Determination of the surface coverage of WO_3/TiO_2 catalysts by CO_2 chemisorption

Nithya Vaidyanathan, Marwan Houalla and David M. Hercules *

Department of Chemistry, Vanderbilt University, Nashville, TN 37235, USA

Received 20 September 1996; accepted 15 November 1996

The surface coverage of a series of WO_3/TiO_2 catalysts prepared by incipient wetness impregnation was monitored by CO_2 chemisorption. The coverage of the TiO_2 support increases from 31 ± 2% for the 3.3 wt% WO_3/TiO_2 catalyst to ca. 86±2% for catalysts with W loadings $\geqslant$ 10.3 wt% WO_3. The leveling off of the surface coverage for the high-loading catalysts has been attributed to the formation of W multilayers or bulk WO_3. The surface coverage values obtained by CO_2 chemisorption were consistent with those measured previously using ion scattering spectroscopy. The apparent suitability of CO_2 chemisorption for monitoring the surface coverage of TiO_2-supported catalyst systems, in contrast to previous results for Al_2O_3-supported systems, will be discussed.

Keywords: TiO_2-supported W catalysts, surface coverage of WO_3/TiO_2 catalysts, CO_2 chemisorption, ion scattering spectroscopy

1. Introduction

Supported tungsten catalysts are active for reactions such as isomerization, hydrogenation and alkene metathesis [1–3]. In addition, they form an important component of catalysts currently used for the removal of nitrogen oxides from flue gases [4]. For these catalysts and other supported systems, knowledge of the surface coverage of the supported phase is of interest. This can be readily conceived for bifunctional catalysts since the surface coverage determines the extent of participation of the support in the reaction. In addition, since surface coverage is directly related to the dispersion, it can be used as an index of catalytic activity or as a control parameter for monitoring catalyst preparation.

Titania-supported tungsten catalysts have been previously studied by a variety of techniques that include Raman spectroscopy [5–9], X-ray photoelectron spectroscopy (XPS) [7–9], X-ray absorption spectroscopy (XANES, EXAFS) [10], infrared spectroscopy (IR) [11], electron microscopy [12,13] and ion scattering spectroscopy (ISS) [14]. However, few studies have been devoted to monitoring the surface coverage of supported WO_3/TiO_2 catalyst systems [6–9,14].

The surface coverages of supported catalysts have been monitored by a variety of conventional and spectroscopic techniques including Raman spectroscopy [6–9], XPS [7–9], IR [15–18], ISS [14,19,20], CO_2 chemisorption [17,18,21–23] and low-temperature CO adsorption [23–26]. The advantages and limitations of these techniques have been discussed elsewhere [23].

Chemisorption of a probe molecule such as CO_2 is, in principle, one of the most simple approaches for surface coverage measurements. This method is based on the observation made by Segawa and Hall [21] that CO_2 selectively chemisorbs on the free alumina portion of the surface of a molybdena–alumina catalyst. However, reports from our laboratory [22] and by others [17,25] have shown that CO_2 chemisorption consistently overestimated the surface coverage for several alumina-supported catalyst systems. Mulcahy et al. [22] attributed this overestimation to the preferential adsorption of the metal oxide or supported species onto the same sites of the support that bind the CO_2 molecules. Similar explanations have been given by other authors [17,25].

Although there are strong indications that the CO_2 chemisorption method has been unsuccessful for alumina-supported catalyst systems, the technique has not been adequately tested for other supports. This might be of interest since a survey of the literature [27] indicates that reasonable coverage values can be calculated from the CO_2 chemisorption results reported for the Mo/TiO_2 system.

The present work will focus on the determination of surface coverage for a series of WO_3/TiO_2 catalysts by CO_2 chemisorption at room temperature and correlation of the results with previously reported values for the same series of catalysts using ion scattering spectroscopy. Although the latter technique has its limitations (the method is based on the assumption of uniform repartition of the supported phase between the inner and outer parts of the catalyst surface), it has been proven effective for surface coverage measurements [14,19,20].

2. Experimental

2.1. Catalyst preparation

Degussa P-25 TiO_2 (78/22 anatase/rutile ratio, pore

---

* To whom correspondence should be addressed.

volume ca. 0.5 cm^3/g, BET surface area 50±5 m^2/g) was mixed with deionized water and dried at 120°C for 8 h. The dried support was then ground with mortar and pestle, sieved to 100 mesh, and calcined in air at 400°C for 12 h before incipient wetness impregnation with ammonium metatungstate (ROC/RIC) solutions. The resulting WO_3/TiO_2 catalysts were then dried at 120°C for 16 h followed by calcination in air at 500°C for 16 h. The series of WO_3/TiO_2 catalysts were recalcined in air at 450°C for 4 h before CO_2 chemisorption experiments.

