

中心原子对Keggin结构杂多阴离子的电子结构和催化性质的影响

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摘要 使用SCC-DV-X α 方法计算了Keggin结构的杂多阴离子(SiMo₁₂O₄₀)⁴⁻, (GeMo₁₂O₄₀)⁴⁻, (AsMo₁₂O₄₀)³⁻的电子结构, 并与文献对(PMo₁₂O₄₀)³⁻

的计算结果作了对比分析。讨论了中心原子对Keggin结构的杂多阴离子的电子结构和催化性质的影响。结果表明, 中心原子对Keggin结构杂多阴离子的电子云、静电势、总态密度的分布影响不明显; 但中心原子不同, 前线轨道HOMO, LUMO的组成有一定差异。四种阴离子的 ϵ LUMO和 ϵ Fermi的相对大小关系为:(AsMo₁₂O₄₀)³⁻>(PMo₁₂O₄₀)³⁻>(GeMo₁₂O₄₀)⁴⁻>(SiMo₁₂O₄₀)⁴⁻, 其氧化能力和催化活性也具有相同的顺序。(XMo₁₂O₄₀)ⁿ⁻(X=Si, Ge, P)中端氧Ot, 桥氧Ob, Mo以及X都具有催化活性, 在催化反应中都可能成为催化活性中心, 而(AsMo₁₂O₄₀)³⁻中仅有As和Ob可作为催化活性中心。

关键词 [杂多酸](#) [硅酸 P](#) [电子结构](#) [钼酸 P](#) [砷酸 P](#) [锆酸 P](#) [催化性能](#) [KEGGIN结构](#)

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Effects of central atoms on electronic structures and catalytic properties of Keggin-type heteropolyanions

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Abstract The electronic structures of Keggin-type heteropolyanions (SiMo₁₂O₄₀)⁴⁻, (GeMo₁₂O₄₀)⁴⁻ and (AsMo₁₂O₄₀)³⁻ have been calculated by the SCC-DV-X α method. According to the comparison among calculating results of the three heteropoly anions and those of (PMo₁₂O₄₀)³⁻ which were adapted from the literature, we discussed the influence of the central atoms on the electronic structures and catalytic properties of Keggin structure anions. The results show that the influences of the central atoms on electron cloud, electrostatic potential, total density of states are not clear. But the central atom can affect the components of the frontier orbitals HOMO and LUMO. The relative sequence of energy of LUMO and Fermi level is as follows: (AsMo₁₂O₄₀)³⁻>(PMo₁₂O₄₀)³⁻>(GeMo₁₂O₄₀)⁴⁻>(SiMo₁₂O₄₀)⁴⁻. The sequences of oxidation and catalytic activity are the same as the above. For (XMo₁₂O₄₀)ⁿ⁻ (X=P, Si, Ge), Ot (terminal oxygen), Ob (bridge oxygen), Ox (central oxygen), Mo and X have the potential to participate in the catalytic reactions, whereas to (AsMo₁₂O₄₀)³⁻, just As and Ob are exclusively active.

Key words [HETEROPOLYACID](#) [SILICIC ACID P](#) [ELECTRONIC STRUCTURE](#) [MOLYBDIC ACID P](#) [ARSENIC ACID P](#) [GERMANIC ACID](#) [CATALYTIC BEHAVIOUR](#)

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