Activation of Carbon Dioxide on ZnO Nanoparticles Studied by Vibrational Spectroscopy†

Heshmat Noei,‡ Christof Wöll,§ Martin Muhler,‡ and Yuemin Wang*,‡,§

Laboratory of Industrial Chemistry and Department of Physical Chemistry I, Ruhr-University Bochum, 44780 Bochum, Germany, and Institute of Functional Interfaces, Karlsruhe Institute of Technology, 76021 Karlsruhe, Germany

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The activation of CO₂ on clean and hydroxylated ZnO nanoparticles has been studied by ultrahigh vacuum FTIR spectroscopy (UHV-FTIRS). Exposing the clean ZnO powder samples to CO₂ at 300 K leads to the formation of a number of carbonate-related bands. A detailed assignment of these bands was carried out using isotope-substitution experiments with C¹₈O₂. On the basis of vibrational and thermal stability data for ZnO single crystal surfaces, a consistent description of the interaction of CO₂ with ZnO powder particles can be provided: (1) on the mixed-terminated ZnO(1010) facets, a tridentate carbonate is formed; (2) on the polar, O-terminated (0001) facets, a bidentate carbonate species is formed via CO₂ activation at oxygen vacancy sites; and (3) additional monodentate or polydentate carbonate species are formed at defect sites such as steps, edges, kinks, and vacancies. The formation of carbonate-related vibrational bands is observed at an exposure temperature as low as 100 K, thus demonstrating the high activity of ZnO nanoparticles with regard to CO₂ activation.

1. Introduction

The activation of CO₂ is a topic of fundamental and applied interest in catalysis, electrochemistry, and environmental chemistry.1–6 Because zinc oxide is used as a catalyst for methanol synthesis from syngas (mixture of H₂, CO, and CO₂),7,8 it is an obvious candidate for activating the rather inert carbon dioxide molecule. In addition to the interesting chemical properties of ZnO, for example, in connection with other catalytic processes such as the water gas shift reaction,9 this transition-metal oxide presently receives a huge amount of attention because of its unique electrical and optical properties.10–16

In past investigations have been reported on CO₂ adsorption on polycrystalline ZnO powder surfaces. In particular, adsorption energies were determined using temperature-programmed desorption (TPD),17 adsorption isotherm measurements,18 and microcalorimetry.19,20 So far, only very few infrared spectroscopy studies have been reported for this system.21 Therefore, the identification of the precise nature of CO₂-related species present on polycrystalline ZnO nanoparticles has remained a challenge, and for most of the bands present in the complex IR spectra recorded for ZnO powders exposed to CO₂, a reliable assignment is missing. Within the so-called “surface science” approach to understanding heterogeneous catalysis, experimental and theoretical studies on well-defined single crystal substrates provide the basis for unraveling the microscopic mechanisms of chemical processes taking place at surfaces of nanoparticles.22 Here this successful approach is applied to the activation of CO₂, the most important greenhouse gas, on polycrystalline ZnO nanoparticles. Vibrational spectroscopy is one of the most informative methods when it comes to a thorough characterization of adsorbates on solid surfaces. Recently, we have systematically investigated the adsorption and subsequent reactions of various molecules on metal oxide single crystal surfaces by employing high-resolution electron energy loss spectroscopy (HREELS).23–31 By combining the vibrational data with other experimental results as well as with theoretical results, we have obtained detailed information about the interaction of CO₂ with differently oriented ZnO surfaces.25,26,31 The corresponding results will be briefly summarized in Section 3.1. To be able to use this information for an understanding of the chemical phenomena occurring at surfaces of ZnO powder particles, we have designed a novel ultrahigh vacuum infrared spectroscopy (UHV-FTIRS) apparatus, which not only allows us to record high-quality IR data at grazing incidence on well-defined oxide single crystal surfaces but also makes it possible to carry out IR experiments in transmission for oxide powder particles.32 The good performance of this UHV-FTIRS apparatus has been demonstrated by investigating the interaction of water with clean, adsorbate-free ZnO powder particles.33 According to the HREELS and thermal stability data obtained for single crystal surfaces, the different bands in the complex OH regime of IR powder data could be assigned in a one-by-one fashion to hydroxyl groups bound to different adsorption sites on the nanoparticle surfaces.

In this article, we report on an investigation of the activation of CO₂ on clean and hydroxylated ZnO nanoparticles at different temperatures by means of UHV-FTIRS. The interaction of CO₂ with ZnO is of complex nature, as evidenced by broad adsorbate-induced IR bands indicating the presence of many different surface species. We will provide a complete assignment of the IR bands, which allows us to gain rather deep insight into the activation of CO₂ on ZnO and to derive a consistent picture describing the vibrational, energetic, and structural properties of carbonate species on surfaces of ZnO powders.

2. Experimental Section

The sample used in this study was polycrystalline ZnO (NanoTek, provided by Nanophase Technologies; purity: >99%). It was prepared by physical vapor synthesis based on the