Use of Zero Point Charge Measurements in Determining the Apparent Surface Coverage of Molybdena in MoO_3/γ-Al_2O_3 Catalysts

Francisco J. Gil-Llambías and A. M. Escudey-Castro

Departamento de Química, Facultad de Ciencia, Universidad de Santiago de Chile, Casilla 5659, Correo 2, Santiago, Chile

Electrophoretic migration measurements of the zero point of charge in MoO_3/γ-Al_2O_3 catalysts have been used to evaluate the 'apparent surface coverage' of molybdena.

The economic relevance of hydrodesulphurization makes MoO_3/γ-Al_2O_3 one of the most interesting catalyst systems being studied.[1,2] López Agudo *et al.*[3] have characterized these catalysts by determining the 'apparent surface coverage' (ASC) of molybdena (*i.e.* the fraction of the alumina support that is covered by the MoO_3 catalyst) based on oxygen chemisorption. Parks[4] has shown that the zero point charge (ZPC) is directly related to the composition of the samples; there is, moreover, experimental evidence that the ZPC measured by electrophoretic migration depends on the surface composition.[5] In this work we have used ZPC measurements to determine the ASC assuming that a relationship exists between the coverage

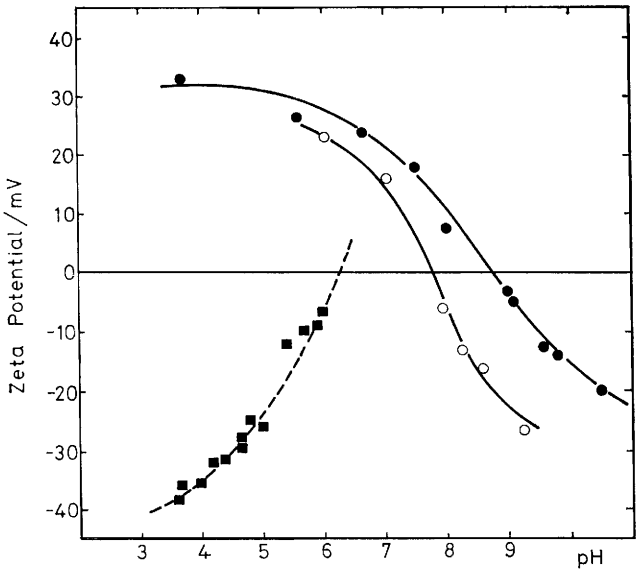

Figure 1. Zeta potential at 295.7 K as a function of suspension pH (●) Al_2O_3, (○) MoO_3/γ-Al_2O_3 (13.8 wt.%), and (■) MoO_3.

by the oxide phase and the ZPC determined by electrophoretic migration.

The measurements of ζ potential were carried out in a Zeta-Meter Inc. (Model ZM-77), using 20 mg of 2 μm catalyst particles ultrasonically suspended in 200 ml of 10^{-3} M KCl solution. (The ultrasonic treatment does not break up the catalyst because strong interaction exists between Al_2O_3 and MoO_3.[6]) A computation program, in BASIC language, was employed to obtain ZPC of the catalysts and the isoelectric point (IEP), of the Al_2O_3. (This was done by fitting points to a polynomial of 4th order.) The IEP of the unsupported MoO_3 was determined by extrapolation of the zeta potential curve. IEP and ZPC values were obtained $\pm$ 0.05 pH units. The catalysts were prepared by 'wet' impregnation of Girdler T-126 alumina with a water solution of ammonium paramolybdate, according to a procedure described in the literature.[3]

The ZPC of samples with more than one species without structural charge, is given by equation (1)[4] where ZPC = point of zero charge of the samples, X_i = molar fraction of each species, and IEP = isoelectric point of each species.

$$ZPC = \Sigma\,(IEP)_i X_i \quad (1)$$

If one assumes that the coverage is related to the ZPC, then for a one-component supported catalyst equation (1) becomes equation (2), where S represents the support, M the supported

$$ZPC = X_S(IEP)_S + X_M(IEP)_M \quad (2)$$

species, and X the surface mole fraction defined in equation (3). M_S and M_M represent the molecular weights of the

$$X_M = (ASC.M_M^{-1})/[(100\text{-}ASC)M_S^{-1} + ASC.M_M^{-1}] \quad (3)$$

support (Al_2O_3 = 101.96 g mol^{-1}) and the supported species (MoO_3 = 143.94 g mol^{-1}), respectively. Thus, the ASC may be given by equation (4).

$$ASC = M_S^{-1}(IEP_S - ZPC)/[(M_M^{-1} - M_S^{-1})(ZPC - IEP_S) + M_M^{-1}(IEP_S - IEP_M)] \times 100 \quad (4)$$

IEP values for Al_2O_3 and MoO_3 as a function of hydration time are included in Table 1. The displacement of IEP with moisture degree is a well known phenomenon;[4] therefore it is necessary to standardize the previous treatment. The experiments were performed with humid samples which ensured a large difference betweeen the IEP of MoO_3(6.25) and of Al_2O_3(8.80).

Table 1. Al_2O_3 and MoO_3 IEP obtained at different times of hydration at 55% relative humidity on $Ca(NO_3)_2 \cdot 4H_2O$.

Sample	t/h	IEP (pH units)
Al_2O_3	0	7.30
Al_2O_3	10	8.40
Al_2O_3	30	8.80
Al_2O_3	40	8.80
MoO_3[a]	0	6.25
MoO_3[a]	40	6.25

[a] Identified by powder X-ray diffraction.

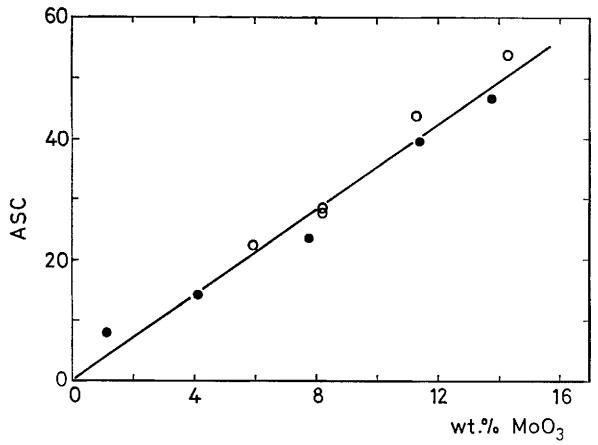

Figure 2. Relationship between 'apparent surface coverage' and MoO_3 loading by (●) zero point charge and (○) oxygen chemisorption (ref. 3) measurements.

As predicted by equation (2) the ZPC values of the catalyst samples fall between the IEP of the support and the IEP of the MoO_3 (see Figure 1). Similar curves were obtained for catalysts with 1.1, 4.1, 7.8, and 11.4 g MoO_3 per 100 g Al_2O_3. At pH values higher than 6.5, unsupported MoO_3 is partially solubilized; it is not then possible to obtain reliable zeta potential values.

Values of ASC obtained by electrophoretic migration and oxygen chemisorption are presented as a function of weight percentage of MoO_3 in Figure 2. The ASC's determined by both methods are in agreement. Therefore electrophoretic migration is proposed to provide a rapid and accurate procedure for the determination of coverages in supported catalysts.

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