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论文

用EXAFS研究pH对Zn(Ⅱ)-TiO_2体系吸附和微观构型的影响

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摘要:

应用延展X射线吸收精细结构(EXAFS)方法, 研究了不同pH对Zn(Ⅱ)在锐钛矿型TiO_2表面吸附产物的微观构型的影响. 宏观的吸附-解吸实验表明, 随着pH值由5.8增大至6.8, 吸附等温线明显升高, Freundlich吸附常数由1.345 L/g增加到15.385 L/g; 而体系的不可逆性逐渐降低, 不可逆吸附系数(TⅡ)由0.43降低到0.23. 不同pH条件下吸附样品的EXAFS结果表明, Zn(Ⅱ)主要通过共用水合离子及TiO_2表面的O原子结合到TiO_2表面上, 第一配位层(Zn—O层)原子间距和配位数随着pH值增大逐渐降低, Zn(Ⅱ)在TiO_2表面吸附形态从六配位向四配位转化; 第二配位层(Zn—Ti层)分析结果表明, 存在2个典型的Zn—Ti原子间距, 即R_1=0.319~0.334 nm(双齿方式结合的强吸附)和R_2=0.366~0.378 nm(单齿方式结合的弱吸附), 随着pH值的升高, 强吸附位(CN1)逐渐减少而弱吸附位(CN2)逐渐增加, 其比值由2.12降低至0.89, 从而导致其在高pH值的条件下吸附量和可逆性明显增大. EXAFS结果从分子水平说明了该体系在不同pH值条件下表现出的可逆性差异是由于微观吸附状态不同所致.

关键词: 延长X射线吸收精细结构; pH; 吸附可逆性; Zn(Ⅱ)

EXAFS Studies of pH Effects on Adsorption and Microscopic Strutures of Zn(Ⅱ) onto TiO_2

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Abstract:

Microscopic structures and thermodynamic characteristics of Zn(Ⅱ) adsorbed onto anatase TiO_2 at different pH were studied using extended X-ray absorption fine structure(EXAFS) spectroscopy. Macroscopic adsorption-desorption experiments indicated that as pH increased from 5.8 to 6.8, the adsorption capacity coefficient(K_F) increased from 1.345 L/g to 15.385 L/g, while the adsorption irreversibility coefficient(TⅡ) decreased from 0.43 to 0.23. EXAFS spectra results showed that Zn(Ⅱ) was adsorbed onto the solid surface in a mixed form of octahedral and tetrahedral hydrous Zn(Ⅱ) ions, which were linked to TiO_2 surface by sharing O atoms. Both the bond length and the coordination number of the first Zn—O coordination sphere decreased as pH increased. Analysis of the second Zn—Ti coordination sphere indicated two Zn—Ti atomic distances: R_1=0.319—0.334 nm and R_2=0.366—0.378 nm, referring to bidentate(stronger adsorption site) and monodentate(weaker adsorption site) complexation respectively. The number of stronger adsorption sites(CN1) decreased while the number of weaker adsorption sites(CN2) increased remarkably with increasing pH, resulting in a drop of CN1/CN2 from 2.12 to 0.89. EXAFS results revealed that the macroscopic adsorption phenomena were directly related to the changes in microscopic adsorption structures of Zn(Ⅱ) on the surface of TiO_2 under different pH conditions.

Keywords: Extended X-ray absorption fine structure; pH; Adsorption reversibility; Zn(Ⅱ)

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