2.2. CO_2 chemisorption

CO_2 uptake was measured at room temperature in a conventional BET volumetric system. About 175 mg of the catalysts were heated to 350°C for 4 h in 10% O_2/He. Following pretreatment, the catalyst samples were evacuated at 350°C for 1 h and cooled to room temperature under high vacuum (1×10^{-5} Torr). Increasing amounts of CO_2 were then introduced into the system and the CO_2 adsorbed by the catalysts was recorded at six different pressures. CO_2 uptake for each catalyst was determined by extrapolating the adsorption isotherm to zero pressure.

From the CO_2 uptake, the surface coverage was calculated using the following equation:

$$\Theta = 1 - \{(CO_2)_{cat}/(CO_2)_{sup}n\}, \qquad (1)$$

where (CO_2) is the CO_2 uptake and n is the fraction of titania in the catalysts (since loadings are reported as wt% WO_3, the fraction of titania in the catalysts decreases as the W loading increases; this necessitates a correction factor, n).

3. Results and discussion

Fig. 1A shows the variation of CO_2 uptake as a function of W loading for WO_3/TiO_2 catalysts. The total amount of CO_2 chemisorbed by the catalysts decreases steadily from about 125 μmol/g to about 23 μmol/g as the W loading increases from 0.0 to 10.3 wt% WO_3. The amount of CO_2 chemisorbed by the TiO_2 support is comparable to the value reported in the literature [27]. There is no significant decrease in the amount of CO_2 chemisorbed with further increase in W loading.

Fig. 1B shows a plot of the surface coverage of the TiO_2 support determined from CO_2 adsorption results using eq. (1). The surface coverage steadily increases from 31 ± 2% for the 3.3 wt% WO_3/TiO_2 catalyst to about 84 ± 2% for the 10.3 wt% catalyst. Thereafter, the coverage levels off at about 86 ± 2%.

Fig. 2 compares the surface coverages obtained from CO_2 chemisorption with those measured by ion scattering spectroscopy reported earlier [14]. Clearly, there is reasonable agreement between the two methods. For a TiO_2 surface area of 50 m^2/g, assuming that the stoichiometry of the reaction between WO_3 and the surface hydroxyls is 1 : 1, a full monolayer coverage would require 8–10% WO_3 [28–30]. The shaded area in fig. 2

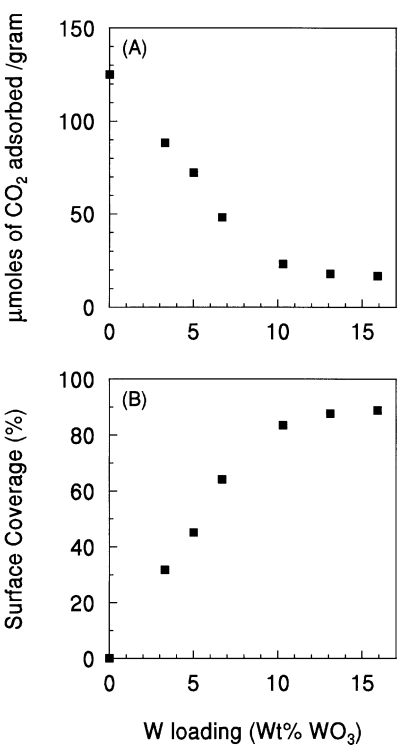

Fig. 1. (A) Total amount of CO_2 adsorbed by TiO_2 and WO_3/TiO_2 catalysts as a function of W loading. (B) Surface coverage of TiO_2 for a series of WO_3/TiO_2 catalysts obtained from the total CO_2 uptake (coverage = $1 - \{(CO_2)_{cat}/(CO_2)_{sup}n\}$).

