition metal atoms linked to each other by edges or corners. In this case, the nuclearity of such entities is an important factor in mild oxygenated product selectivity, since the larger the nuclearity (infinite chains for instance), the lower the selectivity. It is thus noteworthy that $AgMo_3P_2O_{14}$ and $CdMoPO_6$, which exhibit very similar performance in the mild oxidation of propane, involve respectively entities of three and two molybdenum polyhedra. Taking into account the very low specific areas of those compounds, which are related to their method of preparation, these systems can be considered intrinsically very active. The selectivity in mild oxygenated products is also very high. Why these two compounds behave in the same way has to be examined on the basis of the several characterizations conducted.

Structural relationships between the two compounds were first examined to point out eventual common features. Molybdenyl bonds, being considered of peculiar importance toward catalytic activity, were precisely examined. Fine comparison of Figs. 1 and 3 shows that the Mo_2O_{10} bioctahedral unit of $CdMoPO_6$ cannot simply been described as a fraction of the Mo_3O_{14} cluster belonging to the $AgMo_3P_2O_{14}$ structure; the molybdenyl configurations are different in the two cases. Indeed, in the case of $AgMo_3P_2O_{14}$, it appears that the molybdenyl bonds are situated in the square plane of the octahedra (Fig. 1a), whereas, in the case of $CdMoPO_6$, the molybdenyl groups are situated in *trans* configuration relative to this square plane (Fig. 1b). The latter configuration implies the presence at the surface of the catalyst of a short M=O bond, considered as an electron reservoir, contiguous to a vacancy corresponding to a Lewis acid site. Such a pair was previously underlined as primordial in mild oxidation reactions, especially in the case of the well-known $(VO)_2P_2O_7$ compound active in *N*-butane mild oxidation (14). Nevertheless, in the present case, it cannot explain the similar good results obtained for $AgMo_3P_2O_{14}$ and $CdMoPO_6$.

Characterization of the molybdenum oxidation state of the two compounds has shown that, if the two compounds exhibit different molybdenum oxidation states before reaction, they are modified under reactive flow. This modification explains that no clear relation has been observed yet between metal transition oxidation state in the fresh catalyst and catalytic activity (1). *In situ* experiments performed on $AgMo_3P_2O_{14}$ have shown that significant activity (Table 1) and the Mo-*K*-edge modification occur simulta-

neously at 683 K. The concomitance of these two phenomena indicates that the modification of the catalyst is relative to the catalytic reaction itself and not only to the reactive atmosphere. A simple thermal effect of the flow can be rejected since some samples, especially the inactive iron-containing samples, are not modified at all after being submitted to the same reactive conditions. Actually, under the same conditions of temperature and feed, but starting from different initial Mo oxidation states, molybdenum has been partially reduced in the case of $AgMo_3P_2O_{14}$, whereas it has been partially oxidized in case of $CdMoPO_6$. Moreover, from Fig. 4, which represents both $AgMo_3P_2O_{14}$ and $CdMoPO_6$ thresholds, it appears that both catalysts reach the same final state ($Mo^{5.25}$). This point is of peculiar importance since the feed contains propane (reductive reagent) and oxygen (oxidative reagent) in $C_3H_8/O_2 = 3$ proportion, and is thus rather considered a reductive atmosphere. This result confirms that the change is relative to phenomena in direct relation with the reaction itself and not simply to the high-temperature and/or reductive feed effect. The reaction, taking place at the surface of the catalyst, involves the Mars and Van Krevelen mechanism (15). Propane is activated by Mo^{5+} species whereas the insertion of oxygen into the organic compound (oxidation reaction) involves O–Mo^{6+} species. It results in the reduction of the catalyst since the corresponding oxygen belongs to the oxygen network of the solid; the catalyst is further reoxidized by the oxygen of the feed. The evolution of the oxidation state of the transition metal of the catalysts is supposed to depend on the nature of the kinetic determining step. The mechanism involves thus alternatively reduced and oxidized species. The best fit between reactants and surface requires an appropriate ratio between the Mo^{6+} and Mo^{5+} species. Indeed, for instance, a catalyst too easily reducible will not be as selective as the present ones.

It was previously shown from studies performed on isostructural compounds that the nature of the inserted cation in a metal transition phosphate network does not really influence the propane conversion but could modify the selectivity results. Taking into account the very promising results obtained with $CdMoPO_6$, and the fact that iron is known for its ability to insert oxygen (16), iron was introduced into the composition of this structure. The corresponding solid solution was supposed to enhance either, at best, acrolein selectivity, or, at worst, carbon oxide formation. Actually, all the iron-containing samples lead to complete inactivity. This unexpected result indicated that the reaction is inhibited by iron, even in a very small amount. XANES characterization performed on iron-containing samples indicated that molybdenum species remain pentavalent after the treatment. The partial oxidation of molybdenum observed in the case of $CdMoPO_6$ does not occur in the presence of iron. The inhibition of the reaction by iron is thus related to the inhibition of the working of the

Mo^V/Mo^{VI} redox pair. Iron introduced into the samples as Fe^{2+} species might be more easily oxidized in Fe^{3+} than Mo^V in Mo^{VI}. Unfortunately technical problems did not allow us to characterize iron after the reaction.

The reaction takes place only if the properties of the solids allow equilibration of the catalysts to be reached in such a way that the solids have a Mo^V/Mo^{VI} ratio close to 2/3 to 1/3. The ability of a solid to be modified under the feed depends on its composition (eventual competition of several redox couples) and on its structural properties that do or do not allow relaxation phenomena relative to the structural modifications due to the catalytic reaction. In this sense, the reaction is structure sensitive.

