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柳林3#镜煤吡啶残煤大分子结构模型及分子模拟

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Macromolecular structural model of the pyridine extracted residue of vitrain from No.3 coalbed, Liulin and molecular simulation

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摘要 对柳林3#镜煤吡啶抽提残煤(LLR)进行了^{13}C CP/MAS NMR和XPS分析,结合元素分析和工业分析,构建了其大分子模型。LLR结构中芳香部分以蒽为主,脂肪结构主要以脂肪侧链的形式存在,氧原子分别以醚键、羟基和羰基形式存在,氮原子以吡咯和吡啶的形式存在。运用^{13}C NMR预测软件ACD/CNMR predictor计算了大分子结构模型的^{13}C化学位移。与实验^{13}C NMR谱图相比较,对LLR的大分子结构模型进行了修正,获得了^{13}C NMR计算谱能和实验谱图吻合较好的大分子结构模型。采用分子模拟对LLR化学结构模型进行能量优化,结果表明,大分子结构的能量按其大小排序主要为范德华能、键扭转能、键角能与键伸缩能。芳环之间的平行排列在该结构模型中占有很小的比例。最后通过添加周期性边界条件得到该煤的密度为1.22 g/cm^3。量子化学半经验方法(PM 3)模拟结构表明,脂肪侧链中的C-C键较长,因而活性较高;边缘碳原子带有较多的负电荷,易于发生氧化反应;芳香碳原子所带电荷较少,稳定性很高。

关键词: 柳林3#镜煤吡啶抽提残煤 ^{13}C NMR XPS 化学位移 大分子结构模型 量子化学

Abstract: The pyridine extraction residue from LL 3#vitrain (LLR) was studied by ^{13}C CP/MAS NMR and XPS analysis. ^{13}C NMR tests show the structure characteristics of carbon atom and 12 structure parameters. Aromatic structure units are dominated by anthracene; aliphatic C atoms exist in the side-chain; O atoms exist in the form of -O-, C=O and -OH; N atoms exist in pyridine and pyrrole. Macromolecular structure model of LLR is constructed based on the results of proximate and ultimate analysis. ^{13}C chemical shift of LLR macromolecular structure is calculated by ACD/CNMR predictor, then the structure is corrected according to the calculation results. And finally the macromolecular structure which is consistent with the experimental results is obtained. Molecular mechanics (MM) and molecular dynamics (MD) were adopted to simulate the energy-minimum conformation of LLR model. The results show that the order of main energy for LLR model is van der waals>torsion>angle>bond. The simulation results indicate that the parallel aromatic layer structure occupies a small proportion. Finally, LLR density is 1.22 g/cm^3 by enclosing coal model into the periodical boundary condition. Semi-empirical quantum chemistry methods (PM3) simulation indicates that the C-C bonds adjacent to aliphatic side chain C atoms exhibit higher activity. The terminal C atoms are more negatively charged, and therefore prone to undergo oxidation reactions. The aromatic C atoms are characterized by fewer charges and very high stability.

Key words: pyridine extraction residue from LL 3# vitrain ^{13}C NMR XPS chemical shift macromolecular structure model quantum chemistry

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