

ESR, OXYGEN CHEMISORPTION AND ACTIVITY STUDIES ON MoO₃-ZrO₂ CATALYSTS

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Abstract—ESR studies on ZrO₂-supported Mo oxide catalysts indicate the presence of two types of paramagnetic Mo⁵⁺ species on the support surface. The oxygen uptake capacities (at -78°C), as well as the hydrodesulfurization and hydrogenation activities of the catalysts are found to correlate with the Mo loadings on the support. The results are explained with the help of a "patch" model of the Mo oxide phase.

Supported Mo-containing catalysts are used in many important reactions including hydroprocessing, coal liquefaction, hydrogenation (HYD), polymerization and metathesis of olefins. Numerous studies have been devoted towards understanding of the surface structure of the supported Mo oxide phase and its consequence upon the resulting activity and selectivity for certain reactions.^{1,2} Pursuant to our earlier ESR³ and oxygen chemisorption⁴ studies on V₂O₅-Al₂O₃ catalysts an investigation has been made with the Mo-ZrO₂ system by these techniques in order to gain some information on the surface structure of the Mo oxide phase and its relevance to probe reactions like hydrodesulfurization (HDS) of thiophene and HYD of cyclohexene.

EXPERIMENTAL

Catalyst preparation

The ZrO₂ support was prepared by precipitating Zr hydroxide from ZrOCl₂·8H₂O by dilute ammonia solution. The precipitate was freed from chloride ions, dried at 120°C for 24 h and finally

calcined at 540°C for 4 h in air. The supported Mo oxide catalysts were prepared by an incipient wetting technique: a calculated amount of ammonium heptamolybdate (spectroscopic grade, Baker) corresponding to the desired Mo loading on the support was dissolved in that volume of water which corresponded exactly to the total pore volume of the quantity of support used for impregnation. The support was then uniformly wetted by the solution, stirred well for 30 min and allowed to stand for 1 h. The impregnated sample thus obtained was dried at 120°C for 16 h and then calcined in air for 12 h at 540°C.

Chemisorption measurements

A conventional static high-vacuum (up to 10⁻⁶ torr) system, with the facility for reducing the catalysts *in situ* by flowing hydrogen, was used for oxygen chemisorption, which was performed at -78°C, following the procedure of Parekh and Weller.⁵ The same system was used to measure the BET surface areas of the catalysts by N₂ (0.162 nm²) adsorption at -196°C. The details of the experimental set-up and chemisorption procedure have been given elsewhere.⁴

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Activity measurements

Thiophene HDS and cyclohexene HYD were chosen as the model reactions for testing the activities of the catalysts which were sulfided at 400°C for 2 h in a flow of a purified hydrogen and CS₂ mixture before the reactions. For this purpose, a fixed-bed differential flow microreactor operating under normal atmospheric pressure and interfaced with a gas chromatograph by a six-way sampling valve for product analysis was used. The conversions were kept within 10%. The experimental procedure and method of activity calculation have been described elsewhere.⁶

ESR and XRD measurements

The ESR spectra of the catalysts were recorded *in vacuo* (10⁻⁶ torr) and at 25°C on a JEOL FE 3X X-band spectrometer with 100-KHz modulation. The details of sample preparation and the experimental procedure have been elaborated in a previous

paper.³ The X-ray diffractograms were recorded on a Philips PW 1051 diffractometer by using Ni-filtered Cu-K_α radiation.

RESULTS AND DISCUSSION

Representative ESR spectra of the unreduced [(a) and (b)] and the reduced [(c)] catalysts are shown in Fig. 1. A comparison of these spectra with those of Mo-SiO₂ catalysts^{7,8} shows that for the 1% Mo-ZrO₂ catalyst the ESR spectrum due to Mo⁵⁺ represents a "solution-like" behaviour due to incomplete removal of water ($g_{\text{iso}} = 1.975$). For the catalysts with Mo contents higher than 1%, an axially symmetric spectrum appears at the centre of the pattern [Fig. 1(b)] with $g_{\parallel} = 1.910$ and $g_{\perp} = 1.932$ ($g_{\parallel} < g_{\perp}$). The intensity of the anisotropic spectrum increased with increasing Mo loading. Upon reduction, the "solution-like" behaviour almost disappears, while an anisotropic spectrum appeared with maximum intensity for the sample

