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Catalysis Today 61 (2000) 149–155

CATALYSIS TODAY

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Study of H_2S selective oxidation on new model catalysts Influence of composition

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Abstract

Phosphate of transition elements $A_3M_4(PO_4)_6$ (A=Fe, Ni, Zn, Mg, Cu, Cr and M=Fe, V, Cr) are prepared by solid methods, at 1223 K. Their activity in H_2S selective oxidation are compared. In spite of their low specific area, the catalysts develop a good activity (up to 17% of H_2S conversion for surface area lower than $1\,m^2\,g^{-1}$) and an excellent sulphur selectivity (always higher than 95%). Screening experiments show that the best systems always contain Fe as element and, in these cases, Mössbauer characterisations evidence the establishment of Fe^{2+}/Fe^{3+} mixed valency during the reaction. As shown by XANES and XRD results, the ability of the element in the divalent A site to promote the redox mechanism between M^{2+}/M^{3+} and H_2S/S^0 and to prevent sulphidation determines the catalytic activity. © 2000 Published by Elsevier Science B.V.

Keywords: Phosphate; H_2S selective oxidation; Iron mixed valency

1. Introduction

The international restrictions concerning the release of gas containing sulphur into the atmosphere are becoming more and more drastic (200 ppm foreseen in 2000 vs. 1000 ppm presently). For many years, most of hydrogen sulphide (from natural gases or oilfield) is transformed into harmless sulphur using the Claus process [1,2]:

$$H_2S + \tfrac{3}{2}O_2 \underset{(1473\,K)}{\rightarrow} SO_2 + H_2O$$

At the end of this thermal step, the H_2S/SO_2 ratio must be 2/1, in order to optimise the following step:

$$2H_2S + 1SO_2 \rightleftharpoons 3/n\,S_n + 2H_2O$$

(catalytic reaction called “Claus reaction”).

The latter reaction being in equilibrium, the yield of the Claus process is limited to about 97%. The complete transformation of H_2S can be achieved using several processes [3,4]. A possible solution is the Superclaus process, consisting in catalytic selective oxidation of H_2S into sulphur and water, at $T \geq 230°C$, according to: $H_2S+1/2\ O_2 \rightarrow 1/n\ S_n+H_2O$.

Many catalysts have been studied for this reaction, especially iron-containing catalysts. Actually, iron oxide is highly efficient for H_2S oxidation, but scarcely selective. Recently, Li and Shyu [5] showed that mixed antimony/iron oxides exhibit better catalytic performances and sulphur selectivity than single oxide catalysts. Mixed iron/chromium oxides, deposited on α-Al_2O_3, have also been studied [6,7]. The presence of chromium prevents catalyst deactivation. Because

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PII: S0920-5861(00)00363-1

of the toxicity of chromium, a second generation of catalysts has been developed, based on Fe_2O_3/SiO_2 [8]. In this case, the active phase is claimed to be $Fe^{II}SO_4$, i.e. based on Fe^{II} whereas the fresh catalyst contains Fe^{III}. On the other hand, although the H_2S selective oxidation mechanism remains debatable, some authors evidenced a redox mechanism [5,9], according to Mars and van Krevelen kinetics, as in the case of light hydrocarbons mild oxidation reactions.

All these features have prompted us to study binary and even ternary model oxides and investigate this phenomenon. Because of the apparent analogy with the features observed in the selective oxidation of hydrocarbons, model catalysts based on transition element phosphates are chosen in order to get a better understanding of the reaction. Among the phosphate families, $A_3M_4(PO_4)_6$ has been chosen because of the flexibility of its crystalline framework, which implies that cationic substitutions can be performed on either A or M sites. In this structure, the element in A site is divalent and gets an octahedral or bipyramidal coordination. The element in M site, trivalent, is localised in sharing sides octahedra, as shown on Fig. 1. In a recent paper [10], we reported the results obtained with $Ni_3Fe_4(PO_4)_6$ prepared from aqueous solution and calcined at different temperatures. The aim of the work, among others, was to evidence the structure-sensitive character of H_2S selective oxidation reaction in terms of catalyst crystallinity.

