Use of pH Measurements for the Characterization of MoO_3/Al_2O_3 Catalysts

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A new method to estimate the surface coverage of molybdena in MoO_3/Al_2O_3 catalysts based on pH measurements is proposed.

Electrophoretic mobility (EM) has been used to determine the apparent surface coverage and as a technique to characterize supported catalysts.[1,2] Here, we present theoretical and practical considerations to use potentiometric measurements instead of EM for the indicated purpose.

The balance of surface charge density (σ) of a particle without structural permanent charge,[3] and suspended in an indifferent electrolyte (*i.e.* in absence of inner-sphere complexes) is given by eqn. (1),

$$\sigma_H + \sigma_{OS} + \sigma_D = 0 \qquad (1)$$

where $\sigma_H = F(\Gamma_H - \Gamma_{OH})$ = net proton charge density; σ_{OS} = outer-sphere complex charge density (σ_{OHP}); σ_D = the surface charge density associated with the diffuse portion of the electrical double layer.

If $\sigma_H = 0$ the pH value is the point of zero net proton charge (PZNPC), determined through potentiometric measurements. If $\sigma_D = 0$, the pH value is the isoelectric point (IEP) determined by electrokinetic measurements. When the solid surface sites are homogeneous, and both ions of the electrolyte show the same affinity for their respective surface sites, then $\sigma_{OS} = 0$, and PZNPC = IEP. When surfaces are heterogeneous, differences will be observed, but a relationship is established between PZNPC and IEP through σ_{OS}.

Thus, in theory, most studies of catalyst characterization carried out through IEP can also be performed by PZNPC determinations. In the present paper, the theoretical considerations described above are experimentally settled down. Specifically, we establish conditions to determine PZNPC through a single pH measurement and suggest applications to catalyst characterization.

The MoO_3 τ-Al_2O_3 supported catalysts were prepared by the wet impregnation method of Strem τ-Al_2O_3 (98 $m^2\ g^{-1}$) with an aqueous solution of ammonium paramolybdate and then calcined at 823 K.[4]

The Mo content was determined by atomic absorption spectroscopy after sample dissolution.

The IEP was determined with 20 mg of 2 μm size sample ultrasonically suspended in 200 ml of 10^{-3} mol dm^{-3} KCl solution; the mobilities were averaged and the zeta potential calculated using the Helmholtz–Smoluchowski equation.

The PZNPC was determined on the basis of continuous and mass potentiometric titrations[5,6] carried out under nitrogen flow. Continuous data were obtained with 0.70 g of solid suspended in 200 ml of 1.0–10^{-3} mol dm^{-3} of KCl titrated with KOH or HCl, adding 0.30 ml each 30 min (blank titrations were performed similarly). Mass titration was carried out with 2 g of solid, by addition of 200 mg of sample each 30 min to 100 ml of 0.1 mol dm^{-3} KCl, and recording pH *vs.* mass content.

The τ-Al_2O_3 potentiometric titration curves show that PZNPC is coincident with the starting point of the titration and remain invariant under ionic strength changes (the pH where $d\sigma_H/dI = 0$ is named point of zero salt effect). Thus, to determine the PZNPC we needed only the pH measurement of the starting point (in the absence of permanent charge and specific ion adsorption).

The amount of sample and the equilibrium time needed to determine the PZNPC with one single pH measurement were established from pH *vs.* sample addition data (200 mg each 30 min). With the exception of molybdena, the equilibrium pH was reached after the addition of 1.0 g of sample (Fig. 1).

No significant differences were observed on pH data whether 1.0 g or five portions of 200 mg of sample are added to 100 ml of 0.1 mol dm^{-3} KCl under nitrogen flow, after 30 min or 24 h of equilibrium.

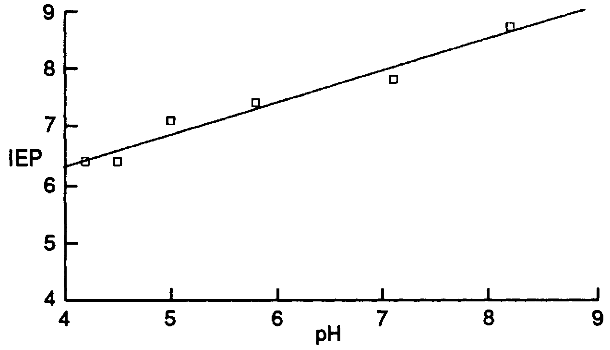

Fig. 2 Relationship between isoelectric point (IEP) and pH

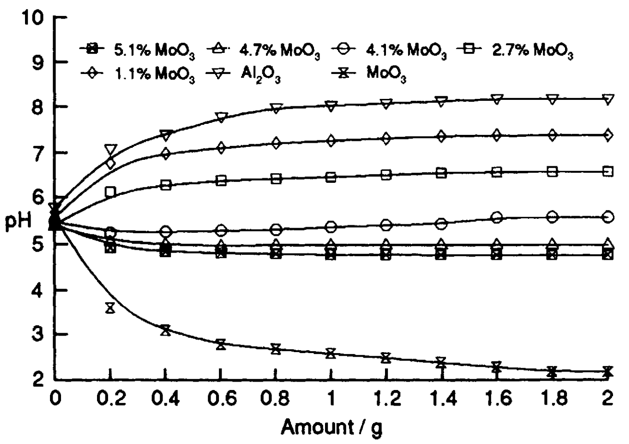

Fig. 1 Suspension pH as a function of amount of solid

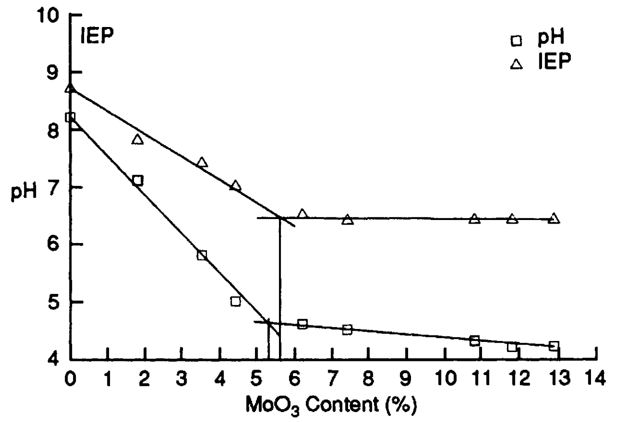

Fig. 3 Isoelectric point (IEP) and suspension pH as a function of molybdena content

Since KCl closely meets the condition of electrolyte affinity, a linear relationship is observed (Fig. 2) that agrees with theoretical considerations; all samples present IEP values higher than PZNPC at the same molybdena content (Fig. 3).

Catalysts show a gradient of IEP values, between the support and MoO_3 IEP values (Fig. 3), that is as a function of the content of the support.

When PZNPC and IEP values are plotted *vs.* MoO_3 content (Fig. 3), the decreasing linear relationship approaches a constant value at about the same molybdena content (5.3 or 5.6% if pH or IEP is used), which means that the maximum apparent surface coverage is reached. The proposed pH measurements methodology compared with IEP determinations has the disadvantage of the amount of sample required (1 g *vs.* 20 mg for IEP), however, it is a very simple method since it does not require special equipment (a pH meter compared with a Zeta Potential meter), and gives similar results.

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