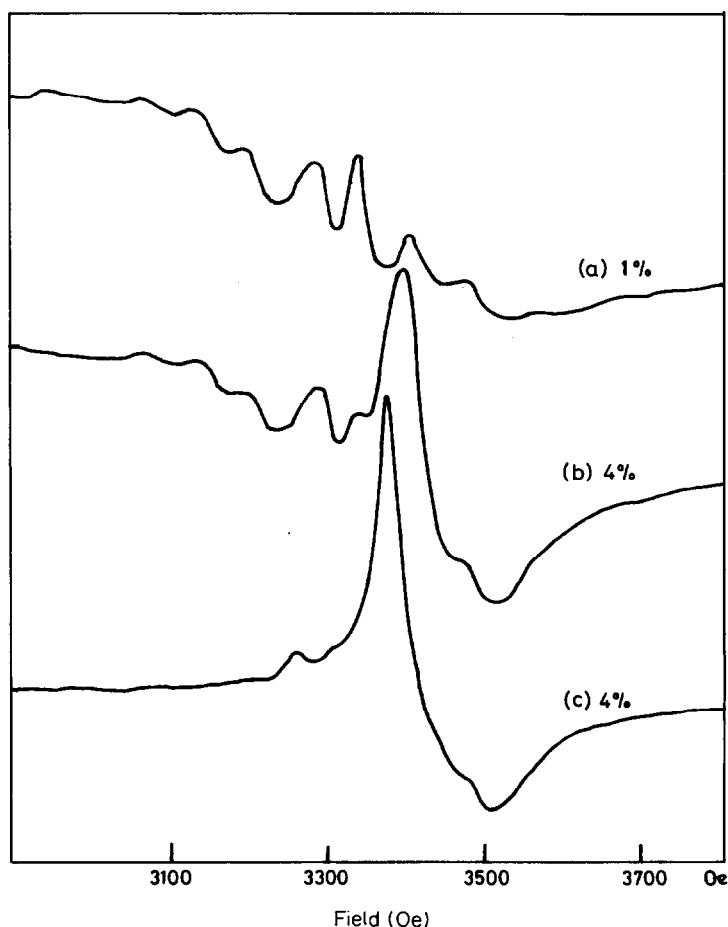


Fig. 1. ESR spectra of unreduced [(a) and (b)] and reduced [(c)] Mo-ZrO₂ catalysts recorded at 27°C and 10⁻⁶ torr.

with 1% Mo loading (not shown in Fig. 1). The intensity of this spectrum, unlike in the case of the unreduced catalysts, decreased rapidly with increasing Mo loading and became asymptotic just above 4% Mo loading.

The oxygen uptake capacities, HDS and HYD activities of the reduced catalysts are given as a function of Mo loading on ZrO₂ in Fig. 2. The oxygen chemisorption (at -78°C) behaviour of the Mo-ZrO₂ catalysts shows a similarity with that of the well-studied Mo-Al₂O₃ catalysts.⁹ As observed from Fig. 2, the oxygen uptake increases as a function of Mo loading up to about 3.5% and then levels off. This saturation level indicates the completion of a monolayer coverage of the "active" ZrO₂ surface by Mo oxide. The monolayer corresponds to about 10 μmol Mo m⁻² of the support surface. This value is about twice as high as the corresponding value for Mo-Al₂O₃ catalysts. The maximum oxygen uptake by the Mo-ZrO₂ catalysts is found to be about 3 μmol m⁻² compared to about 0.3 μmol m⁻² for Mo-Al₂O₃ catalysts. These results therefore, indicate that the Mo oxide is dispersed better on ZrO₂ than on Al₂O₃. This conclusion is made from the higher surface coverage and higher oxygen uptake capacity at the monolayer level of the Mo-ZrO₂ catalysts.