In the present study, activity results of several isostructural compounds are compared. Our purpose is to better understand the apparent positive effect on activity and selectivity of the iron associated element in A site. Catalysts are prepared according to a solid method, at high temperature. This preparation method, which confers to them a very well crystallised framework but a low specific area ($\leq 1\,m^2\,g^{-1}$), allows getting model-catalysts. The elements in A and M sites are various: A=Fe, Ni, Mg, Zn, Cu, Cr and M=Fe, V, Cr. The catalytic performances of the prepared catalysts in H_2S selective oxidation are compared. Mössbauer, DRX and XANES characterisations before and after reaction, completed by the results previously obtained with $Ni_3Fe_4(PO_4)_6$ prepared from aqueous solution, allow us to understand the role of the associated A element.

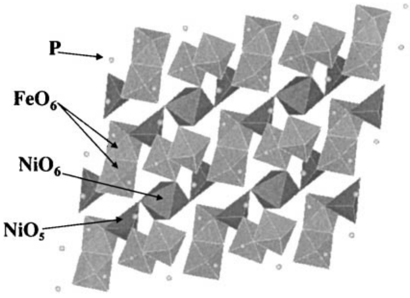

Fig. 1. Projection of $A_3M_4(PO_4)_6$ along (1 0 0).

2. Experimental

2.1. Materials

The powders of precursors (oxides and $(NH_4)_2HPO_4$) are mixed in an agate mortar in the appropriate ratio. The mixture is then heated at 673 K in air to eliminate NH_3 and H_2O. In case of different elements in A and M sites (for example $Cu_3Fe_4(PO_4)_6$), samples are then calcined at 1223 K in air. When A and M are the same element (for example in case of $Fe_3Fe_4(PO_4)_6$), the preparation implies the synthesis of the divalent compound. Thus, after adding appropriate amount of M^0, samples are heated under vacuum, at 1223 K according to the literature [11,12]. The preparation of $Ni_3Fe_4(PO_4)_6$ by liquid method has been previously detailed [10]. Fe_2O_3 oxide ($22\,m^2\,g^{-1}$) and Fe/Cr=0.5 ($78\,m^2\,g^{-1}$) mixed oxide were provided by Rhône-Poulenc and prepared from citrates.

2.2. Characterisations

Catalysts were characterised before and after reaction by X-ray diffraction, Mössbauer spectroscopy and XANES. X-ray diffraction patterns of the samples were registered using Cu–Kα radiation. The powder Mössbauer spectra were registered on a constant acceleration spectrometer, with a ^{57}Co source in Rh matrix. The isomer shift (IS) values were given with respect to that of α-iron at room temperature. The X-ray absorption spectra at Fe, Cu, Cr, Ni K-edges were recorded at room temperature in a classical transmission mode at the EXAFS I station (channel cut monochromator) using the synchrotron radiation of the DCI storage ring of LURE (ORSAY, FRANCE) working at 1.85 GeV with a 250 mA current.

2.3. Catalytic tests

Catalytic tests were carried out, under atmospheric pressure at 503 K, in a fixed bed flow quartz microreactor containing 50 mg of granules (∅=0.4–1 mm). The reactants were H_2S (1.2%) and O_2 (0.8%) diluted in N_2 (97.8%) and the W/F about 0.4 g h mol^{-1}. After trapping of water and condensed sulphur, the inlet and outlet gases were analysed using a Varian 3400 CPG, with a Porapak column and an FPD detector. Hydrogen sulphide conversion (conv.) and sulphur selectivity (sel.) are defined as:

Conv.=(moles of H_2S reacted/moles of H_2S fed)×100.

Sel.=[(moles of H_2S reacted−moles of SO_2 produced)/(moles of H_2S fed)]×100.

