



A simple method for CO chemisorption studies under continuous flow: Adsorption and desorption behavior of Pt/Al₂O₃ catalysts

Canan Karakaya^a, Olaf Deutschmann^{a,b,*}

^a Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany

^b Institute for Catalysis Research and Technology, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany

ARTICLE INFO

Article history:

Received 26 April 2012

Received in revised form 17 August 2012

Accepted 18 August 2012

Available online 25 August 2012

Keywords:

Metal dispersion

CO chemisorption

Pt/Al₂O₃

Adsorption

Desorption

ABSTRACT

A simple and rapid method for the determination of metal dispersion of technical catalysts is presented, which is based on temperature-programmed desorption (TPD) of pre-adsorbed CO in a continuous-flow reactor at atmospheric conditions. A commercial Pt/Al₂O₃ diesel oxidation catalyst is studied as an example. In the TPD spectra, desorption of CO as well as CO₂ is considered. Furthermore, a pulse adsorption technique is applied to better understand the adsorption–desorption behavior and the oxidation of CO. Metal dispersion based on the TPD methods presented agrees well with data derived from H₂ and CO chemisorption measurements using commercial set-ups.

© 2012 Elsevier B.V. All rights reserved.

1. Introduction

Gas adsorption is a very frequently used method for the characterization of heterogeneous catalysts in order to quantify the active surface area of the supported metal catalysts such as Pt, Pd, and Rh [1,2] and determine the metal dispersion of fresh and used catalysts. In exhaust gas after-treatment, for instance, the reduction in conversion of pollutants due to on-road aging of the catalysts (Pt, Pd, and Rh) is directly related to the total number of adsorption sites available for CO chemisorption [3,4]. The effects of catalyst agglomeration, loss, and poisoning on the overall reaction rate could be governed by a single scalar, i.e., the number of active sites available for CO chemisorption.

Metal dispersion is expressed as the ratio of the total number of metal atoms on the metal surface accessible to the adsorbate species to the total number of metal atoms in the sample [5]. H₂ and CO are the most frequently used probe molecules [6,7]. In the past, the understanding of surface properties of transition metals and metal oxides was often based on the studies of ultra-high vacuum conditions (UHV). However, chemisorptive and catalytic properties at atmospheric conditions may significantly differ from those at UHV conditions [6].

The aim of this study is to establish a simple and rapid chemisorption technique for the quantification of metal dispersion on different types of supported metal catalysts as well as of the different structures such as monoliths, pellets, and granules, without using a sophisticated apparatus and UHV conditions. Such a technique can not only help to understand the catalytic behavior under operating conditions, i.e., at atmospheric pressure and in flow, but also the same apparatus can be used to repeatedly study the kinetics and Temperature Programmed Desorption (TPD) upon certain treatments (aging, poisoning, and storage of adsorbates). Here, we present exemplary results for diesel oxidation catalysts (DOC) based on Pt/Al₂O₃ washcoated on honeycomb-structured cordierite monoliths. In order to compare the dispersion data, which were achieved by means of our method with data from commercial devices, the monoliths were crushed and used in a fixed-bed reactor configuration. The method also works well with intact monolithic structures without any modification.

CO TPD under continuous flow has been studied before. Foger and Anderson [8] showed that a considerable amount of CO₂ was detected when TPD of chemisorbed CO was carried out on Pt/Al₂O₃ catalysts. They also showed that a considerable amount of CO₂ desorbed above 450 K and the desorption spectra reached their maxima at 820 K. It was generated by a reaction between CO and the residual water that originated from the dehydrated γ -alumina support [8]. Dropsch and Baerns worked with Pd/Al₂O₃ catalyst and showed that CO₂ was generated via the Boudouard reaction of CO when CO₂ reached a significant level above 500 K [9]. Another study performed by Lear et al. showed that CO oxidation was

* Corresponding author at: Institute for Chemical Technology and Polymer Chemistry, Karlsruhe Institute of Technology (KIT), D-76131 Karlsruhe, Germany. Tel.: +49 721 608 43064; fax: +49 721 608 44805.

E-mail address: deutschmann@kit.edu (O. Deutschmann).

significant above 500 K and reached its maximum at around 760 K when water gas shift reaction took place between chemisorbed CO and the hydroxyl groups associated with the alumina support [10]. Föttinger et al. also showed that WGS reaction is generated between the adsorbed CO and OH species on the support of Pd/Al₂O₃ catalyst [11].

In our study, we also observed a considerable amount of CO₂ desorption during CO chemisorption TPD on a Pt/Al₂O₃ catalyst. To investigate the origin of the CO₂ formation, a CO pulse technique was applied to measure the adsorbed amount of CO and quantify the desorbed amount of CO and CO₂. Adsorption studies were carried out at different temperatures to investigate the oxidation behavior of the adsorbed amount of CO on the surface. Dispersion results based on our CO and CO₂ signals were compared with CO and H₂ dispersion data obtained in commercial devices. Additionally, CO oxidation was studied in the same continuous-flow apparatus by measuring the CO conversion as a function of temperature.

2. Experimental

2.1. Catalyst

The catalyst studied is a commercial honeycomb-structured diesel oxidation catalyst (DOC) made of cordierite with 0.114 wt.% Pt loading dispersed in an Al₂O₃ washcoat (DOC20). The specific surface area of the catalyst is determined by nitrogen adsorption at 77 K with the Brunauer Emmett Teller (BET) method. The BET measurements are carried out in a Belsorb Mini II apparatus.