This raises two questions. How are the solids structurally modified to relax the molybdenum oxidation state variations? What kind of factor determines the ability of such a compound to attain this state? If XRD data indicate that the structures are preserved after reaction, EXAFS experiments performed on the $AgMo_3P_2O_{14}$ and $CdMoPO_6$ compounds indicate that the structure is slightly modified.

In the case of $AgMo_3P_2O_{14}$, EXAFS results previously reported had shown that the molybdenyl shell is modified as expected from the observed reduction (decreases in molybdenyl bond number and length). Indeed, general properties of Mo^{VI} and Mo^V coordination spheres (12) indicate that Mo(VI) species, in either octahedral or bipyramidal coordination, exhibit two short bond, whereas Mo(V) species, always in octahedral coordination, exhibit only one very short $Mo=O$ bond. Moreover, the length of molybdenyl bonds is slightly longer in the case of Mo^{VI} species than Mo^V species. Nevertheless, to explain the increase in molybdenum coordination despite reduction, the substitution of few O^{2-} by hydroxyl groups can be proposed. Indeed, taking into account the decreasing number of $Mo=O$, the opening of such an oxo group into a $Mo–OH$ group during reaction can be proposed. Actually, this phenomenon would formally correspond to the transformation of Lewis acid sites into Brønsted acid sites. Such a phenomenon was previously observed in the VPO/TiO_2 system for the same reaction (17). In the present case the modification of the molybdenum oxidation state appears finely related to a modification of the acid–base properties of the surface. Actually, the bifunctional character of such an oxidation reaction is not simply related to successive elementary steps involving either acidobasic character or redox character: the mechanism, even not well known, probably involves concerted steps. Moreover, the oxygen insertion ability is relative to the nucleophilic character and, thus, to the basicity of the surface. There is obviously a close relation between acid–base properties and redox properties in this system. Moriceau *et al.* have recently reported that the selectivity in mild oxygenated products is correlated to the optical basicity of the solid (18). According to them, $AgMo_3P_2O_{14}$ and $CdMoPO_6$ equilibrated catalysts exhibit very similar optical basicity properties with respective values of 0.75 and 0.74. The sim-

ilar performance of both equilibrated catalysts must thus be linked both to their same final molybdenum oxidation state and to their common basic properties.

As far as $CdMoPO_6$ is concerned, two levels of structural modification have to be considered. First, the contribution of the molybdenyl ions is increased whereas the sixfold coordination is kept. This evolution, opposite that of $AgMo_3P_2O_{14}$, is in agreement with the transformation of a few Mo^V species into Mo^{VI} centers. Second, the second coordination sphere is also modified. This modification is attributed to an increase in the contribution of the second molybdenum shell and, thus, to a clustering of the Mo_2O_{10} units. To interpret such a clustering, and although the polycrystalline X-ray diffraction pattern does not indicate any modification (this is not sensitive to slight structural modification), one might think about creation of defaults such as crystallographic shear and glide planes accompanied by the departure of a few phosphate groups. Unfortunately, it was not possible to check the first part of this hypothesis, as the sample was not stable under the electronic microscopic beam. Nevertheless, even if X-ray diffraction did not indicate the formation of any crystalline phase in sufficient quantities to diffract, fine observation of the sample with a binocular indicates the apparition of very few white granules that could correspond to CdP_2O_7. It was checked that the latter compound is completely inactive for this reaction. One can imagine the existence of a few Mo^{VI} species inside a $CdMoPO_6$ sample containing crystalline defaults. This interpretation must be related to the results reported for pure $(VO)_2P_2O_7$ sample, which is used as a catalyst for *N*-butane mild oxidation; even if this phase is supposed to exclusively exhibit V^{IV} species, it was shown that, under peculiar conditions the active phase remains single-phase and involves few V^V species which are compensated by crystalline defaults (19, 20). Such a result is consistent with our interpretation for the $CdMoPO_6$ system and contradicts the previous current assumption that the formation of multiphase systems is the lone way to explain that the metal transition atoms coexist in both oxidized and reduced forms in the active phase (14, 21). Our results show that the active phase can correspond to a single- phase system involving mixed valency. This mixed valency is either intrinsic to the structure, as in case of $AgMo_3P_2O_{14}$, or compensated by creation of defaults.

CONCLUSION

Characterizations performed on silver and cadmium molybdenum phosphates lead to the conclusion that their similar catalytic performance toward propane mild oxidation reaction must be linked to their peculiar ability to reach a convenient balance between Mo^V and Mo^{VI} species and to relax the corresponding electronic effects occurring during reaction. There is a close fitting of the ratio between Mo^V and Mo^{VI} species under the reactive flow which is

independent of the initial molybdenum oxidation state value, but has to be compensated by minor local modifications of the molybdenum atoms' surrounding and/or creation of defaults. One of the key factors for such a reaction concerns the presence of an efficient mechanism of isolation of the active sites to avoid the overoxidation phenomenon: a convenient surface structure allowing the control of the architecture of the active surface and/or the reconstruction of the surface during the reaction. Actually, the phosphate groups limiting the size of the active site allow this convenient regulation. The electronic and geometric adaptations are indeed facilitated by the organization of the atoms in clusters involving two or three centers. In the case of clusters of larger nuclearity the selectivity drastically decreases, and in the case of isolated molybdenum atoms (surrounded by only phosphate groups), electronic exchanges or circulation inside the framework are stopped, resulting in inhibition of the reactivity. The nature of the countercation can also influence the electronic exchange. Cations involving fixed valency can simply modify the electronic density around molybdenum atoms and thus influence the selectivity. Other cations, namely, transition metal atoms such as iron, involving by itself redox properties, can directly interfere or even inhibit the establishment of molybdenum mixed valency and, consequently, the catalytic reaction because of its preferential and easier redox transformation.

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