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Effect of the preparation method on the surface coverage of Mo/Al_2O_3 catalysts

José Goldwasser [1], Carlos Scott, M. Josefina Pérez Zurita

Centro de Catálisis, Petróleo y Petroquímica, Escuela de Química, Facultad de Ciencias,
Universidad Central de Venezuela, Apartado postal 47102, Los Chaguaramos,
Caracas 1020-A, Venezuela

Marwan Houalla and David M. Hercules

Department of Chemistry, Materials Research Center, University of Pittsburgh,
Pittsburgh, PA 15260, USA

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Two series of Mo/Al_2O_3 catalysts were prepared by equilibrium adsorption and incipient wetness impregnation methods. The effect of preparation method on the surface coverages of the calcined catalysts was investigated by the combined use of CO_2 chemisorption, low temperature CO adsorption and ion scattering spectroscopy (ISS). For a given Mo loading, the CO_2 and CO adsorption results showed little difference between the two preparation methods. As previously noted, the CO_2 chemisorption method overestimated the Mo surface coverage. In contrast to the adsorption methods, the ISS technique gave different Mo surface coverage values for a given Mo content of the two series of catalysts. This apparent discrepancy was attributed to different repartition of the Mo phase between the internal and external surfaces which can only be detected by ISS. This interpretation is supported by the observed agreement between the coverage values measured from ISS and low temperature CO adsorption for presumably uniform catalysts obtained by the equilibrium adsorption method.

Keywords: surface coverage; Mo and Al oxides; CO_2 chemisorption; CO adsorption; ion scattering spectroscopy (ISS)

1. Introduction

The importance of molybdena–alumina catalysts in key industrial processes such as hydrotreating and hydrodesulphurization is well established [1]. Knowledge of the Mo surface coverage in these catalysts is often desirable since this parameter directly reflects the dispersion of the supported phase and the extent of participation of the support in a given reaction. Different techniques have been

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[1] To whom correspondence should be addressed.

used for assaying the surface coverage of molybdenum species over alumina. These include X-ray photoelectron spectroscopy (XPS) [2–5], laser Raman spectroscopy (LRS) [6–8], infrared spectroscopy [9,10], chemisorption of CO_2 [11–16], ion scattering spectroscopy (ISS) [17,18] and low temperature adsorption of CO [19–21].

In a recent paper, the advantages and limitations of the above mentioned techniques for measuring surface coverages of molybdena–alumina catalysts have been discussed [18]. It was noted that the joint use of ion scattering spectroscopy and low temperature CO adsorption is a promising approach for monitoring surface coverages. The use of CO_2 significantly overestimated the coverage of molybdena–alumina catalysts. The catalysts used in the study [18] were prepared by equilibrium adsorption. This method consists of adsorbing Mo from dilute aqueous solutions of $(NH_4)_6Mo_7O_{24}$ at a fixed pH over an extended period of time. The loading is controlled by varying the pH of the Mo solution. However, supported catalysts are generally prepared by incipient wetness impregnation. This preparation method involves contacting the support with a solution containing the precursor salt using a predetermined volume of water sufficient to fill the pores. Due to the short contact time between the alumina and the molybdenum solution, inhomogeneities in the repartition of the Mo phase may occur.

The purpose of the present work is to investigate the effect of preparation method (equilibrium adsorption vs. incipient wetness) on the surface coverage of Mo/Al_2O_3 catalysts as monitored by ion scattering spectroscopy, low temperature adsorption of CO and CO_2 chemisorption.

2. Experimental

2.1. CATALYSTS

γ-alumina (Ketjen CK-300), BET surface area 210 m^2/g, was used as the support. The equilibrium adsorption series was prepared by the method described by Wang and Hall [22]. Details of the preparation procedure are given elsewhere [23]. The incipient wetness series was prepared by impregnation of the support with aqueous solutions of $(NH_4)_6Mo_7O_{24}\cdot 4H_2O$ (BDH reagent grade). Following adsorption or impregnation, the catalysts were dried for 2 h at 373 K and calcined for 5 h at 773 K. The Mo loadings prepared by both methods expressed as wt% Mo and Mo at./cm^2 are reported in table 1.