2.2. Experimental set-up

A continuous-flow reactor set-up was designed to be used for both adsorption and desorption studies under atmospheric pressure as shown in Fig. 1. Ar, H₂, and CO gases are fed to the reactor by mass flow controllers (MKS) for the continuous-flow applications. An automated six-port valve (VICI Valco Instruments Co. Inc.) configuration is applied to generate pulses for the adsorption studies. When the six-port valve is at position A, it is connected to a vacuum pump and the sample loop (0.26 cm³) is evacuated. Then the loop is filled with pure CO at constant pressure (600 mbar) and room temperature. Having thus defined volume, pressure, and temperature, 6.3×10^{-3} mmol CO is loaded in the sample loop. By changing the six-port valve's position to B, this defined amount of CO in the sample loop is pulsed to the reactor. The system works with different structures of catalyst supports, such as pellets, powders, or monoliths. For this purpose, two different reactor configurations are established. In this study, the catalyst was crushed and placed in a 10 mm outer diameter (OD) quartz reactor to reduce dead volume. For monolithic structures, a 25.4 mm OD quartz reactor is used instead. The catalyst is positioned in the center of the reactor and fixed there with quartz wool.

The reactor is housed in a temperature-controlled furnace and the temperature inside the catalyst bed is measured by a K-type thermocouple (NiCr-Ni, 3 mm thick). The system has a by-pass line with 6 mm OD made of stainless steel, which is designed for sample loop calibrations. Flow directions between the reactor and the by-pass line can be controlled by three-way valves. The outlet gas is connected to a chemical ionization mass spectrometer (MS) (Airsense 500, V&F) and an infrared detector (IR) (BINOS 100, Emerson Process). MS is used for detailed investigations, and O₂, CO, and CO₂ species are detected, whereas for repeated measurements, IR is chosen to measure CO and CO₂ species. The effect of high signal-to-noise ratio of MS signals to the metal dispersion calculations is also examined. Continuous-flow CO chemisorption measurement

at room temperature is repeated by using IR with 500 ml/min flow rate. The result is given in Supplementary data in Fig. 1.

Flow direction between MS and IR is controlled by means of a three-way valve configuration.

2.3. Measurements without catalyst

For the quantification of amount of possible adsorbed CO by the sealings and quartz wool, the reactor is first operated without catalyst. The empty reactor (10 mm OD with quartz wool) is subjected to the continuous-flow CO adsorption measurement. The pre-treatment procedure described in Section 2.4 is applied and a TPD measurement is carried out. CO, CO₂, and O₂ species are analyzed in the outlet gas composition by using an MS.

2.4. Continuous-flow TPD studies

The amount of 1 g of the crushed monolith catalyst is placed in a quartz tube reactor leading to a 30 mm catalyst bed. The total flow rate in the reactor is always 1 SLPM (standard liter per minute at 293 K and 1 atm).

Before the analysis, the catalyst is subjected to a pre-treatment procedure. For this purpose, the catalyst is first oxidized by 21 vol.% O₂ (Air Liquide, 99.95% purity), diluted in Ar (Air Liquide, 99.996% purity), with a total flow rate of 1 SLPM for 1 h at 773 K. After flushing with Ar for 30 min, the catalyst is reduced by 4 vol.% H₂ (Air Liquide, 99.996% purity) in Ar at 673 K for 1 h.

For the TPD measurement, the reactor is cooled down to room temperature (290 K). Then, 1 vol.% CO (Air Liquide, 99.97% purity), diluted in Ar, is fed to the reactor for 1 h to saturate the metal surface. Physisorbed CO is removed by flushing with Ar gas for another 30 min at room temperature. TPD is performed with a heating rate of 28 K/min from room temperature to the maximum temperature of 790 K under continuous Ar flow. The heating rate of 28 K/min was chosen for achieving a better signal/noise ratio. Similar heating rates were also used in literature (3–50 K/min) [8–10,12]. The heating rate only affects the desorption profile of the peaks. Higher heating rates yield sharp peaks, whereas lower heating rates result in wider peak shapes. 28 K/min is the maximum heating rate of the oven and yields reasonably sharp peak spectra that permit repeatable analyses.

The outlet gas composition is monitored during the TPD.

2.5. CO pulse adsorption at room temperature

To investigate the origin of CO₂ peaks derived during continuous-flow CO TPD measurements, a CO pulse technique is applied at atmospheric pressure and room temperature. First, the pre-treatment procedure described in Section 2.4 is applied for the continuous-flow TPD measurements. CO pulses are injected by means of the automated six-port valve configuration. The defined amount of pure CO (6.30×10^{-3} mmol) is pulsed to the reactor in 1 SLPM Ar carrier gas. Between the pulses, the reactor is kept under 1 SLPM Ar flow. The outlet gas composition is monitored by the MS. Desorption of CO and CO₂ species is detectable as Gaussian peaks. The pulsation is continued until desorption peaks reach the saturation value. In practice the pulsation was terminated when two consecutive CO peaks resulted in an equal amount of CO observed according to the peak area. The CO pulsation is followed by a TPD measurement carried out between the temperatures of 290 K and 790 K with a fixed ramp of 28 K/min.

2.6. CO pulse adsorption at high temperatures

CO pulse adsorption measurements are also carried out at higher temperatures. After the same pre-treatment procedure as

Download English Version:

<https://daneshyari.com/en/article/40720>

Download Persian Version:

<https://daneshyari.com/article/40720>

[Daneshyari.com](https://daneshyari.com)