3. Results and discussion

3.1. Catalytic performance

Table 1 shows the screening results. In some cases, a slight deactivation occurred during the first 2 h of experiment, but after the steady state was reached, no deactivation occurred during 20 h, which is a real improvement, compared to unsupported iron simple oxide [6] tested in the same conditions. In spite of their low specific area ($<1\,m^2\,g^{-1}$), all the catalysts exhibit a real activity, but conversion differs with regard to composition. Selectivities are excellent in any case, always above 97%. Iron-containing samples are always active, except when the A site is occupied by copper ($Cu_3Fe_4(PO_4)_6$). Catalysts without iron are less active, except in case of $Cr_7(PO_4)_6$ (16% of H_2S conversion). This result is however lower than that obtained with the corresponding sample containing iron mixed valency, $Fe_7(PO_4)_6$: 26%.

Compared to systems previously studied, phosphate matrix seems to improve the intrinsic activity of iron systems (Fe_2O_3 ($22\,m^2\,g^{-1}$) compared to $Fe_7(PO_4)_6$ or even $Cr_3Fe_4(PO_4)_6$ compared to Cr/Fe mixed oxide ($78\,m^2\,g^{-1}$) [6]). Indeed, $Cr_3Fe_4(PO_4)_6$ is intrinsically very active and, which is an important point, does not deactivate: 15% of H_2S conversion for approximately $1\,m^2\,g^{-1}$, vs. 25% for $78\,m^2\,g^{-1}$ in case of Fe/Cr oxide (Fe/Cr=0.5). These good catalytic results, obtained on model phosphate catalysts, are not so surprising if one refers to numerous works concerning the catalytic activity of phosphate compounds in oxidation reactions of light hydrocarbons [13,14]. Although the reactive molecule is different, one must note that many authors suggest that H_2S selective oxidation is governed by a Mars and Van Krevelen mechanism, as many hydrocarbons oxidation reactions. Structure-sensitive effects are also thus expected in that reaction.

We have recently shown that catalytic performance of $Ni_3Fe_4(PO_4)_6$ is improved by using aqueous precursors during the preparation step [10]: with a low calcination temperature (450°C), one can reach $78\,m^2\,g^{-1}$ of specific area and 80% of H_2S conversion, keeping a sulphur selectivity above 90%. Nevertheless, we evidenced that the specific activity, about 1% conv. g m^{-2}, (with respect to the specific area of the sample) of samples prepared by solution method remains constant, when samples are completely amorphous ($T<823$ K). It progressively increases up to 4% conv. g m^{-2} for samples calcined at higher temperatures, with respect to the increase in their crystallinity. However, it remains lower than the value obtained in case of the sample prepared at 1223 K by solid method, and consequently very well crystallised: 17% conv. g m^{-2}. The results showed that H_2S selective oxidation is structure-sensitive in terms of sample crystallinity. The results presented here show another aspect of H_2S selective oxidation

Table 1
Catalytic results of model phosphate catalyst in H_2S selective oxidation

Catalyst	Zn_3V_4 $(PO_4)_6$	Fe_3V_4 $(PO_4)_6$	Mg_3Fe_4 $(PO_4)_6$	Zn_3Fe_4 $(PO_4)_6$	Cu_3Fe_4 $(PO_4)_6$	Fe_2O_3	Ni_3Fe_4 $(PO_4)_6$	Fe_7 $(PO_4)_6$	Cr_3Fe_4 $(PO_4)_6$	Cr_7 $(PO_4)_6$	Zn_3Cr_4 $(PO_4)_6$	Fe/Cr=0.5
Conv. (%)	6	14	16	12	3	40	17	26	15	16	2	25
S_n sel. (%)	97	98	100	100	100	20	97	97	100	100	100	100

