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Structure sensitivity of cyclopropane hydrogenolysis on carbon-supported platinum

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ABSTRACT

There has been debate in the past as to whether or not cyclopropane hydrogenolysis is a structure sensitive reaction. This paper addresses the structure sensitivity of cyclopropane hydrogenolysis on Pt using K^+ addition to Pt/C and compares the results to those for CO hydrogenation, a classic structure insensitive reaction. Kinetic parameters determined for both reactions show the effect of K^+ on Pt to be limited to simple site blockage at the reaction conditions used. Determination of the site ensemble size (number of contiguous surface metal atoms) required for reaction using Martin's model suggests that cyclopropane hydrogenolysis requires a site ensemble size of ca. 7, whereas the structure insensitive CO hydrogenation reaction requires only an ensemble size of ca. 1. In addition, evidence suggests that K^+ decorates Pt non-uniformly.

1. Introduction

The reaction of cyclopropane with hydrogen has been studied extensively on a wide variety of metal catalysts [1–8], and in particularly Pt [1,3,9–13]. This hydrogenolysis reaction, termed so due to the characteristic ring opening of cyclopropane, has been observed to yield three different sets of products depending on the metal and conditions used:

$$cC_3H_6 + H_2 \rightarrow C_3H_8 \quad (1)$$

$$cC_3H_6 + 2H_2 \rightarrow CH_4 + C_2H_6 \quad (2)$$

$$cC_3H_6 + 3H_2 \rightarrow 3CH_4 \quad (3)$$

Reactions (2) and (3), termed "selective" and "non-selective hydrocracking", respectively, have been observed to occur on metals such as Fe, Os, and Ru with a shift toward the latter reaction as temperature increases [3,5,7,8]. However, on metals such as Pt, Pd, Ir, and Rh, only reaction (1) has been observed [3,4,11,13].

The structure sensitivity of the three cyclopropane reactions has been widely debated in the literature; and within this debate, the structure sensitivity of reaction (1) on Pt has particularly been discussed. Early works by Boudart et al. [9] and Kahn et al. [12] comparing the specific activity of the hydrogenolysis reaction as a function of metal surface area and dispersion showed the turnover frequency (TOF) to vary by a factor of only 2 for various loadings of Pt on alumina/silica and for certain Pt single crystal planes investigated. Based on the hypothetical vast difference in surface structural characteristics of the metal between supported and single crystals of Pt, the authors concluded that the reaction was structure insensitive to particle size, nature of support, or method of preparation. Later, work by Gallaher et al. [4] on La_2O_3-supported Rh, which, like Pt, is only active for reaction (1), showed the reaction rate to increase linearly with an increase in Rh dispersion and suggested that the activity vs. dispersion on a TOF basis is constant and similar in behavior to that of other structure insensitive reactions.

On the other hand, Oteroschipper et al. [13] confirmed the factor of 2 difference in TOF observed by Boudart et al. [9] but found it to be beyond experimental uncertainty for a wide range of dispersed Pt/SiO_2 catalysts. They concluded that, for this difference to be real, the reaction must be at least moderately structure sensitive. Similar conclusions have been suggested in more recent works by Jackson et al. [11] and Sajkowski et al. [6], in which the activity of cyclopropane hydrogenolysis appeared to depend on the particle size of the various supported Pt and Ru catalysts investigated. It should be noted that, while Ru is active for reactions (1) and (2), both reactions appear to have the same rate determining step, which is the ring opening of cyclopropane and formation of a common intermediate [6].

It should be pointed out that the "structure sensitivity" of a particular reaction entails not just (a) an effect of particle size related to crystal planes exposed on the observed rate or TOF of the reaction. Parameters that can also affect the rate of a structure sensitive reaction are as follows: (b) coordination numbers of the active metal surface atoms in the active sites and (c) the number of contiguous metal surface atoms or ensemble size required for reaction. A general

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change in particle size and/or dispersion can potentially change the characteristics of all three parameters above and, depending on how "structure sensitive" the specific reaction is, the effect on the resulting reaction kinetics can be moderate to significant. In addition to particle size, the shape of a metal particle may also be an issue. However, a more specific investigation of structure sensitivity of a reaction on a metal catalyst can be made without varying metal particle size but by decoration of the metal surfaces using an additive or poison that effectively blocks surface metal atoms.

This paper reports, for the first time, the results of an investigation into the structure sensitivity of cyclopropane hydrogenolysis on Pt using a series of K^+-doped Pt/C catalysts prepared via sequential impregnation of the pre-reduced supported metal catalyst to prevent modification of the particle size distribution. Potassium was chosen due to evidence suggesting the promoter-metal interactions to be limited to simple site blocking on Pt and other noble metals if impregnated sequentially [14,15]. The methodology of this investigation is similar to that of Hoost and Goodwin [15] and utilizes the statistical dependence of the rate of structure sensitive reactions on simple site blockage originally established and reviewed in detail by Martin [16] in determining the approximate ensemble size required for reaction. In addition, results for the hydrogenation of CO, a classic structure insensitive reaction, on the K^+-modified Pt/C catalysts are also presented to contrast to those for cyclopropane hydrogenolysis. Due to the low temperature required for cyclopropane hydrogenolysis, if this reaction were shown to be structure sensitive, it could be used to characterize Pt catalyst surfaces in catalysts not stable at higher temperatures, such as Nafion-Pt/C, which is used as the anode catalyst in proton exchange membrane fuel cells (PEMFCs).

