

Absolute surface coverage of tungsten–alumina catalysts

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Absolute surface coverages (θ) of a series of tungsten–alumina catalysts prepared by the equilibrium adsorption method were determined by ion scattering spectroscopy (ISS) and low-temperature CO adsorption. The θ_{CO} values for the W catalysts were very similar to those obtained with the ISS method, for a given W loading. A linear increase in W coverage with increasing W loading, reaching $\sim 55\%$ coverage for the 13.1% W solid, was observed. The calculated W cross-sections ($22.0\text{--}24.5 \text{ \AA}^2/\text{W}$) were in agreement with other reports in the literature. Due to the inherent limitations of each method, the combined use of ISS and low-temperature CO adsorption is recommended for estimating absolute surface coverages in tungsten–alumina catalysts.

Keywords: tungsten, absolute surface coverage, ISS, low-temperature CO adsorption

1. Introduction

Supported tungsten based catalysts have been used extensively in important industrial processes such as hydrodesulfurization and hydrotreating [1,2]. Numerous studies have been devoted to the characterization [3–12] and understanding of the catalytic properties of the W–alumina system [2,3,13–15]. As for any metal supported catalyst, the knowledge of the surface coverage (θ) of the catalysts is of great importance, since it can be used as an index of the catalytic activity or as a control parameter for monitoring catalyst preparation.

Different techniques have been used to assess the surface coverage in tungsten–alumina catalysts [4–7,9,12,15]. Of these, X-ray photoelectron spectroscopy (XPS) has been one of the most frequently used techniques [4,9,12]. The XPS method is based on monitoring the variation of the intensity ratio of two peaks associated with the W phase (e.g., W 4f) and with the alumina (e.g., Al 2p) as a function of the bulk W/Al ratio. Formally, the results should be compared with those predicted from a theoretical model. For submonolayer coverages, a linear plot should be obtained with intercept at the origin. A change in the slope is taken as an indication of completion of the monolayer and the formation of discrete WO_3 particles. From the W content required for a full monolayer coverage, the W cross-section can be estimated. The reported values [4,9,12,14] are within the $22.3\text{--}24.1 \text{ \AA}^2/\text{W}$ range. The main limitations of the XPS method are the inherent uncertainties of the theoretical

model used and the assumption that only for W content exceeding the nominal monolayer value can WO_3 be formed. An additional shortcoming of this method is its inability to measure partial surface coverages.

The W surface coverage has also been monitored by Raman spectroscopy (see for example the detailed characterization work by Wachs and coworkers [5–7]). The LRS method is based on the assumption that in a series of tungsten–alumina catalysts, the threshold of appearance of WO_3 particles corresponds to a full monolayer coverage. Early data [6] showed that for an alumina support with $180 \text{ m}^2/\text{g}$, monolayer coverage was reached at $\sim 30\%$ WO_3 ($16.2 \text{ \AA}^2/\text{W}$), after calcination at 773 K. More in situ LRS work [7a], showed that the monolayer value had been exceeded for loadings above 20% WO_3 on a $180 \text{ m}^2/\text{g}$ alumina ($27.7 \text{ \AA}^2/\text{W}$). In a more recent study [7b], 28% WO_3 over a $180 \text{ m}^2/\text{g}$ alumina was taken as the monolayer value ($17.8 \text{ \AA}^2/\text{W}$). While this method has been proven useful for the determination of the molecular structure of the different tungsten species found in tungsten(VI) oxide–alumina catalysts [5–7,27–30], it may not be totally suitable for surface coverage determinations, since it assumes that a full monolayer coverage is required before the appearance of WO_3 species. Furthermore, as with the XPS method, the technique is not suitable for the determination of partial coverages.

Recently, two techniques have been proven useful for determining absolute surface coverages of different alumina supported transition metal oxides: ion scattering spectroscopy (ISS) and low-temperature CO adsorption. The former is based on monitoring the signal

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associated with the support on addition of the metal oxide phase. Due to its extreme surface sensitivity (ca. 2 Å), it is assumed that the ISS signal originating from the support cannot be detected for a full monolayer coverage. The technique has been proven successful in monitoring the surface coverage of Mo [16–18], V [19], Cr [20] and Re [21] supported on alumina. The low-temperature CO adsorption method is based on the selective adsorption of CO on the uncovered portion of the totally dehydroxylated alumina surface. This method has been used for measuring coverages of Mo [17,18,22,23,31] and Re [24] supported on alumina catalysts. Due to the inherent limitations of each method, *vide infra*, joint use of both techniques was recommended.

The main purpose of the present work is to explore the usefulness of the ISS and low-temperature CO adsorption methods for estimating absolute surface coverages of a series of tungsten–alumina catalysts.

2. Experimental

2.1. Catalysts

γ -alumina (American Cyanamid, BET surface area = 205 m²/g) was used as the support. The catalysts were prepared by the equilibrium adsorption method. An ammonium metatungstate solution (0.055 M in monomeric anion) was used as the tungsten promoter. The pH of the impregnation solution was adjusted with HNO₃ or NH₄OH. Adsorption of tungsten oxyanions was carried out for 24 h, after which the solutions were filtered. The solid was dried in air overnight at 393 K and calcined in air at 773 K for 16 h. The W content of the catalysts was determined by X-ray fluorescence spectroscopy (XRF).