on phosphate catalysts: their structure-sensitivity in terms of composition. Actually, the disparity of the results shows the sensitiveness of the reaction to the nature and to the oxidation state of the associated A–M elements. As shown in Table 1, all iron-containing catalysts develop a good catalytic activity, except $Cu_3Fe_4(PO_4)_6$. This latter result can be amazing considering the industrial use of copper and iron-based catalysts in H_2S oxidation or Claus processes [15,16]. It can be noted that the best catalyst contains initially the mixed iron valency. The good result of $Cr_7(PO_4)_6$ may be also related to the presence of Cr^{2+}/Cr^{3+} in the starting catalyst. The two vanadium-containing samples ($Fe_3V_4(PO_4)_6$ and $Zn_3V_4(PO_4)_6$) develop different activities (respectively 14 and 6% of H_2S conversion). The positive effect of iron might be evoked, but intrinsically vanadium is more active than chromium. For the same cation in A site, i.e. Zn, the activities of the transition elements are:

$Cr<V<Fe$, with respectively 2, 6 and 12% of H_2S conversion.

3.2. Characterisations

3.2.1. XRD

XRD spectra of the samples have been indexed following the references of isostructural phosphate ASTM files available in literature [11,12,17]. On fresh catalysts, the XRD pattern corresponds to the $[M_4(PO_4)_6]_\alpha$ family; no traces of remaining precursors oxides (Fe_2O_3, CuO, MgO) were detected. It should be pointed out that, because of the low symmetry of the $[M_4(PO_4)_6]_\alpha$ structure (triclinic), the XRD powder diffraction patterns do not allow to differentiate either solid solution such as $(A_{3-x}M_x)^{II}(M_{4-x}A_x)^{III}(PO_4)_6$, or mixed phases such as $A_3Fe_4(PO_4)_6$ and $Fe_7(PO_4)_6$. XANES and Mössbauer characterisations will refine the results. No modification of the diffraction lines was observed after reaction, except in the case of $Cu_3Fe_4(PO_4)_6$. This point is detailed further.

3.2.2. Mössbauer

Samples containing iron in the trivalent M site (except $Zn_3Fe_4(PO_4)_6$) were characterised, at room temperature, before and after catalytic test. The spectra were fitted using the MOSFIT program [18] and the percentages of Fe^{2+} and Fe^{3+} were calculated and are reported in Table 2.

Table 2
Mössbauer data of model phosphate catalysts before and after reaction

Catalyst	Before reaction				After reaction			
	IS[a]	QS[b]	Iron charge	%	IS	QS	Iron charge	%
$Fe_7(PO_4)_6$	0.28	0.65	3+	61	0.28	0.65	3+	61
	0.99	1.68	2+	29	0.99	1.68	2+	29
	1.04	1.98	2+	10	1.04	1.98	2+	10
$Ni_3Fe_4(PO_4)_6$	0.43	0.57	3+	40	0.38	0.50	3+	38
	0.43	0.94	3+	48	0.40	0.90	3+	42
	1.14	2.71	2+	12	1.22	2.53	2+	20
$Mg_3Fe_4(PO_4)_6$	0.27	0.64	3+	55	0.27	0.64	3+	62
	0.46	0.78	3+	39	0.45	0.77	3+	27
	1.29	2.28	2+	6	1.32	2.18	2+	11
$Cr_3Fe_4(PO_4)_6$	0.34	0.89	3+	43	0.34	0.89	3+	44
	1.21	2.29	2+	46	1.21	2.29	2+	45
	1.27	2.79	2+	11	1.29	2.79	2+	11
$Cu_3Fe_4(PO_4)_6$	0.42	1.08	3+	43	0.29	0.84	3+	19
	0.42	0.82	3+	47	0.44	0.78	3+	38
	1.25	2.66	2+	10	1.31	2.38	2+	43

[a] Isomer shift ($mm\,s^{-1}$).

[b] Quadrupolar splitting ($mm\,s^{-1}$).

Mössbauer spectra of $Cu_3Fe_4(PO_4)_6$ before and after reaction are reported in Fig. 2. It can be clearly seen that the intensity of the doublet at V (velocity)$=2.25\,mm\,s^{-1}$, corresponding to divalent iron, is greatly increased after reaction, at the expenses of Fe^{3+} doublets intensity.

