Catalysis Letters 63 (1999) 131–133

Determination of the surface coverage of Re/Al_2O_3 catalysts by ion scattering spectroscopy and low-temperature CO adsorption

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Received 9 June 1999; accepted 17 September 1999

The surface coverage of a series of rhenia–alumina catalysts prepared by equilibrium adsorption was determined by low-temperature CO adsorption. The results show a linear increase in the coverage of the Re oxide on the alumina support up to 24% with increasing Re loading from 0 to ca. 5.6 wt%. This is consistent with a uniform build-up of the surface species. The coverage values measured by this method agreed very well with those obtained by ion scattering spectroscopy.

Keywords: Re/Al_2O_3 catalysts, low-temperature CO adsorption, ion scattering spectroscopy, coverage measurements, equilibrium adsorption

1. Introduction

A large number of catalysts consist of a surface metal oxide phase (oxides of Mo, W, Re) supported on a high surface area carrier (e.g., Al_2O_3). The performance of these catalysts is often a function of the coverage of the supported phase. Thus, it is of interest to develop a reliable methodology for monitoring the surface coverage. In principle, there is a plethora of techniques which can be used for monitoring the coverage of supported oxides. However, some of these techniques are at best effective in detecting the point of full coverage (e.g., Raman spectroscopy). Others have been shown to overestimate the coverage (CO_2 chemisorption on alumina-supported systems) [1–3] or to yield values which appear to be dependent on the pretreatment temperature (infrared analysis of the –OH region) [2,4].

Recently, two techniques have shown promise in estimating the coverage of supported oxides: ion scattering spectroscopy (ISS) and low-temperature CO adsorption. The ISS method is based on monitoring the signal associated with the support on addition of the metal oxide phase. Because of the extreme surface sensitivity of the technique (ca. 2 Å), it is assumed that the ISS signal originating from the support cannot be detected for a full monolayer coverage. This technique has been successfully used for monitoring the surface coverage of MoO_3/Al_2O_3 [5], V_2O_5/Al_2O_3 [6], CrO_3/Al_2O_3 [7] and Re_2O_7/Al_2O_3 catalysts [4]. The low-temperature CO adsorption method was developed for alumina-supported systems. It is based on the selective adsorption of CO on the uncovered (free) part of the dehydroxylated alumina surface. The technique has been used for measuring the coverage of MoO_3/Al_2O_3 catalysts [3,8].

It should be noted, however, that both techniques, despite their potential, exhibit some limitations. For example, the ISS method is based on the assumption of a uniform repartition of the supported phase between the inner pores and the external parts of the catalyst particles. The low-temperature CO adsorption method requires a complete dehydroxylation of the support. This is usually achieved by a high-temperature pretreatment which might alter the morphology of the support and the nature or dispersion of the support species. Taking into consideration the inherent limitations of each technique, we have recently [9] proposed a methodology for monitoring the coverage of supported oxides based on the joint use of ISS and low-temperature CO adsorption measurements. This approach was evaluated for Mo/Al_2O_3 and W/Al_2O_3 catalysts [9,10]. The purpose of the present work is to extend the study to the Re/Al_2O_3 system. The latter is reportedly one of the most active catalysts for olefin metathesis [11,12]. However, the exact nature of the active site remains, to date, a matter of discussion [13–15].

2. Experimental

2.1. Catalysts

The Re/Al_2O_3 samples were prepared by equilibrium adsorption from aqueous solutions of NH_4ReO_4 at various pH's. γ-alumina (American Cyanamid, BET surface area $= 205\ m^2/g$) was used as a support. The impregnated catalysts were dried overnight at 393 K and then calcined in air for 16 h at 773 K. Rhenium content was determined

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by X-ray fluorescence spectroscopy. More details are given elsewhere [4].

2.2. Ion scattering spectroscopy

The ISS spectra were acquired using a 3M model 525 ISS spectrometer. A base pressure of 3×10^{-8} was achieved prior to backfilling with ^{4}He. The primary ion energy was 2000 eV. The current density and the beam diameter were 2×10^{-7} A/cm^2 and ca. 1 mm, respectively.

The surface coverages were evaluated from the experimental $(I_{\mathrm{Al}}/I_{\mathrm{O}})_{\mathrm{cat}}$ intensity ratios using the following equation:

$$(I_{\mathrm{Al}}/I_{\mathrm{O}})_{\mathrm{cat}} = K(1-\theta),$$

where K is a constant equal to the $(I_{\mathrm{Al}}/I_{\mathrm{O}})$ ratio for the alumina support $(I_{\mathrm{Al}}/I_{\mathrm{O}})_{\mathrm{al}}$,

$$\theta = 1 - (I_{\mathrm{Al}}/I_{\mathrm{O}})_{\mathrm{cat}}/(I_{\mathrm{Al}}/I_{\mathrm{O}})_{\mathrm{al}}.$$

It is assumed that the Al peak cannot be detected for full monolayer coverage and the oxygen signal I_{O} remains essentially constant for all catalysts. More details about the methodology are given elsewhere [4,9].

