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Hydrodesulfurization Catalysts: Electrophoretic Study of Mo(or W)–Co, Mo(or W)–Ni, and Mo(or W)–Ca Sulfided Phases

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When $CoMoO_4$, $NiMoO_4$, $CaMoO_4$, $CaWO_4$, $NiWO_4$, and $CaWO_4$ are treated at 400°C for 3.5 h in a 10% H_2S/H_2 flow, which are experimental conditions commonly used for the sulfidation of hydrodesulfurization catalysts, the products obtained are the sulfides MoS_2, WS_2, Co_9S_8, NiS, and CaS, respectively. The increase of the sulfidation temperature of unsupported Co–Mo samples prepared by the homogeneous sulfide precipitation procedure, leads to a displacement of the cobalt located at the surface of the Co–Mo–S phase.

INTRODUCTION

An interface between a solution and a suspended particle leads to a perturbation of the molecular environment of the solution in the interfacial region, resulting in a separation of charge. This perturbation then leads to an electrified solid–liquid interface which can be characterized by its surface charge.

According to the double layer theories the surface charge is neutralized by ions located in a fixed layer, called the Helmholtz double layer, and by ions located in a diffuse layer called the Gouy double layer. Although the diffuse layer is bound to the surface, the main part of it is within the solvent; therefore, it can be moved from the surface as a result of an external force. The frontier between both layers is called the plane of shear, and its potential is the zeta potential (ZP). Although the zeta potential is actually lower than the potential of the Helmholtz plane it can be considered a good approximation of it. The value of ZP can be determined through electrokinetic experiments by measurements of electrophoretic mobility, which can be used to calculate the ZP values using the Helmholtz–Smoluchowski equation.

The surface charge, surface potential, and consequently the ZP is a function of the potential determining ion (PDI) concentration. As the PDI of an oxide particle are H^+ and OH^- the ZP values depend on suspension pH. Ions, other than H^+ and OH^-, may be adsorbed and particle surface then also develop surface charge. From electrokinetic experiments the development of the surface charge, because of adsorption of H^+ and OH^- and other charged species which are not PDI, is observed. This is called the net surface charge. The pH value of a solution in which the net surface charge vanishes is called the isoelectric point (IEP) which, at constant ionic strength and in the absence of ions that may be specifically absorbed, depends on the particle surface composition.

From these basic ideas, the zeta potential and consequently the IEP, may be used to study the surface of heterogeneous catalysts, with the advantages, when compared to classical techniques, that the IEP and ZP are functions of the layer exposed to the liquid which is the most important layer during the heterogeneous reaction.

As was mentioned above the isoelectric point of a solid surface has a value that is characteristic of the surface; therefore,

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knowing the electrophoretic behavior of a solid we may, for example, distinguish between a sample that has a mixture of two solids, as occurs in a sulfured Co–Mo sample prepared by comaceration (CM) of other samples that have only one solid, as occurs with the Co–Mo samples prepared by high sulfide precipitation (HSP) (*1*).

The results of that study (*1*) were in agreement with those of Delmon *et al.* (*2*), which were also from electrophoretic measurements, since in both studies it was proved that the products obtained depend strongly on the preparation procedure.

On the other hand, the IEP of a mixture of two solids strongly banded, has an IEP that is between the IEP of both solids; therefore, we may know, for example, the coverage of a supported phase on a carrier. We worked using this property in the determination of coverages of phases like MoO_3, MoS_2 (*3*), $CoAl_2O_4$ $NiAl_2O_4$ (*4*), WO_3 (*5*), and V_2O_5 (*6*) on γ-Al_2O_3 and observed that the results obtained from electrophoretic measurement are in agreement with those obtained from other more classical techniques such as oxygen chemisorption (*7*) or CPS (*6*).

The aim of the present study was twofold. For the hydrodesulfurization (HDS) of crude oil fraction or coal-derived liquid, catalysts of supported molybdenum or tungsten are used. In the oxide state of the Co–Mo/γ-Al_2O_3 catalysts the existence of a monolayer of molybdenum, bulk MoO_3, Co_3O_4, and $CoAl_2O_4$ has been described in addition to other phases in smaller proportion as $CoMoO_4$ and $CaMoO_4$ was proved. This last phase is formed from impurities of Ca^{2+} that commonly exist in the alumina carrier.

In its active state the monolayer of molybdenum leads to MoS_2 (*8*) or to a sulfided monolayer (*9*) depending on the conditions of the sulfiding treatment. The bulk Co_3O_4 is transformed into Co_9S_8, while $CoAl_2O_4$ cannot be reduced. The $CoMoO_4$ seems to lead to Co_9S_8 and MoS_2 (*10*). The products of the sulfidation of $CoWO_4$, $NiMoO_4$, $NiWO_4$, $CaMoO_4$, and $CaWO_4$ are actually unknown. It could be that the sulfidation of these compounds would produce two phases as it seems to be for the $CoMoO_4$ (*10*) or, on the contrary, they would form only one phase similar to Co–Mo–S (*11*).