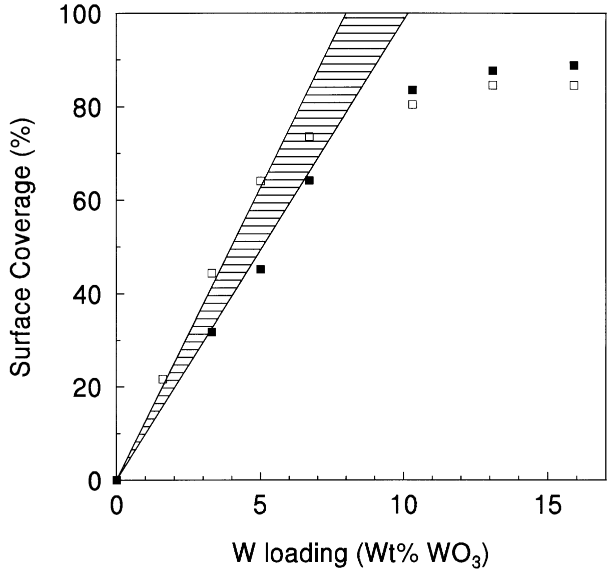

Fig. 2. Comparison of the surface coverage of TiO_2 for a series of WO_3/TiO_2 catalysts obtained using (□) ISS and (■) CO_2 chemisorption. The shaded area indicates the predicted range for W coverages, assuming monolayer dispersion. See text for details.

shows the predicted range of coverages for the series of WO_3/TiO_2 catalysts, assuming a monolayer-like dispersion. It is seen from fig. 2 that for W loadings $\leqslant 10.3$ wt% WO_3, the coverage values determined by the two techniques fall within the range of the predicted values for monolayer dispersion [28–30]. The leveling-off of the surface coverage of TiO_2 for higher W loadings is consistent with the formation of W multilayers or bulk WO_3.

It is interesting to note that the surface coverage values from CO_2 chemisorption correlate fairly well with those obtained previously using ion scattering spectroscopy. This is in contrast to Al_2O_3-supported catalyst systems, where the CO_2 chemisorption method consistently overestimated the surface coverage [17,18,22]. As mentioned earlier, the inadequacy of the CO_2 chemisorption method for the determination of the surface coverage of alumina-supported catalysts has been attributed to that initial additions of the supported species are preferentially adsorbed on the same sites that bind CO_2. These sites adsorb CO_2 in an *irreversible* manner, and represent only a small fraction of the total adsorption sites of the alumina support [22,23]. In contrast, CO_2 adsorption on TiO_2 has been shown to be almost completely reversible [31–35]. Thus, for titania-supported systems, the CO_2 chemisorption method is based on monitoring the *reversibly adsorbed* CO_2. Furthermore, a larger fraction of the titania surface is involved in the adsorption process compared to alumina (2.4 μmol of CO_2/m^2 for titania vs. 0.7 $\mu mol/m^2$ for alumina [23]). The fact that the CO_2 chemisorption method yields reasonable coverage values for WO_3/TiO_2 catalysts can be taken as an indication that the W species interact in a random fashion with the titania sites that reversibly adsorb CO_2.

4. Conclusion

It has been shown that CO_2 chemisorption can be used successfully for monitoring the coverage of WO_3/TiO_2 catalysts. The surface coverage of the TiO_2 support measured by the CO_2 chemisorption method increased from 32±2 to 84±2% as the W loading increases from 3.3 to 10.3 wt% WO_3. The coverage levels off with further increases in the W loading indicating formation of W multilayers or bulk WO_3.

The surface coverage values obtained by CO_2 chemisorption were consistent with those measured previously using ion scattering spectroscopy. For catalysts with W loadings $\leqslant 10.3$ wt% WO_3, these results were also in reasonable agreement with the predicted coverage values for monolayer dispersion. The apparent suitability of the use of CO_2 chemisorption for monitoring the surface coverage of WO_3/TiO_2 catalysts, in contrast to previous results relative to the Al_2O_3-supported systems, has been attributed to a non-selective interaction of the W species with the titania sites that reversibly adsorb CO_2.

Acknowledgement

The authors acknowledge financial support for this work from the US Department of Energy, Grant DE FG02-87ER13781.

References

[1] T. Yamaguchi, Y. Tanaka and K. Tanabe, J. Catal. 65 (1980) 442.

[2] R. Thomas, E.M. van Oers, V.H.J. de Beer, J. Medema and J.A. Moulijn, J. Catal. 76 (1982) 241.

[3] J.C. Mol and J.A. Moulijn, in: *Catalysis – Science and Technology*, Vol. 8, eds. J.R. Anderson and M. Boudart (Springer, Berlin, 1987) p. 69.

[4] M. Imanari, Y. Watanabe, S. Matsuda and F. Nakajima, *Proc. 7th Int. Congr. on Catalysis*, eds. T. Seiyama and K. Tanabe (Elsevier, Amsterdam, 1981) p. 841.