2. Experimental

2.1. Catalyst preparation

A commercial carbon-supported Pt (Pt/C) with a nominal Pt loading of 20 wt.% was purchased from BASF and used as received. It was confirmed by BASF that the carbon black support (Vulcan XC-72) was purchased in-bulk from Cabot Co. and used directly for the synthesis of the Pt/C catalyst.

A portion of the purchased Pt/C catalyst were impregnated sequentially via incipient wetness with aqueous KNO_3 solutions of varying concentrations to prepare a series of K^+-doped catalysts with theoretical $(K/Pt_T)_{atom}$ ratios of 0, 0.1, 0.2, 0.4, and 0.8, where Pt_T stands for the total amount of Pt available. In order to obtain a more uniform distribution of the potassium for each batch, the KNO_3 (Sigma Aldrich, 99.999% purity) was dissolved in 30 mL of distilled water and added drop-wise to the catalyst until incipient wetness was achieved. The wet catalyst was then placed in a static oven at 90 °C for ca. 20 min to dry and the process was repeated until the entire solution has been used. The K^+-free Pt/C catalyst was treated with only distilled water to check for possible effects from the impregnation process. After impregnation, the material was dried at 90 °C overnight in a static air oven, then crushed, and sieved to obtain a catalyst particle size distribution of 60–180 μm. Nominal Pt and K compositions were confirmed via elemental analysis (performed by Galbraith Laboratories) for all catalysts. The K^+-modified Pt/C catalysts are designated as *xx*K/Pt to indicate $(K/Pt_T)_{atom} = xx/100$. It should be noted that the $(K/Pt_T)_{atom}$ ratio is based on the total amount of Pt in the catalyst.

2.2. Characterization methods

2.2.1. BET

Physical characteristics of the catalysts such as BET surface area, pore size, and pore volume measurements were performed in a Micromeritics ASAP 2020 unit. Samples of as-received Pt/C and K^+-promoted Pt/C catalysts were degassed under vacuum (10^{-3} mm Hg) at 110 °C for 4 h prior to analysis. Results were obtained from N_2 adsorption isotherms at -196 °C.

2.2.2. Static H_2 chemisorption

Static chemisorption experiments using H_2 were performed at 35 °C in a Micromeritics ASAP 2010 equipped with a chemisorption controller station. Catalysts were first reduced in H_2 at 80 °C for 3 h followed by an evacuation at 80 °C (10^{-5} mm Hg) for another 3 h prior to the start of the analysis. A low reduction temperature of 80 °C was chosen in order to be able to apply the results of this study to an investigation of temperature sensitive catalysts such as Nafion® supported on Pt/C. Nafion® polymer is an integral part of PEMFC Pt/C catalysts but is structurally unstable at higher temperatures. While no Nafion® was present on the Pt/C catalyst investigated here, the low reduction temperature was used to adhere to conditions employed for fuel cell catalysts. Temperature-programmed reduction (TPR) results has shown Pt/C catalysts to be fully reduced at these conditions [17]. After evacuation, the temperature was adjusted to 35 °C and the H_2 isotherms were obtained from 50 to 450 mm Hg at increments of 50 mm Hg. Volumetric uptakes of CO or H_2 on the catalysts were determined from the total adsorption isotherm of the specified gas by extrapolating the linear portion of the isotherm in the higher pressure region to zero pressure. These values were then used in determining total available Pt surface atom concentration (Pt_S) and metal dispersion by assuming stoichiometric ratios of 1:1 for H/Pt_S. Calculation of average Pt particle size was carried out using the metal dispersion approximated from the chemisorption results and has been shown to correlate very well with the average Pt particle size results obtained from TEM images [17].

2.2.3. TEM and XRD

Transmission electron microscopy (TEM) images of Pt/C and K^+-promoted catalysts were obtained using a TEM-Hitachi 9500, which offers 300 kV high magnification TEM and is designed for atomic resolution. Preparation of copper sample grids is explained in detail elsewhere [17]. Approximate Pt particle sizes of the catalysts were obtained by averaging diameters of 100+ particles from the TEM images. The results were further confirmed via X-ray Diffraction (XRD) (Scintag XDS 2000 powder diffractometer equipped with Cu Kα radiation) with a scanning range from 20° to 85° and a step-size of 0.02°/min.

2.3. Cyclopropane hydrogenolysis

Cyclopropane hydrogenolysis reaction rate results were obtained at 30 °C and 1 atm utilizing a conventional plug flow, micro-reactor system similar to the one described in Ref. [17] with a tubular quartz reactor with an internal diameter of ca. 5 mm. Due to the high activity of Pt for this reaction [3], low amounts of catalysts and a low partial pressure of C_3H_6 (American Gas Group, UHP) in the feed stream were required in order to achieve differential conditions for adequate kinetic analysis. To this end, 1.5–5 mg of the *xx*K/Pt catalysts (depending on activity) were diluted uniformly with 38.5–35 mg of XC-72, respectively, to achieve a catalyst bed of ca. 1 cm in thickness. Prior to reaction, the catalysts were reduced in 100 sccm of H_2:Ar (50:50) (National Specialty Gases, UHP) for 3 h at 80 °C and 1 atm. After reduction, the temperature was decreased from 80 °C to 30 °C and stabilized. Reaction was initiated by flowing a gas mixture of C_3H_6:H_2:Ar (1:50:149) (total flow = 200 sccm) through the catalyst bed and allowing the reaction to stabilize for 5 min before sampling the gas effluent with a Varian 3800 GC equipped with FID and a Restek RT-QPLOT column (30 m, 0.53 mm ID). It is meaningful to note