3.2.3. XANES

The XANES spectra at Cu K-edge are presented in Fig. 3. For chromium compounds, the energy values at Cr K-edge have been extracted from XANES spectra and are presented in Table 3. XANES characterisations at vanadium K-edge are in progress and are not reported here.

3.2.4. Discussion

3.2.4.1. Samples before reaction. Firstly, Mössbauer results evidence the presence of Fe^{2+} before reaction, in samples containing theoretically only Fe^{3+}. This phenomenon is confirmed by XANES characterisations at Fe K-edge. El Kira et al. [11]

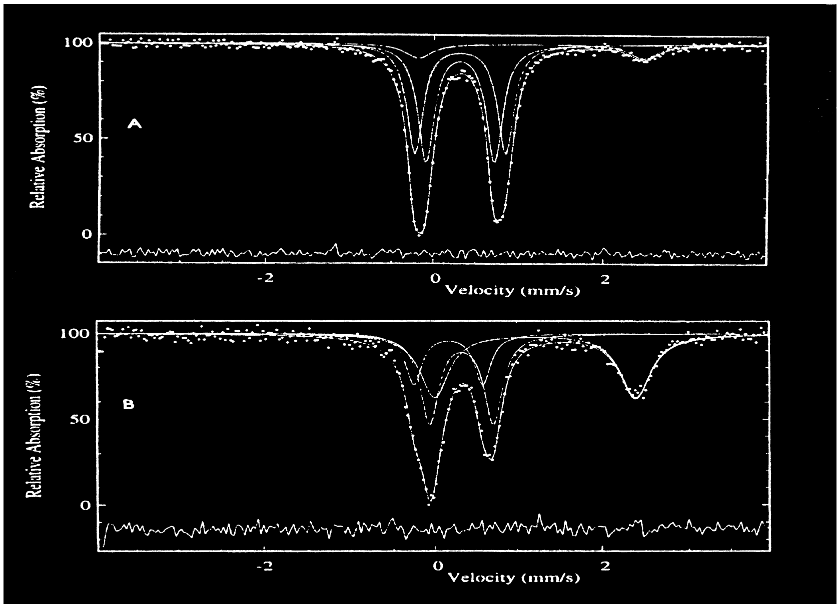

Fig. 2. Mössbauer spectra of $Cu_3Fe_4(PO_4)_6$ before and after catalytic test.

have already observed it on $Ni_3Fe_4(PO_4)_6$. The authors underlined the difficulty of preparing a single phased sample and evidenced the presence of a small quantity of $Ni_{2-x}Fe_xP_2O_7$, at the origin of Fe^{2+} Mössbauer signal. In our case, XRD spectra do not show any diffraction lines corresponding to this compound, indicating that, if it is present, its amount is lower than 5% (weight). Another explanation could be related to the competition between iron and the other elements (Mg, Cu or Ni) to get the more usual octahedral coordination. This would result in the formation of the solid solution $A_{3-x}{}^{II}Fe_x{}^{II}Fe_{4-x}{}^{III}(PO_4)_6$, completed by εP_2O_5 and εAO oxide, whose small amounts are undetectable by XRD. In this case, the five-coordination of Fe^{2+} atoms is not observable by simple Mössbauer characterisations. Nevertheless, the five-coordination of iron in iron phosphate compounds is not scarce [14].

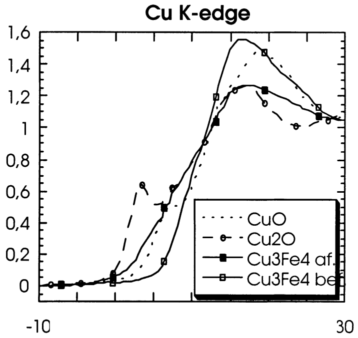

Fig. 3. XANES spectra at Cu K-edge of $Cu_3Fe_4(PO_4)_6$ before and after reaction, comparison with CuO and Cu_2O references.