2.2. REAGENTS

CO and CO_2 were Matheson high purity. A freeze–pump–thaw technique, described previously [24] was used for purification purposes. The methodology used for CO_2 chemisorption [16], CO adsorption [21] and ISS experiments [18] has been previously described, but will be repeated here for the sake of completion.

Table 1
Experimental surface coverages determined by ISS

Series[a]	Mo loading		Al/O	θ_{ISS}[b]	Mo_{cs}[c] ($Å^2$/Mo)
	wt% Mo	(Mo/cm^2) × 10^{-13}			
–	0.0	0.0	1.47	0.00	–
EA	1.0	3.0	1.38	0.061	20.3
EA	3.9	12.4	1.10	0.25	20.2
EA	6.0	19.7	0.86	0.41	20.8
EA	8.0	27.2	0.70	0.53	20.8
IW	1.7	5.2	1.15	0.22	42.3
IW	5.5	17.9	0.71	0.52	29.1
IW	8.8	30.3	0.55	0.63	20.8
IW	13.0	48.2	0.40	0.73	15.1

[a] EA: equilibrium adsorption; IW: incipient wetness.
[b] For calculation, see text.
[c] Mo cross-section.

2.3. ADSORPTION EXPERIMENTS

The CO and CO_2 adsorption experiments reported here are the averages of at least two runs. The results were always within 5–7%.

(A) *CO_2 chemisorption.* Prior to the adsorption measurements, the catalysts were first pretreated with O_2 (60 cm^3/min) for 16 h at 773 K and then evacuated at the same temperature for 4 h. The CO_2 volumetric measurements were performed by two different methods in a BET-type system [16]. In method 1, the amount of CO_2 irreversibly held at room temperature was measured volumetrically. Method 2 consisted in measuring the amount of CO_2 desorbed at 773 K following the adsorption step. The procedures are described in detail elsewhere [16,25,26]. The two values served for cross-checking purposes and were essentially identical for all catalysts.

(B) *CO adsorption.* The CO adsorption experiments were performed in the above mentioned BET-type system. The catalyst was first pretreated with O_2 (60 cm^3/min) at 773 K for 16 h. After evacuating the catalysts at 1200 K for 3 h ($< 1 \times 10^{-5}$ Torr) the CO adsorption isotherms were obtained at 77 K. The double isotherm method [27] was used to calculate the irreversibly held CO.

2.4. ISS EXPERIMENTS

ISS spectroscopy was performed with a 3M model 525 ISS spectrometer. Samples were pressed into 6 × 15 mm^2 pellets at a pressure of 2000 kg/cm^2 and, after calcination at 773 K in air, they were mounted on double sided tape on a probe for insertion into the spectrometer. A base pressure of 3×10^{-8} Torr was achieved before backfilling with ^4He to 8×10^{-6} Torr. The energy of the primary beam was

2000 eV. Ten spectra were collected over 40 min to minimize sputtering effects. Al/O ISS intensity ratios were measured after linear background subtraction. The intensity of a peak was obtained by linear regression to time zero from a plot of peak height vs. ion beam exposure time. The reported results are the averages of two experiments. A maximum error of 20% was obtained for the low loading catalysts.

2.5. METHODOLOGY FOR SURFACE COVERAGE MEASUREMENTS

(A) The surface coverages based on the adsorption of CO(θ_{CO}) and CO$_2$(θ_{vol}) were calculated from

$$\theta = 1 - \frac{Q_{cat}}{Q_{alumina}(1 - 1.5\,\%Mo/100)}, \tag{1}$$

where Q_{cat} and $Q_{alumina}$ are the adsorption uptakes for the catalyst and the support respectively and %Mo is the Mo content in wt%. Eq. (1) is similar to that used by Zmierczak et al. [4].

(B) The surface coverages (θ_{ISS}), based on ISS measurements, were calculated from the experimental Al/O intensity ratios using eqs. (2) and (3), according to refs. [17,28],

$$(I_{Al}/I_O) = K(1 - \theta_{ISS})\,. \tag{2}$$

Since $(I_{Al}/I_O)_{alumina} = K$ for the alumina ($\theta = 0$) then

$$\theta_{ISS} = 1 - \frac{(I_{Al}/I_O)_{cat}}{(I_{Al}/I_O)_{alumina}}, \tag{3}$$

where $(I_{Al}/I_O)_{cat}$ and $(I_{Al}/I_O)_{alumina}$ are the experimental intensity ratios for the catalyst and the support, respectively. In this model it is assumed that the oxygen signal remains essentially constant as the alumina surface is covered by Mo. This assumption has recently gained experimental support [29].