2.2. Methods

The methodology used for the ISS experiments [17] and for the low-temperature adsorption of CO [23] has been previously described, but will be outlined here for the sake of completion.

2.2.1. ISS experiments

ISS spectroscopy was performed with a 3M model 525 ISS spectrometer. Samples were pressed into 6 × 15 mm² pellets at a pressure of 2000 kg/cm² 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. 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 expo-

sure time. The reported results are the average of two experiments.

2.2.2. Low-temperature CO adsorption

The CO adsorption experiments were performed in a conventional BET-type system [23]. The catalyst was first pretreated with dry O₂ (60 cm³/min) at 773 K for 16 h. After evacuating the catalysts at 1200 K for 3 h (< 2 × 10⁻⁵ Torr) the CO adsorption isotherms were obtained at 77 K. The double isotherm method [25] was used to estimate the irreversibly held CO. A freeze–pump–thaw technique was used to purify the CO.

2.3. Methodology for calculating surface coverages

The number of W atoms per cm² of alumina was calculated according to

$$W/\text{cm}^2 = \%W \times 3.274 \times 10^{15} / 205(1 - 1.26 \times \%W/100), \quad (1)$$

where %W is the wt% W in the catalyst. The term in parentheses is the weight fraction of support in the catalyst based on three oxygens per W in the calcined catalyst.

The surface coverages (θ_{ISS}), based on ISS measurements, were calculated from the experimental Al/O intensity ratios using the following equations, according to refs. [17–21]:

$$(I_{\text{Al}}/I_{\text{O}}) = K(1 - \theta_{\text{ISS}}). \quad (2)$$

Since $(I_{\text{Al}}/I_{\text{O}})_{\text{alumina}} = K$, then

$$\theta_{\text{ISS}} = 1 - [(I_{\text{Al}}/I_{\text{O}})_{\text{cat}} / (I_{\text{Al}}/I_{\text{O}})_{\text{alumina}}], \quad (3)$$

where $(I_{\text{Al}}/I_{\text{O}})_{\text{cat}}$ and $(I_{\text{Al}}/I_{\text{O}})_{\text{alumina}}$ 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 W. This assumption is well supported in the literature [17,21,26].

The surface coverage based on the adsorption of CO (θ_{CO}) was calculated from

$$\theta_{\text{CO}} = 1 - [Q_{\text{cat}} / Q_{\text{alumina}} \times (1 - 1.26 \times \%W/100)], \quad (4)$$

where Q_{cat} and Q_{alumina} are the adsorption uptakes for the catalyst and the support, respectively. Eq. (4) is similar to that used in ref. [23].

3. Results and discussion

Figure 1 shows characteristic ISS spectra for the support and the tungsten–alumina catalysts. The peaks at $E/E_0 = 0.41, 0.59$ and 0.93 are due to oxygen, aluminum and tungsten, respectively. Table 1 reports the experimental (Al/O) intensity ratios and the corresponding tungsten surface coverages as a function of W content. It

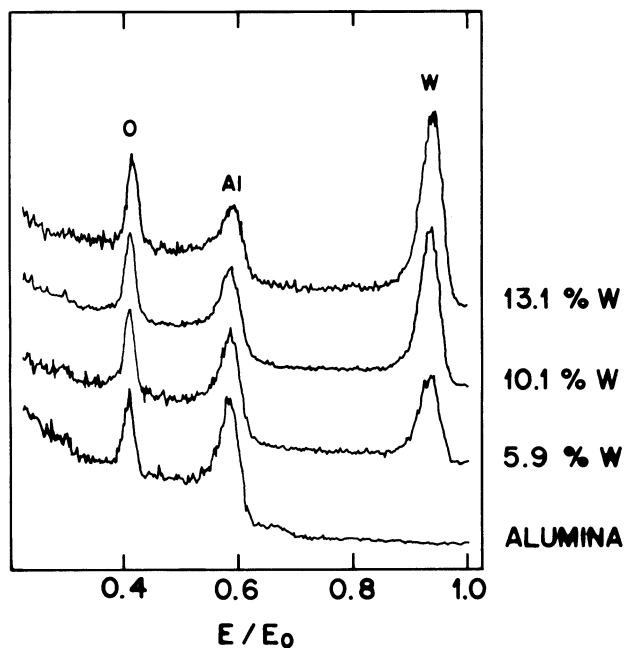


Figure 1. Ion scattering spectroscopy spectra for the alumina and the tungsten–alumina catalysts.

can be seen that the Al/O intensity ratios decrease, as expected, with increasing tungsten content. The calculated coverages increase in a linear fashion (figure 2). These data yield similar values for the calculated W cross-sections.

