The interaction of carbon monoxide with clean and surface-modified zinc oxide nanoparticles: A UHV-FTIRS study

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Abstract

The interaction of CO with differently modified polycrystalline ZnO has been studied by FTIR spectroscopy under ultrahigh vacuum conditions (UHV-FTIRS). After exposing the clean, adsorbate-free ZnO nanoparticles to CO at 110 K we observe an intense vibrational band at 2187 cm$^{-1}$, which is assigned to a majority of CO species bound to the Zn$^{2+}$ sites on the mixed-terminated ZnO(1 0 1 0) surface. After the exposure of CO$_2$-pretreated ZnO nanoparticles to CO at 110 K, a new CO band is observed at 2215 cm$^{-1}$, which originates from CO species adsorbed on the “free” Zn sites embedded within the (2 × 1) tridentate carbonate structure on the ZnO(1 0 1 0) surface. UHV-FTIRS data recorded at different sample temperatures demonstrate that the binding energy of CO on polycrystalline ZnO is substantially increased in the presence of pre-adsorbed CO$_2$. The presence of hydroxyl species on the ZnO powder particles does not lead to substantial changes of the CO vibrational bands detected at 110 K under UHV conditions.

Keywords: Vibrational spectroscopy, Carbon monoxide, Zinc oxide, Infrared spectroscopy, Carbon dioxide, Hydroxyl groups, Heterogeneous catalysis

1. Introduction

The interaction of carbon monoxide with zinc oxide is an important topic in heterogeneous catalysis, because CO is the carbon source for the methanol production from syngas (CO/CO$_2$/H$_2$) over ZnO catalysts [1]. Furthermore, CO is a very useful probe molecule to monitor the structure of metal oxide surfaces [2,3]. In the past, a number of infrared spectroscopy (FTIR) studies focused on the adsorption of CO on ZnO powder samples [4-8]. The adsorption energy of CO on polycrystalline ZnO was determined by applying temperature-programmed desorption (TPD) [4,9,10] and microcalorimetry [9-13]. In addition, the interaction of CO with different ZnO single crystal surfaces has been investigated in detail (for a review see Ref. [14]).

With regard to the identification of adsorbate-induced vibrational bands observed for ZnO powders the recent success in measuring high-resolution electron energy loss spectroscopy (HREELS) data for various molecular adsorbates on ZnO single crystal surfaces constitutes a significant progress (see reviews Refs. [15,16] and references therein). In order to carry out an unambiguous identification of IR bands observed for powder particles by comparison to the data available for single crystal surfaces we have used a novel ultrahigh vacuum infrared spectroscopy (UHV-FTIRS) apparatus, which allows for the investigation of both surfaces of well-defined oxide single crystals and of powder particles in grazing incidence reflection and transmission, respectively [17]. By combining the single crystal HREELS results with the UHV-FTIRS powder data, the interaction of H$_2$O and CO$_2$ with ZnO nanoparticles has been investigated in detail [18,19]. Interestingly, it was found that the binding energy of CO on polycrystalline ZnO is largely increased in the presence of pre-adsorbed CO$_2$, as confirmed by TPD and microcalorimetry results [20]. For the single crystal surface, this unexpected effect could be explained by the presence of tridentate carbonate species on the mixed-terminated ZnO(1 0 1 0) surface, which leads to an increase of the Lewis acidity of the embedded Zn$^{2+}$ cations [20].

In this work, we present detailed vibrational spectroscopic data for the adsorption of CO on the clean, CO$_2$-pretreated and hydroxylated surfaces of ZnO nanoparticles by employing UHV-FTIRS. The high-quality IR data allow for rather detailed conclusions on the interaction of CO with differently modified ZnO powder samples.

2. Experimental

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 oxidation of...