3. Results and discussion

Fig. 1 shows the Mo surface coverages for the two series of catalysts prepared by incipient wetness and equilibrium adsorption methods, measured from CO$_2$ uptake. It can be readily seen that for a given Mo loading, the Mo surface coverage estimated from CO$_2$ chemisorption appears to be little affected by the preparation method. Recall that the use of CO$_2$ chemisorption has been shown to significantly overestimate the Mo surface coverage [10,15,16,18,20]. This was explained in terms of CO$_2$ and the molybdenum species competing for the most basic hydroxyl groups of the support, which comprise less than 10% of the total amount of OH groups.

Also included in fig. 1 are the surface coverages (θ_{CO}) measured by low temperature CO adsorption and taken from refs. [18,21]. Note that similar coverage values

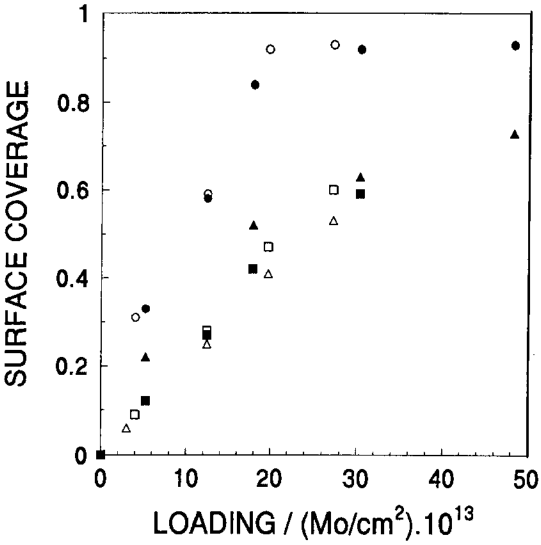

Fig. 1. Plot of surface coverages of molybdena–alumina catalysts as a function of Mo loading. (□) CO, (△) ISS, (○) CO_2, equilibrium adsorption series. (■) CO, (▲) ISS, (●) CO_2, incipient wetness preparations.

are obtained for both sets of catalysts. The Mo cross-sections calculated from these values (20.6–22.2 Å^2) agree with earlier studies [2,17,18,20,21]. These results and the CO_2 chemisorption data suggest that the surface structures of catalysts obtained by incipient wetness and equilibrium adsorption are very similar. This finding is consistent with previously reported Raman spectroscopy results [8,30] indicating that the structure of supported molybdenum oxide is independent of the preparation method.

Fig. 2 shows the ISS spectra for the equilibrium adsorption and incipient wetness series. The peaks at $E/E_0 = 0.41, 0.59$, and 0.86 are due to O, Al and Mo, respectively. Table 1 reports the experimental (Al/O) intensity ratios and the corresponding Mo surface coverages as a function of Mo loading. Also included in table 1 are the corresponding Mo cross-section values. As expected, a decrease in the Al/O intensity ratio (i.e. increase in the coverage) is observed with increasing metal loading for both series of catalysts. The variation of the ISS surface coverages (θ_{ISS}) for both series with increasing metal loading is shown in fig. 1. Note the good agreement between θ_{CO} and θ_{ISS} for the equilibrium adsorption series and the difference between the corresponding values for the incipient wetness series. It is also clear that higher surface coverage values are obtained from ISS for the incipient wetness series. The differences in the coverages between the two series, particularly for low MO loadings, largely exceed the experimental error associated with these measurements. These results should be contrasted with those obtained from CO_2 chemisorption and low temperature CO adsorption which show essentially no difference in the surface coverage of both series.

