

Finding of a New Type of Dioxygen Adsorbed Species Formed in Copper-Ion-Exchanged MFI-Type Zeolite and Its Analysis Based on Calorimetric, Spectroscopic, and Theoretical Methods

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Transition metal dioxygen adducts have attracted the wide attention of chemists or biochemists for decades. The main attractive features of such studies are derived from the importance of these species in various kinds of catalytic reaction processes, such as biocatalytic and synthetic oxidations. If we focus our attention on the solid catalysts, transition metal-ion-exchanged zeolites samples (especially copper-ion-exchanged MFI-type zeolite: CuMFI) are very intriguing materials because they act as the active materials for NO decomposition. This behavior relies on the prominent structural and electronic states of the monovalent copper-ion exchanged in MFI-type zeolite. Therefore, it attracts a wide attention from the viewpoint of the interaction of the monovalent copper ion with dioxygen, because the dioxygen formed plays a prominent role in the redox reaction related to the states of copper ion. In order to know the potential application of CuMFI in the selective oxidation catalyst, we investigated, in the first stage, the interaction of CuMFI with dioxygen and found a new prominent adsorption feature of dioxygen on CuMFI; this species was formed even after O₂ adsorption onto CuMFI at lower pressure of 0.1 Pa and at around 300 K and this reaction was equilibrated within 40 seconds. The formed species gives the peculiar absorption band centered at 31000 cm⁻¹, XAFS band at 2.2 and 2.9 Å, and IR band at 2198 cm⁻¹ (tentatively assigned to overtone band), as well as 143 kJ mol⁻¹ as the adsorption energy; the formed species is attributed to the one bridging between two copper ions existing in the near neighbor, i.e., Cu₂(m-1,2-O₂). In addition, this species is efficiently transformed its state to the oxygen-bridged species, i.e., Cu₂(m-O)₂, bis(m-oxo)dicopper species, which gives the absorption band at around 22000 cm⁻¹, under the irradiation of light in the region of 29000-33000 cm⁻¹. The adsorption models of these two species were constructed to reasonably explain the respective data and also certified on the basis of DFT calculation. It was also found that the bis(m-oxo)dicopper species acts as the activation catalyst for CH₄ under irradiation of UV light. The prominent features observed of CuMFI for dioxygen adsorption are very specific and this material is expected to act in the similar way to the oxidation catalysts found in biomaterials, from the viewpoint of its similarity to the biological system.