The formation of a Co–Mo sulfided active phase in which both metals are in a MoS_2-like structure, with the Co atoms occupying sites on its surface, has also been described (*11*). This structure, called "Co–Mo–S" phase, was deduced from Mössbauer emission spectroscopy (MES), although its existence was also recently revealed by electrophoretic migration measurement of unsupported sulfided Co–Mo catalysts (*1*). In this last study, the electrophoretic behavior of one sample of sulfided unsupported Co–Mo catalysts, prepared by the homogeneous sulfide precipitation (HSP) method (*11*), shows the presence of only one kind of particle, with an isoelectric point different from those corresponding to the pure Co_9S_8 and MoS_2 phases. Moreover, the IEP of this kind of particle was not located between the IEP of the pure phases. In that study (*1*) it was proposed that these particles would be Co–Mo–S phase.

It could be, however, that increasing the sulfidation temperature of the "Co–Mo–S" phase leads to the formation of two phases as in the samples prepared by the CM method (*12*). In fact, as was mentioned above, the sulfidation of $CoMoO_4$ seems to lead to MoS_2 and Co_9S_8 (*11*). Candia *et al.* (*13*) show, on the contrary, that in Co–Mo/γ-Al_2O_3 catalysts calcined between 400–700°C, the Co–Mo–S phase only changes its surface structure. They show (*13*), moreover, from NO adsorbing measurements, that the amount of cobalt located at the Co–Mo–S surface decreases with the increase of the temperature treatment, while the configuration of the Mo atoms is not significantly affected. Segregation of Co_9S_8 from Co–Mo–S phase by an increase of the sulfidation temperature of Co–Mo/γ-Al_2O_3 was also suggested (*14, 15*).

Consequently the aims of the present study were: (a) to know the products of the sulfidation of any compounds present in a low proportion in the HDS catalyst, when they are sulfided under the same experimental conditions as was used in the sulfidation of catalysts and (b) to know the evaluation of the Co–Mo–S phase with the increase of the sulfidation temperature. To reach both aims proposed, electrophoretic measurement was used; therefore, the information obtained takes into account only the surface of the formed phases.

EXPERIMENTAL

Zeta potential. Determinations of the zeta potential were made using an electrophoresis instrument (Zeta-Meter ZM-77), basically constituted by an AO microscope in a Riddick Type II UVA Cell, with Pt–Ir cathode and a cylindrical Mo anode. The samples were studied using 200 mg of 2-μm hydrated sample particles ultrasonically dispersed in 200 ml of 10^{-3} M KCl solution. The pH values were adjusted with either 10^{-3} M HCl or KOH solution. Both electrophoretic migration rate and zeta potential are related by the Helmholtz–Smoluchowski equation.

Sample preparation. The precursors were prepared by coprecipitation at pH = 10 of ammonium heptamolibdate (Merck P.A.) or ammonium tungstate (Hopkins Williams) and cobalt nitrate (Merck P.A.) or nickel nitrate (Merck P.A.) or calcium nitrate (Merck P.A.) and calcinated for 4.5 h at 550°C. The products obtained were identified by X-ray diffraction in $CoMoO_4$, $NiMoO_4$, $CaMoO_4$, $CoWO_4$, $NiWO_4$, or $CaWO_4$, respectively. The samples were then treated at 400°C for 3.5 h in a 10% H_2S/H_2 flow. Both the preparation and the sulfidation of the samples were made using the same procedure that is commonly used with supported catalysts.

Unsupported sulfided Co–Mo samples were prepared by the homogeneous sulfide precipitation method in which a mixture of cobalt nitrate and ammonium heptamolibdate, with a desired atomic Co/Mo ratio, is poured into a hot (60–70°C) solution of 20% ammonium sulfide under vigorous stirring. The solids obtained are then heated in a flow of 2% H_2S/H_2 at a rate of 1.5°C/min until the desired temperature is reached and kept at this temperature for 4 h.

TABLE 1

Isoelectric Point (IEP) of the Products of the Sulfidation of same Precursors Presents in Hydrodesulfurization Catalysts

Precursor	Number of phases	IEP	
$CoMoO_4$[a]	Two	3.0	2.4
$NiMoO_4$[a]	Two	3.0	2.8
$CaMoO_4$[a]	Two	2.9	2.4
$CoWO_4$[a]	Two	2.4	2.2
$NiWO_4$[a]	Two	2.3	2.8
$CaWO_4$[a]	Two	2.5	2.6
MoO_3	One	2.9	—
WO_3	One	2.4	—
CoO	One	—	2.0
NiO	One	—	2.8[b]
CaO	One	—	2.5 ± 0.3

[a] Identified by XR.
[b] From Ref. (*2*).