2.3. Low-temperature CO adsorption measurements

CO adsorption measurements were carried out in a BET-type system. The catalysts were first pretreated in O_2 at 773 K for 16 h and then evacuated at 1200 K for 3 h. The CO adsorption isotherms were obtained at 77 K. The irreversibly held CO was obtained by the double-isotherm method. The methodology for surface coverage measurements from CO adsorption data was described earlier [9].

3. Results and discussion

Low-temperature CO adsorption results showed a steady decrease in CO uptake with increasing Re content (table 1, figure 1(a)). This is indicative of increased coverage of the alumina and is consistent with CO adsorption occurring selectively on the uncovered alumina surface. Figure 1(b) shows the variation of the surface coverage estimated from CO adsorption results as a function of Re content. A linear increase in the coverage up to 24% is observed with increasing Re loading from 0 to ca. 5.6 wt% Re. The observed

Table 1
CO uptakes and surface coverages of Re/Al_2O_3 catalysts determined by low-temperature CO adsorption.

%Re	Loading[a] (Re atoms/cm^2 $\times10^{13}$)	CO uptake (μmol/g-cat)	Surface coverage[b]	Cross-sectional area (Å^2)
0	–	1054	–	–
1.45	2.33	958	7.5	32.2
2.07	3.35	932	9.2	27.5
3.07	5.4	889	12	24
3.88	6.44	837	16.3	25.4
4.33	7.23	785	17.9	24.8
5.56	9.44	744	24	25.4

[a] Loadings calculated from the following expresion: Re atoms/cm^2 = %Re $\times$ $3.23 \times 10^{15}/205(1 - 1.30 \times \%\mathrm{Re}/100)$.

[b] For calculation, see text.

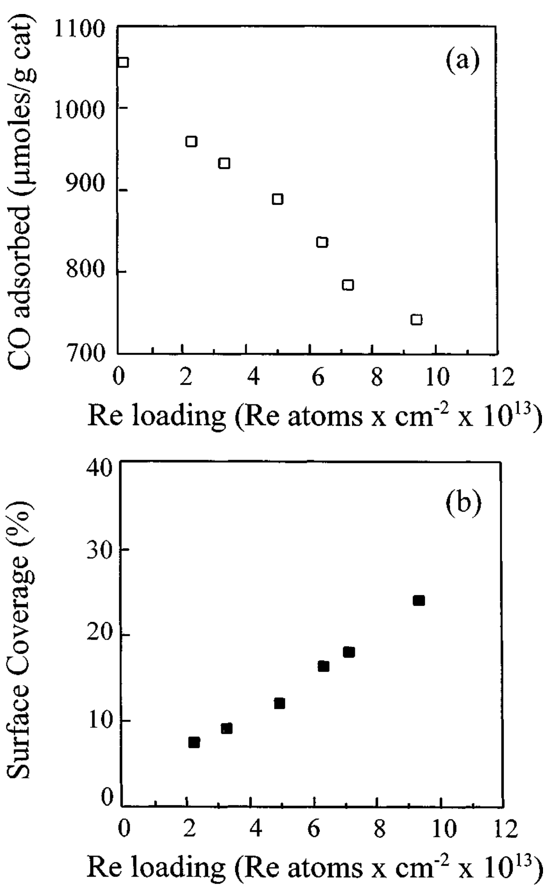

Figure 1. (a) Low-temperature CO adsorption results for a series of Re/Al_2O_3 catalysts. (b) Surface coverages of Re/Al_2O_3 catalysts measured from CO adsorption results.

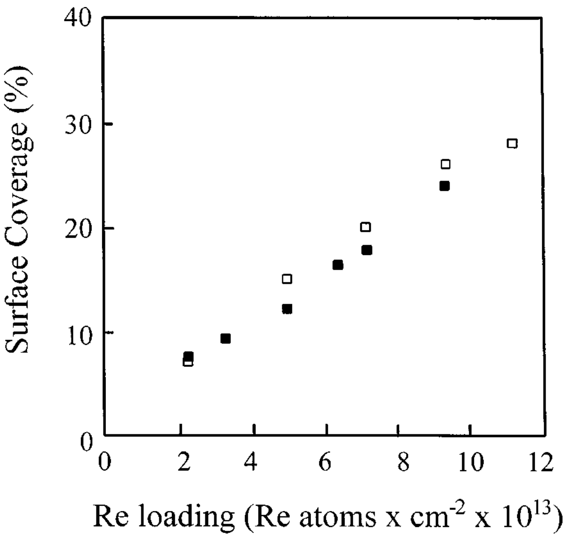

Figure 2. Surface coverages of Re/Al_2O_3 catalysts determined by low-temperature CO adsorption (■) and ISS (□).

linearity of the coverage with increasing Re content is consistent with a uniform build-up of the supported phase.

Figure 2 compares the coverage values measured by low-temperature CO adsorption with those obtained by ISS [4]. It can be readily seen that for a given Re loading, both techniques yield similar coverage values. The Re cross-sections calculated from the corresponding surface coverages (24–32 Å^2)/Re were comparable with those previously reported for the Re/Al_2O_3 system [16–18]. These results, together with those previously reported for the Mo/Al_2O_3 and W/Al_2O_3 systems [9,10], indicate a promising potential for the proposed methodology for surface coverage measurements.

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