The case of the sample containing Cr and Fe is more delicate: actually, the affinity of chromium to get a trivalent charge enables the formation of a solid solution $(Cr_{3-x}Fe_x)^{II}(Fe_{4-x}Cr_x)^{III}(PO_4)_6$, explaining the presence of iron mixed valency in the fresh catalyst. XANES data show that the edge of $Cr_3Fe_4(PO_4)_6$ value is about 10.70 eV, close to the Cr_2O_3 value (10.97 eV) and much higher than that of $Cr_7(PO_4)_6$ which presents mixed chromium valency (E=9.16 eV). Thus, the $Cr_3Fe_4(PO_4)_6$ sample mainly contains Cr^{3+} and very few Cr^{2+}. This result is in agreement with the Mössbauer characterisation, which evidences the presence of large amount of Fe^{2+} in the sample. One must conclude that the preparation has led to the formation of at least a major phase $Fe_3Cr_4(PO_4)_6$ and a minor one $Fe_7(PO_4)_6$.

In any case, and taking into account that small amounts of some phases could be present in our samples, we have verified that the catalytic activity

Table 3
Edge energy values at Cr K-edge for Cr containing samples. Comparison with Cr metal and Cr_2O_3 references[a]

Sample (eV)	Cr metal	Cr_2O_3	Zn_3Cr_4		Cr_3Fe_4		$Cr_7(PO_4)_6$	
			Before	After	Before	After	Before	After
Edge energy	4.68	10.97	10.69	10.47	10.70	10.15	9.16	9.05
Error	0.21	0.30	0.13	0.19	0.17	0.15	0.13	0.13

[a] To clarify the legends, some phosphate samples are designated by A_3M_4 instead of $A_3M_4(PO_4)_6$.

cannot be due to Fe_2O_3 (not sulphur selective), neither to $FePO_4$ nor $AFeP_2O_7$ samples (not active in H_2S selective oxidation).

3.2.4.2. Samples after reaction. In the cases of $Fe_7(PO_4)_6$ and $Cr_7(PO_4)_6$, no modification of the relative amount M^{2+}/M^{3+} is observed after reaction (Tables 2 and 3, respectively). In $Ni_3Fe_4(PO_4)_6$, $Mg_3Fe_4(PO_4)_6$ and $Cu_3Fe_4(PO_4)_6$ samples, the amount of Fe^{2+} increased after reaction (Table 2): a reduction of the iron oxidation state occurred during the catalytic reaction. This phenomenon is confirmed by XANES spectra at Fe K-edge (not reported here). Since Mössbauer spectra were recorded under air, one cannot exclude a partial re-oxidation of the iron. Actually, the exact Fe^{2+}/Fe^{3+} ratio in the equilibrated catalyst should be estimated by in-situ characterisations, technically difficult to realise because of the formation of liquid sulphur during the reaction. One must remember that the establishment of the iron mixed valency, in $Ni_3Fe_4(PO_4)_6$ prepared by liquid method, has also been evidenced in our previous study [10]: in the case of $Ni_3Fe_4(PO_4)_6$ calcined at 773 K, the amount of Fe^{2+} rises from 0% before reaction up to 30% after reaction.

It should be underlined that iron valency remains unchanged in the $Cr_3Fe_4(PO_4)_6$ sample after reaction, in contrast to compounds referred above. Taking into account that this sample was shown to be probably multiphased and even to exhibit pre-existing iron mixed valency in large amounts, this result can be compared to the unchanged mixed valency in $Fe_7(PO_4)_6$ and $Cr_7(PO_4)_6$ compounds after reaction. Finally, it seems that no modification of mixed valency occurs when it pre-exists in the fresh material.

Cr K-edge energy value of $Cr_3Fe_4(PO_4)_6$ sample shows a slight decrease of the energy value after reaction (E=10.15 vs. 10.70 eV). This variation is higher than the change of the edge energy observed for $Zn_3Cr_4(PO_4)_6$ (E=10.47 vs. 10.69 eV), which is not active in H_2S selective oxidation.