X-Ray diffraction patterns. They were obtained using a Philips–Norelco instrument with Cu$K\alpha$ radiation and Ni filter.

RESULTS AND DISCUSSION

In Table 1 the IEP of the products of the sulfidation of the precursors ($CoMoO_4$, $NiMoO_4$, $CaMoO_4$, $CoWO_4$, $NiWo_4$, and $CaWO_4$) as well as those of some other sulfides is given. It shows that the sulfidation of molybdates and tungstates studied lead to two phases. It shows, moreover, that the IEP of both kinds of particles agree with the IEP expected. For example, from the results obtained by Scheffer *et al.* (*10*) the sulfidation of the $CoMoO_4$ leads to MoS_2 and Co_9S_8; therefore, we may expect that both kinds of particles have respective IEP close to the MoS_2 and Co_9S_8. This hypothesis is in agreement with the values shown in Table 1 and Fig. 1a although actually the

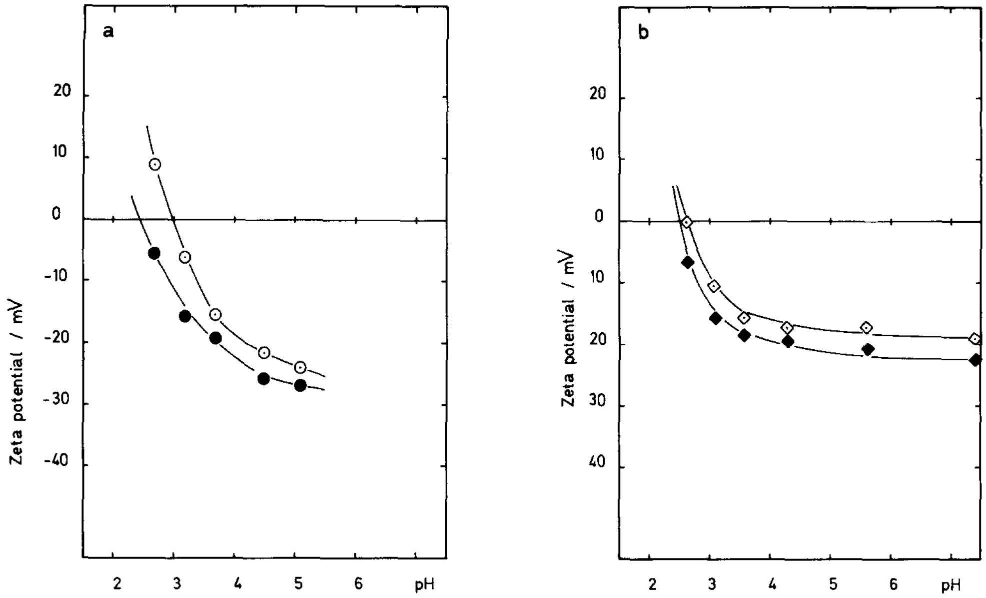

FIG. 1. Zeta potential at 22.5°C as a function of the suspension pH of (a) $CoMoO_4$ and (b) $CaWO_4$ sulfided at 400°C for 3.5 h 10% H_2S/H_2 flow.

IEP of the Co_9S_8 is slightly smaller than one of the sulfides formed from $CoMoO_4$. This difference may be due to a surface contamination of the Co_9S_8 with MoS_2, which has an IEP higher than the Co_9S_8; the phases formed from the other molybdates and tungstates, agree more satisfactorily as shown in Table 1.

The IEP of the sulfided CaO was not determined more precisely because there are some experimental difficulties for working at a pH lower than 2.5. On the other hand, both kinds of particles formed from $CaWO_4$ have IEP which are too close (see Table 1). This might be considered an impediment to using the electrophoretic method in order to find two kinds of particles. Figure 1b shows that, in spite of this difficulty, the zeta potentials of both phases at pH distant from the IEP, are quite different.

Finally, it is possible to conclude that the sulfidation of the molybdate or tungstates of cobalt, nickel, and calcium lead to the formation of two phases with surface characteristics to MoS_2 or WS_2 and Co_9S_8, NiS or CaS, respectively. The possibility of the presence of bulk oxide cannot be totally rejected because, as was mentioned above, the IEP is a surface property. In fact, the formation of bulk CaS is doubtful under the experimental conditions commonly used for the sulfidation.