Table 2 shows the CO uptake as a function of the tungsten loading. It can be seen that the amount of irreversibly held CO decreases as the W loading increases. This result can be understood in terms of coverage of the Al^{3+} sites (free alumina surface) by the tungsten species. The latter are known to replace the hydroxyl groups of the support [10–12], thus decreasing the available OH groups that can be dehydroxylated at high temperature and reducing the number of uncovered Al^{3+} ions, necessary for CO adsorption [22,23]. The results for θ_{CO} are shown in table 2 and in figure 2. A linear increase in the surface coverage with increasing W loading is observed. The θ_{CO} are very similar to those obtained with the ISS method, for a given W loading. The observed linearity of the coverage with increasing W content is consistent with a uniform build-up of the supported phase, as suggested earlier [4,7,9,12].

Table 1
ISS data for γ -alumina and tungsten–alumina catalysts

wt% W	W(atoms)/ cm^2 ($\times 10^{-13}$)	Al/O ^a	θ_{ISS}	Cross-sectional area (\AA^2)
0.0	0.00	1.44	0.00	–
5.9	10.24	1.10	0.24	23.4
10.1	18.54	0.80	0.44	23.7
13.1	25.05	0.64	0.56	22.4

^a Al/O intensity ratios.

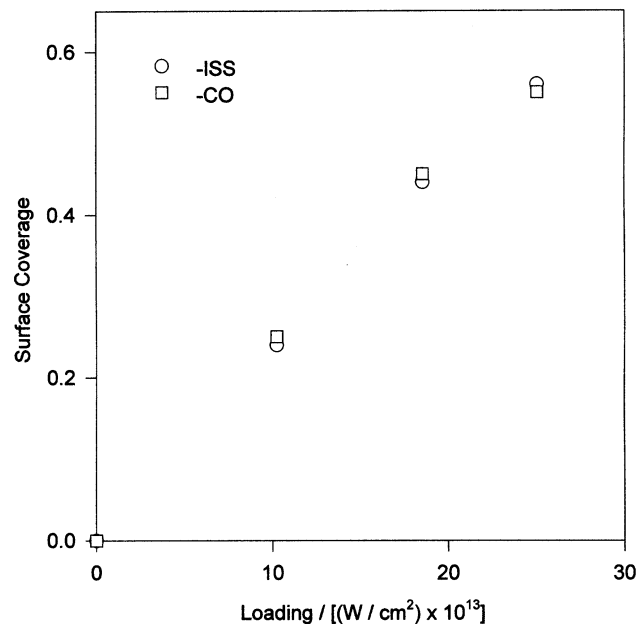


Figure 2. Plot of surface coverages as a function of W loading.

The above results agree with several characterization studies of tungsten–alumina catalysts [4–7,9,12,13,27–30], where up to ~ 13 wt% W, the tungsten forms well dispersed monomeric species.

As observed, the W cross-sections for the catalysts used in the present work (~ 22 – $24.5 \text{ \AA}^2/\text{W}$) are comparable to other reports, where the XPS or LRS methods were used ($23.1 \text{ \AA}^2/\text{W}$ [4] (XPS), $22.3 \text{ \AA}^2/\text{W}$ [9,14] (XPS), $24.1 \text{ \AA}^2/\text{W}$ [12] (XPS) and $27.7 \text{ \AA}^2/\text{W}$ [7a] (LRS)).

As attractive as the use of the ISS and low-temperature adsorption of CO methods may seem for estimating absolute surface coverages, both techniques have inherent limitations. In the case of the CO adsorption, total dehydroxylation of the surface is needed in order to calculate the surface coverage, thus high-temperature pretreatment is necessary. This can induce changes in the morphology as well as the surface area of the support. It can also lead to the formation of tungsten compounds such as $\text{Al}_2(\text{WO}_4)_3$ or loss of tungsten (although due to its high thermal stability, this is unlikely).

ISS as a technique is hardly routine and the instrument not widely available. Owing to its extreme surface sensitivity, ISS can only analyze the outer part of the cat-

Table 2
Low-temperature adsorption of CO data for γ -alumina and tungsten–alumina catalysts

wt% W	W(atoms)/ cm^2 ($\times 10^{-13}$)	CO uptake ($\mu\text{mol}/\text{g}_{\text{cat}}$)	θ_{CO}	Cross-sectional area (\AA^2)
0.0	0.00	879	0.00	–
5.9	10.24	605	0.25	24.4
10.1	18.54	424	0.45	24.3
13.1	25.05	333	0.55	22.0

alyst surface. Thus, for the coverage results to be valid, a uniform repartition of the supported phase between the inner pores and the external parts of the catalyst particles, must be assumed. This has been proven untrue for molybdena–alumina catalysts prepared by the incipient wetness technique [18].

In view of the above discussion joint use of both techniques (ISS and low-temperature CO adsorption) is suggested.

4. Conclusions

The combined use of low-temperature CO adsorption and ISS proved to be effective for estimating absolute surface coverages (θ) of tungsten–alumina catalysts. The θ_{CO} values for the W catalysts were very similar to those obtained with the ISS method, for a given W loading. A linear increase in W coverage with increasing W loading, reaching $\sim 55\%$ coverage for the 13.1% W solid, was observed. The calculated W cross-sections ($22\text{--}24.5 \text{ \AA}^2/\text{W}$) agreed with other reports in the literature.

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