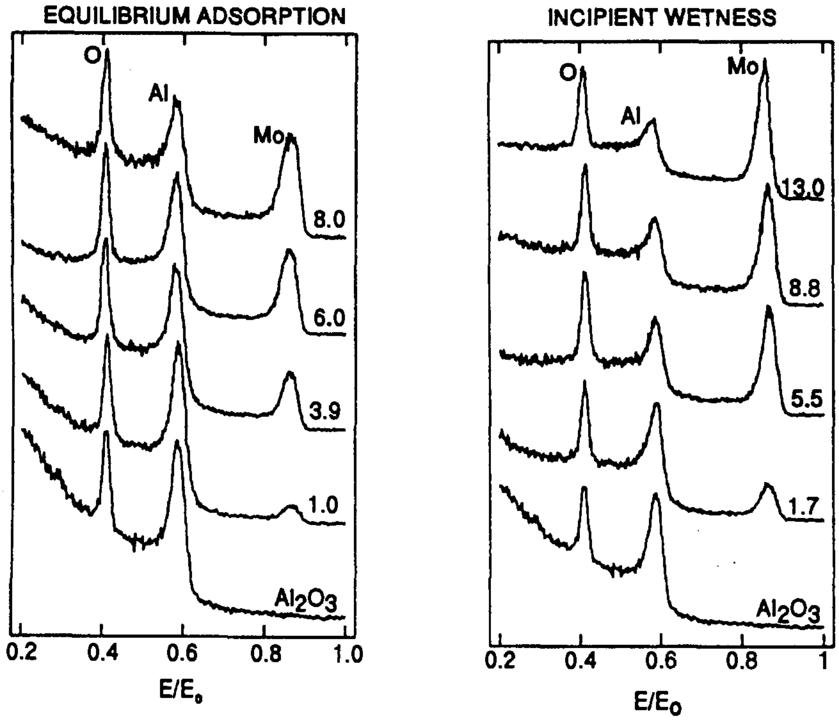

Fig. 2. ISS spectra for the alumina and molybdena–alumina catalysts. The numbers in the figures refer to the Mo loadings expressed as wt% Mo.

The apparent discrepancy between the ISS and adsorption results can be attributed to the surface sampled in both techniques. CO and CO_2 molecules can access the entire surface (internal and external) whereas ISS because of its extreme surface sensitivity can only analyze the outerparts of the catalysts particles. Thus, for the ISS coverage results to be valid, a uniform repartition of the supported phase between the inner pores and the external parts of the catalyst particles is assumed. Keeping this in mind, the observed difference in the coverage data (θ_{ISS}) obtained for both series of catalysts can be attributed to different repartition of the active phase. Catalysts obtained by the equilibrium adsorption method should be more uniform. This is supported by the agreement between the ISS and CO based coverages. The reproducibility of these preparations is illustrated by the excellent agreement between the θ_{ISS} values measured in the present work and those of similar preparations reported earlier [17]. The Mo cross-section values calculated from these coverages (table 1) are in turn consistent with those generally reported or estimated for the Mo system (ref. [17] and references therein). Catalysts prepared by the incipient wetness method, because of the short contact time between the alumina and the molybdenum solution, are more likely to be inhomogeneous. An enrichment of molybdenum species on the external parts of the support could explain the higher coverage values obtained for the incipient wetness catalysts. In support of this interpretation are the unreasonably high MO cross-section values measured for the low loadings catalysts obtained by incipient wetness impregnation (30–40 $Å^2$/Mo) (table 1) compared to values generally reported in the literature (ca. 20 $Å^2$/Mo) [17].

4. Conclusions

Surface coverages of Mo/Al_2O_3 catalysts obtained by equilibrium adsorption and incipient wetness impregnation methods were investigated by low temperature CO adsorption, CO_2 chemisorption and ion scattering spectroscopy (ISS). For a given Mo loading, the CO and CO_2 adsorption results showed little difference between the two preparation methods. The coverages measured by CO_2 chemisorption were, however, significantly higher than those obtained from adsorption of CO. These results were consistent with an earlier finding that CO_2 chemisorption method overestimated the Mo surface coverage.

In variance with the adsorption methods, the ISS technique gave different Mo surface coverage values for a given Mo content of the two series of catalysts. This can be explained in terms of a different distribution of the Mo phase between the inner pores and the outer parts of the catalysts particles which can only be detected by ISS. This interpretation is supported by the observed agreement between the coverage values measured from ISS and low temperature CO adsorption for presumably uniform catalysts obtained by the equilibrium adsorption method.

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