The surface structure and consequently the electrophoretic behavior of an unsupported Co–Mo samples prepared by the HSP method (*11*) and sulfided at different temperatures has two possibilities: (a) at a fixed sulfidation temperature the Co–Mo–S phase is decomposed, forming Co_9S_8 and MoS_2. If this is correct then at sulfidation temperatures lower than of decomposition only one kind of particle, with an IEP close to the Co–Mo–S phase, must be found by electrophoretic measurements, while at higher sulfidation temperatures two kinds of particles, with IEP close to Co_9S_8 and MoS_2, must be found, (b) the surface configuration of the Co–Mo–S phase changes gradually with the sulfidation temperature from the Co–Mo–S phase to one close to MoS_2 structure. If this is correct then we must find, by electrophoretic measurements, a dependence of the IEP with the sulfidation temperature, from the IEP of the

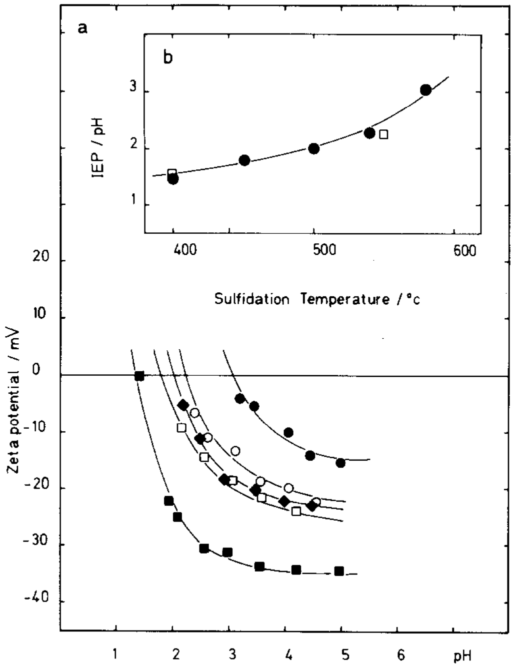

FIG. 2. (a) Zeta potential at 22.5°C as a function of the suspension pH of a Co–Mo unsupported samples sulfided at (■) 400°C, (□) 450°C, (◆) 500°C, (○) 540°C, and (●) 580°C. (b) Dependence of the isoelectric point (IEP) with the sulfidation temperature of a sample with an atomic ratio (●) Co/Mo = 0.15 and (□) Co/Mo = 0.50.

Co–Mo–S phase sulfided at low temperature (~1.5 for Co–Mo–S prepared at 400°C) to a IEP close to that of the MoS_2.

Actually, the IEP of the MoS_2 is 2.1 which is too close to the IEP of the Co–Mo–S prepared at 400°C; therefore, we may not find a sufficiently clear shift. Fortunately, the IEP is a property that changes radically due to traces of impurities; therefore if we were to know of experimental conditions in which the MoS_2 could have a IEP higher than 2.1, then we would find a clearer shift. Previously (*1*) we inform that the IEP of the MoS_2 is ~3.0 because, as was shown by Delmon (*2*), the experimental conditions used by us in the preparation of those samples were not sufficient to remove the adsorbed pure rhombic sulfur, which has an IEP of 3.1–2.7. The S^0 can be removed from the surface of MoS_2 by subsequent treatment under vacuum at 673 K (*2*). Thus, if we use the same experimental conditions of the previous study (without vacuum at 673 K) we should find a clearer shift.

In Fig. 2 the electrophoretic behaviour of an unsupported Co–Mo sample with an atomic ratio Co/Mo = 0.15 prepared by the HSP method (*11*), sulfided at 400, 450, 500, 540, or 580°C is summarized. In Fig. 2b some results obtained with a sample with an atomic ratio Co/Mo = 0.50 are also included.

In all the samples studied in the present research only one kind of particle was detected. Indeed, in the samples with low cobalt content (atomic ratio Co/Mo = 0.15) the Co_9S_8 formed from the Co–Mo–S phase might not be found; however, in the sample with high cobalt content (atomic ratio Co/Mo = 0.50) it would be. Thus, the first possibility described above must be rejected. Figure 2 shows that the IEP of the samples shift from ~1.5 to ~3.0 due to increases of the sulfidation temperature. This agrees with the second possibility.

Thus, we propose that the increase of the sulfidation temperature leads from a Co–Mo–S phase with a surface rich in cobalt to a Co–Mo–S phase with a surface poor in cobalt, close to a MoS_2 surface. This leads, therefore, to an increase of the cobalt content into the Co–Mo–S phase but without an important segregation of Co_9S_8.

It is possible to conclude therefore, that there is an agreement between the behaviour described from diffuse reflectance, magnetic susceptibility and MES measurements, of sulfided supported Co–Mo samples calcined at different temperatures (*13*) and that described in the present study from electrophoretic measurements for sulfided unsupported Co–Mo samples, sulfided at different temperatures.

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