Thermodynamics of Carbon Monoxide Adsorption on Polycrystalline Titania Studied by Static Adsorption Microcalorimetry

Xinyu Xia,* Wilma Busser, Jennifer Strunk, and Martin Muhler

Laboratory of Industrial Chemistry, Ruhr-University Bochum, D-44780 Bochum, Germany

Received May 24, 2007. In Final Form: July 18, 2007

The adsorption of CO on polycrystalline TiO2 was investigated by static adsorption microcalorimetry. The initial differential heat of adsorption (q_{diff}) of CO on polycrystalline titania is 40 kJ/mol, and the standard adsorption entropy (ΔS{sub std}) is ~104 J mol{sup -1} K{sup -1}. These results are consistent with those derived from temperature-programmed desorption and FTIR results in the literature. The good reproducibility of the isotherms and the stable q_{diff} indicate that the lattice oxygen and hydroxyl groups on titania surface are basically not reactive to adsorbed CO.

1. Introduction

Titania is a widely used support material in heterogeneous catalysis, and its surface properties have been investigated extensively. (See refs 1–3 and references therein.) The titania-supported gold catalyst is the most deeply studied gold catalyst. The heat of adsorption of CO on the 110 face of rutile TiO2 (110) has been extensively. (See refs 1–3 and references therein.) The titania-supported gold catalyst is the most deeply studied gold catalyst. The heat of adsorption of CO on the 110 face of rutile TiO2 (110) has been extensively. (See refs 1–3 and references therein.)

* Corresponding author. Current address: Department of Chemical Engineering, University of California at Berkeley, Berkeley, California 94720. E-mail: xinyu_xia@berkeley.edu.


2. Experimental Section

The titania powder used in this work was Degussa P25 with a surface area of 55 m{sup 2}/g. Its surface has a patchwise structure consisting of 10% rutile and 90% anatase. Before the calorimetric measurement, two samples (0.3 g for each) were pretreated for 4 h in dilute oxygen (99.97% O{sub 2} in Ar, O{sub 2} purity 99.995%, Ar purity 99.999%), one at 250 °C and the other at 400 °C, in order to check the effect of thermal pretreatment. After pretreatment, each sample was sealed in a capsule filled with pretreating gas.

The microcalorimetry system and experimental procedures are similar to those in our previous work.12 After the sample capsule was introduced into the sample cell, the whole microcalorimeter setup was baked for 72 h at 145 °C. The sample capsule was crushed with the linear-motion feedthrough, followed by evacuation for 30 min. The adsorption temperature was 30 °C, and the purity of CO adsorptive gas was 99.997%. N{sub 2} (99.9999%) was used as the nonadsorptive gas for pressure compensation.

Adsorption on each sample was measured twice to test the reversibility. Between the two adsorption measurements, the sample was evacuated overnight at 30 °C. To obtain the hydrated sample, each sample after two periods of CO adsorption was exposed to saturated water vapor at 40 °C for 24 h in the microcalorimeter setup, followed by evacuation at 120 °C for 72 h. Adsorption of CO on two hydrated samples was also measured at 30 °C.

3. Results and Discussion

Figure 1 shows the isotherms of CO adsorption on titania samples after different pretreatment. The coverage increases nearly proportionally with pressure in all measurements, which is to say that they are all Henry isotherms (the deviation will be discussed below). This means that the surfaces are far from saturation under the experimental pressure, no matter whether the adsorption is on an energetically homogeneous or heterogeneous surface.14 For a given pressure, the equilibrium coverage on the hydrated sample is the lowest, and on the 400 °C pretreated sample, it is the highest, indicating that the adsorption sites are preferably occupied by hydroxyl groups. The isotherms of repeated measurements show that the adsorption is reversible at room temperature under the experimental vacuum (<10{sup -3} Pa in the adsorption cell and <10{sup -7} Pa near the pump). There are...