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Adsorption of CO on $Cr_2O_3(0\,0\,0\,1)$

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Abstract

The adsorption of CO molecules on the Cr-terminated (0 0 0 1) surface plane of Cr_2O_3 is studied theoretically by means of quantum chemical cluster calculations and experimentally by thermal desorption spectroscopy and infrared reflection absorption spectroscopy. The combination of these approaches yields a detailed picture of the CO/$Cr_2O_3(0\,0\,0\,1)$ adsorption. In the low coverage limit, CO is strongly bound (chemisorbed) and occupies a O_3-hollow position, i.e. it is adsorbed above a threefold hollow site in the first full oxygen layer, with the CO axis oriented along a line connecting two Cr ions at the surface and tilted strongly against the surface normal. CO molecules in this position desorb at 175 K, which corresponds to an adsorption energy of 45 kJ/mol, and exhibit a blue shift of the CO stretching frequency of about 35 cm^{-1} with respect to CO in the gas phase (from 2143 to 2178 cm^{-1}). At higher coverages, a second desorption peak at 105 K is found which is accompanied by a small red shift of -10 cm^{-1} of the CO stretching frequency. This adsorption state corresponds to a physisorption of CO with an adsorption energy of 28 kJ/mol and is tentatively assigned to CO molecules adsorbed parallel to the surface above one O^{2-} anion in the oxygen layer.

Keywords: Chromium; Carbon monoxide; Clusters; Thermal desorption spectroscopy; Infrared absorption spectroscopy; Ab initio quantum chemical methods and calculations