In case of $Ni_3Fe_4(PO_4)_6$, no modification of the oxidation state of Ni is observed by XANES characterisations, although the partial reduction of Fe^{3+}–Fe^{2+} could have been relaxed by partial oxidation of Ni^{2+}–Ni^{3+}. Moreover, in case of $Mg_3Fe_4(PO_4)_6$ and $Zn_3Fe_4(PO_4)_6$, the fixed valency of Mg and Zn elements (+2) can certainly not compensate the partial reduction of iron. Thus, one must admit that the iron mixed valency is not relaxed by the element located in A site. It can be supposed that the nature of the A element influences the redox potential of Fe^{3+}/Fe^{2+} couple toward the other redox couple participating in the reaction: H_2S^{-II}/S^0. The feature of such a couple redox mechanism has been recently developed by Davidov et al. [19] on α-Fe_2O_3. A question arises however: how can the crystalline structure remain unchanged in spite of such iron partial reduction? One could propose (i) a partial dismutation of the system leading to $Fe_7(PO_4)_6$+$A_3M_4(PO_4)_6$+AO, not detected by XRD or (ii) a modification of only the catalyst surface. XPS study should be performed to clarify this point.

XANES characterisation at Cu K-edge of $Cu_3Fe_4(PO_4)_6$ (see Fig. 3) shows a strong reduction of Cu^{2+} to Cu^+ after reaction. A linear combination of $Cu^{II}O$ and $Cu_2{}^{I}O$, compared to the spectra of $Cu_3Fe_4(PO_4)_6$, reveals the presence of 18% of Cu^+. Thus, the simultaneous reduction of Cu^{2+} to Cu^+ and of Fe^{3+} to Fe^{2+} is inconsistent with the existence of $A_3M_4(PO_4)_6$ crystalline framework. In fact, XRD characterisation evidences the disappearance of the main lines of the structure and the raising of new lines relative to CuS or α-Cu_2S. The great sensitiveness of copper and iron toward H_2S molecule [20–22] explains the competition of both couples to interact in the redox mechanism. The simultaneous reduction of Cu^{2+} and Fe^{3+}

prevents the formation of the active site and breaks the structure. Formation of copper sulphide leads, at this temperature, to deactivation, as already observed on simple oxides [6].

A previous work dealing with the mild oxidation of propane on molybdenum phosphate evidenced the establishment of mixed molybdenum valency in case of $AgMo_3(PO_7)_2$ [23], promoted by the presence, in the structure, of sharing-side octahedra. In our case, the electronic exchanges, inducing the coupled redox mechanism, are facilitated by the crystalline framework containing also sharing-side iron octahedra (see Fig. 1). Actually, we have shown [24] that iron phosphate containing isolated iron octahedra, such as $KFeP_2O_7$ or $Cd_{2.5}Fe(P_2O_7)_2$, are much less active in H_2S selective oxidation than $A_3M_4(PO_4)_6$. These electronic exchanges are promoted when the mixed valency is much present in fresh catalyst as in the cases of $Fe_7(PO_4)_6$, $Cr_7(PO_4)_6$ and the $Cr_3Fe_4(PO_4)_6$ sample, the redox couples involved being Fe^{2+}/Fe^{3+} or Cr^{2+}/Cr^{3+} and H_2S/S^0. When the divalent A site is occupied by copper, the competition between Cu^+/Cu^{2+} and Fe^{2+}/Fe^{3+} leads to the simultaneous partial reduction of Cu^{2+} and Fe^{3+} under the reactive flow. This destroys the framework and leads to the formation of CuS and Cu_2S, which contribute to catalyst deactivation. Finally, Ni^{2+}, Mg^{2+} or Zn^{2+} cations must influence the Fe^{2+}/Fe^{3+} redox potential to induce the selective oxidation of H_2S. Moreover, in this phosphate configuration, their lower affinity to form sulphides prevents the framework destruction.

Acknowledgements

E. Laperdrix thanks ADEME for financial support.

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