

石油沥青质含硫结构的XANES导数光谱研究

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Speciation and quantification of sulfur compounds in petroleum asphaltenes by derivative XANES spectra

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摘要 采用X射线近边结构谱(XANES)研究沥青质中硫的存在形态,针对沥青质的未知复杂混合体系特性,采用高阶导数谱图分析方法,提高XANES的分辨率,准确分析沥青质中硫的存在形态;采用反正切和高斯函数分峰拟合、定量解析谱图,针对不同氧化态硫 $3p$ 轨道空余状态不同引起 $1s \rightarrow 3p$ 跃迁几率不同,提出峰面积修正因子,以准确分析体系中各形态硫的相对含量。结果表明,石油沥青质中硫主要存在形式为硫醚、噻吩、亚砷、噻吩砷和硫酸酯,常减压渣油沥青质中基本不含硫醚。

关键词: 沥青质 硫 X射线吸收近边结构谱 高阶导数谱图

Abstract: The XANES spectrum is employed to study the sulfur functional groups in asphaltenes. Since the asphaltenes are complicated mixture, it is difficult to distinguish different classes of sulfur compounds in asphaltenes. Therefore, the higher order derivative spectra of sulfur XANES were introduced in order to improve sulfur XANES resolution and to qualitatively analysis sulfur functional groups in asphaltenes. Sulfur XANES spectra were deconvoluted by using of several Gaussian and arctangent functions to quantify the sulfur species. In order to convert peak area percentages to atomic percentages, the relative $1s \rightarrow 3p$ transition probabilities of different sulfur classes must be considered. The areas of the different Gaussian peaks were calculated and revised for their oxidation state-dependent absorption cross-section. The contribution of sulfur species to total sulfur was calculated by the corrected peak areas. The result showed that sulfur species in asphaltenes of atmospheric and vacuum residue were mainly in form of thiophene, sulfoxide, thiophene sulfone and sulfate, while hardly contained sulfide.

Key words: asphaltenes sulfur XANES higher order derivative

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