[5] S.S. Chan, I.E. Wachs, L.L. Murrell, L. Wang and W.K. Hall, J. Phys. Chem. 88 (1984) 5831.

[6] S.H. Han, H.S. Kim and K. Kim, Bull. Korean Chem. Soc. 12 (1991) 80.

[7] G.C. Bond, S. Flamerz and L. van Wijk, Catal. Today 1 (1987) 229.

[8] M.A. Vuurman, I.E. Wachs and A.M. Hirt, J. Phys. Chem. 95 (1991) 9928.

[9] R.B. Quincy, M. Houalla and D.M. Hercules, Fresenius J. Anal. Chem. 346 (1993) 676.

[10] F. Hilbrig, H.E. Göbel, H. Knözinger, H. Schmelz and B. Lengeler, J. Phys. Chem. 95 (1991) 6973.

[11] G. Ramis, G. Busca, C. Cristiani, L. Lietti, P. Forzatti and F. Bregani, Langmuir 8 (1992) 1744.

[12] A. Burrows, C.J. Kiely, R.W. Joyner, H. Knözinger and F. Lange, in: *Materials and Processes for Environmental Protection*, Mater. Res. Soc. Symp. Proc. 344 (1994) 33.

[13] A. Burrows, R.W. Devenish, R.W. Joyner, C.J. Kiely, H. Knözinger and F. Lange, in: *Electron Microscopy and Analysis 1993*, Inst. Phys. Conf. Ser. 138 (1993) 481.

[14] J.N. Fiedor, M. Houalla, A. Proctor and D.M. Hercules, Surf. Interf. Anal. 23 (1995) 234.

[15] W.S. Millman, M. Crespin, A.C. Cirillo, S. Abdo and W.K. Hall, J. Catal. 60 (1979) 404.

[16] O.V. der Meer and P. Mars, J. Catal. 42 (1976) 79.

[17] N.-Y. Tøpsoe and H. Tøpsoe, J. Catal. 139 (1993) 631.

[18] M.A. Eberhardt, M. Houalla and D.M. Hercules, Fresenius J. Anal. Chem. 350 (1994) 570.

[19] F.M. Mulcahy, M. Houalla and D.M. Hercules, Anal. Chem. 62 (1990) 2232.

[20] M.A. Eberhardt, M. Houalla and D.M. Hercules, Surf. Interf. Anal. 20 (1993) 766.

[21] K. Segawa and W.K. Hall, J. Catal. 77 (1982) 221.

[22] F.M. Mulcahy, K.D. Kozminski, J.M. Slike, F. Ciccone, S.J. Scierka, M.A. Eberhardt, M. Houalla and D.M. Hercules, J. Catal. 139 (1993) 688.

[23] V. Sazo, L. Gonzalez, J. Goldwasser, M. Houalla and D.M. Hercules, Surf. Interf. Anal. 23 (1995) 367.

[24] M.I. Zaki, B. Vielhaber and H. Knözinger, J. Phys. Chem. 90 (1986) 3176.

[25] A.L. Diaz and M.E. Bussell, J. Phys. Chem. 97 (1993) 470.

[26] V. Sazo, C. Scott, M.J. Perez Zurita, E.J. Eljuri and J. Goldwasser, J. Catal. 148 (1994) 392.

[27] D.S. Kim, Y. Kurusu, I.E. Wachs, F.D. Hardcastle and K. Segawa, J. Catal. 120 (1989) 325.

[28] V.H.P. Boehm and H. Herrmann, Anorg. Allg. Chem. 352 (1967) 156.

[29] A.J. van Hengstum, Thesis, Twente University of Technology, Enschede, The Netherlands (1984).

[30] J.A.R. van Veen, F.T.G. Velmaat and G. Jonkers, J. Chem. Soc. Chem. Commun. (1985) 1656.

[31] C. Morterra, A. Chiorino, F. Boccuzi and E. Fisicaro, Phys. Chem. 124 (1981) 211.

[32] K. Tanaka and J.M. White, J. Phys. Chem. 86 (1982) 4708.

[33] B.D. Yates, J. Phys. Chem. 65 (1961) 746.

[34] C. Morterra, A. Chiorino, A. Zecchina and E. Fisicaro, Gazz. Chim. Ital. 109 (1979) 683.

[35] M. Primet, P. Pichat and M. Mathieu, J. Phys. Chem. 75 (1971) 1216.