The HDS and HYD activities of the catalysts [curves (b) and (c) of Fig. 2] show a sharp rise as a function of Mo loading up to the monolayer level. Beyond this level, the activities show a very slow rise as a function of Mo loading. A closer look at Fig. 2 also reveals a good correlation of both HDS and HYD activities with the oxygen uptake capacities of the catalysts. These results indicate, therefore, that: (1) the HDS and HYD active sites, i.e. the coordinatively unsaturated sites (CUS), are titrable by oxygen chemisorbed at low temperatures; and (2) beyond the monolayer coverage, further addition of the active component, i.e. Mo oxide, does not contribute to the generation of active CUS upon which oxygen chemisorption, HDS and HYD reactions can take place.

Based on the "patch" model of Hall,² the nature of the oxygen chemisorption sites on Mo-Al₂O₃ catalysts has recently been discussed by Nag.⁹ It has been envisaged that at lower Mo loadings small patches of Mo oxide, two layers thick and with Mo in an octahedral coordination, are formed on the support surface. Upon reduction, CUS are generated by the removal of oxygen from the edge and corner sites of the patches. These are the sites upon which oxygen chemisorption, HDS and HYD reactions

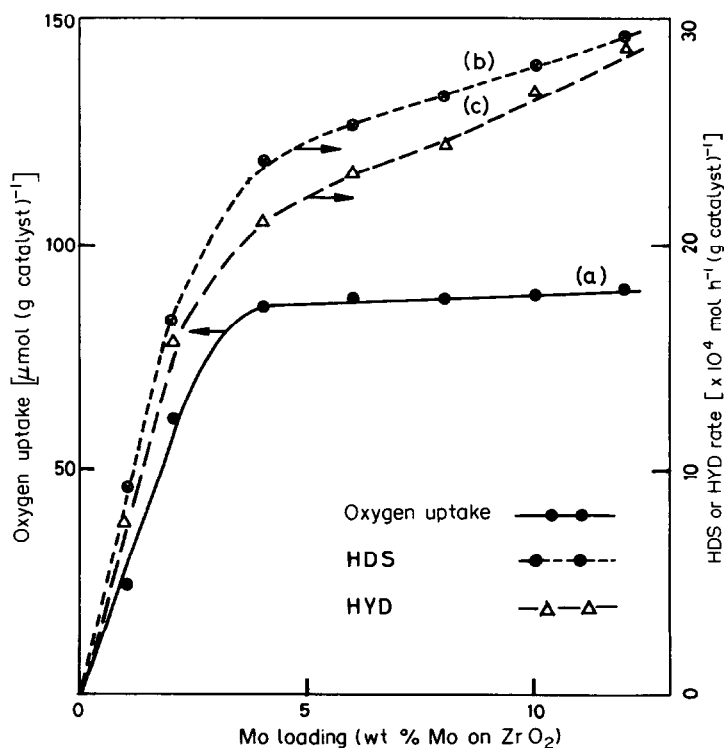


Fig. 2. Oxygen uptake at -78°C (a), hydrodesulfurization (HDS) of thiophene at 420°C (b) and hydrogenation (HYD) of cyclohexene at 400°C (c). Activities as a function of Mo loading. All the data are corrected for the contributions by the support.

take place. It has also been proposed that as the Mo loading increases the number of these patches increases with attendant increase in the number of CUS up to the monolayer level. Beyond the monolayer level the patches grow three-dimensionally, thus decreasing the dispersion of Mo oxide. It is proposed that a similar mechanism operates in the Mo-ZrO₂ system, and the present results can be explained with the help of the above concepts. Thus the initial increase and subsequent levelling off in the oxygen uptake capacity of the catalysts as a function of Mo loading are due to generation of new CUS up to the monolayer level and a subsequent decrease in the edge and corner CUS beyond the monolayer level due to crystal growth. Since the HYD and HDS activities are correlated with the CUS, their initial increase and subsequent levelling off tendencies can be understood by the same mechanism. It is worth mentioning here that, indeed, XRD lines of reduced Mo oxide were detectable only with samples containing Mo oxide at greater than the monolayer level.

Several conclusions can be derived from this present work: (1) as in the case of the Mo-Al₂O₃ system, the CUS of highly dispersed Mo oxide on ZrO₂ responsible for HDS and HYD reactions can be titrated by low-temperature oxygen chemisorption; (2) low-temperature oxygen chemisorption data can precisely determine the Mo level where the

formation of a monolayer reaches completion; and (3) Mo oxide is dispersed better on the ZrO₂ support than on the Al₂O₃ support.

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