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NiMoS加氢脱硫催化剂的合成及其表面非化学计量硫物种的研究

Study on the synthesis of NiMoS hydrodesulfurization catalysts and the surface non-stoichiometric sulfur species

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**Study on the synthesis of NiMoS hydrodesulfurization
catalysts and the surface non-stoichiometric sulfur species**

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摘 要

作为最重要的催化材料之一，Ni/Co 促进的 MoS₂ 或 WS₂ 催化剂已被广泛应用于各种油品的加氢脱硫(HDS)工艺过程。另一方面，由于环保法规对燃油硫含量规定日益严苛，高效的深度 HDS 催化剂越来越受到关注。近年来，Topsøe 及其合作者通过对 Co (Ni)/Mo 硫化物作用机理进行细致研究，提出了 Co-Mo-S 相模型。然而，由于实际 HDS 催化剂表面结构的复杂性，对于 Co-Mo-S 结构与催化本征活性之间的关系目前仍存在诸多争议。在 Co-Mo-S 相模型的基础上，对负载型及非负载型硫化物的光谱学研究发现，催化剂表面存在非化学计量硫(S_x)物种及 SH 基团。然而，非化学计量硫物种与反应气氛趋向平衡的过程在反应的最初始阶段快速进行，因而这一硫物种对 HDS 活性的影响不易引起关注。本论文的重点在于研究非化学计量硫动态平衡及其对 NiMoS 活性相结构与 HDS 性能的影响。

本文对于 NiMoS 活性模型提出一种新的理解，揭示 NiMoS 活性相边缘与反应气氛之间存在一个硫动态平衡。实验结果表明，硫化态 NiMoS 催化剂表面存在可被还原的非化学计量硫物种 S_x (由 S²⁻、S₂²⁻及 S⁰等组成)，当 S_x 未被还原分解而覆盖于 NiMoS 边缘位点时，未能形成硫阴离子空位，从而导致催化剂 HDS 活性显著下降。进一步的研究表明，在合适的温度下，S_x 物种能够被 H₂ 还原为 H₂S、H₂S₂、S₂ 和 S₃ 等，且这一还原过程是可逆的。在 S_x 物种的还原过程中，NiMoS 边缘的 S-S 键被 H₂ 裂开，生成 SH 基团并进一步加氢释放出 H₂S，从而伴随着催化剂表面硫含量的下降。还原后，表面活性金属 Mo 和 Ni 处于配位不饱和(CUS)状态，NiMoS 边缘生成 CUS 位点，吸氢能力提高，且表现出 Lewis 酸性，使得 CO、吡啶和噻吩的吸附增强，进而导致催化剂对于含硫化合物催化加氢和直接脱硫的活性提升。在有机含硫化合物的 HDS 反应中，含硫反应物通过获取 SH 基团上的 H 原子进行加氢反应，且其 S 原子转移至 NiMoS 边缘的空位上，随后被加氢脱除，从而使 NiMoS 结构恢复至其初始状态。这一循环过程促使 NiMoS 边缘非化学计量硫物种 S_x 的硫化还原反应可逆地进行，即所谓的催化剂表面“硫动态平衡”。

在 HDS 反应过程中，非化学计量硫处于动态平衡，并且这一平衡状态与反应气氛及反应温度相关。在此基础上，初步研究了 NiMoS 催化剂表面非化学计量硫物种 S_x 动态平衡反应的热力学规律，定量测定结果表明 S_x 物种与气相 H_2S 分压及反应温度的关系可用经典的热力学平衡方程及 van't Hoff 等压方程描述。由于可能存在的硫溢流现象，相比于非负载型 NiMoS 催化剂，NiMoS/ Al_2O_3 负载型催化剂上的 S_x 表现出较高的随 H_2S 分压及反应温度变化的敏感性且其还原反应的焓变也较大。总之，本课题致力于探明决定表面非化学计量硫物种 S_x 的存在状态及浓度的各种因素及其对 NiMoS 结构的影响，建立反应温度/ H_2S 分压—活性相 S_x 浓度—HDS 活性三者的定量关系。本研究有助于加深对 NiMoS 催化剂活性相本质的理解，且将为油品深度 HDS 催化剂的研究和开发提供科学依据。

另一方面，NiMoS 催化剂被广泛应用于石油产品 HDS 过程，但是，目前关于 Ni/Co 促进的 MoS_2 特定纳米结构催化剂的报道仍然较少。作为潜在的工业 HDS 催化剂，NiMoS 纳米材料的发展受到密切关注。因此，本论文系统研究了花状 NiMoS 纳米催化剂的合成及其催化 HDS 活性，其主要结果如下。

以廉价的单质硫作为硫源及水合肼作为还原剂，采用简便的水热生长法成功合成了由纳米薄片组装的均一 NiMoS 三维纳米花，其中单质硫和水合肼添加量以及水热时间和水热温度对 NiMoS 纳米花状结构有着重要影响。采用 SEM、TEM、XRD、Raman 和 XPS 等分析方法对这一纳米材料的结构与形貌进行表征，结果表明 NiMoS 花状结构由厚度约为 6–12 nm 的超薄纳米片组装而成。这种花状分级结构在相邻纳米薄片之间存在充足的孔隙空间，利于反应物分子的快速传输扩散。HRTEM 观测结果发现纳米薄片上弯曲的短 MoS_2 微晶片层呈现错位、畸变与中断的特征，呈现出富缺陷的结构，这种结构将促使更多的 Ni-Mo-S 边缘活性位点的产生与暴露。因其高活性位密度，所制得的 NiMoS 纳米花催化剂在噻吩加氢脱硫及 4,6-二甲基二苯并噻吩深度加氢脱硫反应中表现出优异的催化活性。以上结果表明，采用水热生长法合成纳米薄片自组装的花状 NiMoS 复合材料是可行的，且该复合材料在油品的深度 HDS 过程中具有潜在的应用价值。

关键词：加氢脱硫；非化学计量硫；硫平衡；SH 基团；NiMoS；纳米花

Abstract

As one of the most important applications, catalysts based on Ni/Co promoted molybdenum disulfide have been widely used for the hydrodesulfurization (HDS) process in petroleum refining, and growing concern is directed towards more effective catalysts for deep HDS due to increasingly stringent environmental regulations for the sulfur content in transportation fuels. Over the years, the genesis and functioning of Co (Ni)/Mo catalysts have been thoroughly investigated by Topsøe and colleagues in which an edge-decorated Co(Ni)MoS phase model has been suggested. However, the relationship between the intrinsic activity and the Co(Ni)MoS structure has not been understood sufficiently yet, due to the great complexities of the surface structure of practical HDS catalysts. On the basis of the Co(Ni)MoS phase model, the existence of non-stoichiometric sulfur species and SH groups on the surface of sulfide HDS catalysts have been proven by the spectroscopic studies. Whereas, the effect of non-stoichiometric sulfur (S_x) on the HDS activity does not draw so much attention, since the evolution of S_x content proceeds rapidly at the very beginning of HDS reaction. The present work focuses on the sulfur dynamic equilibrium between the NiMoS edge and the gas phase, and its influence on NiMoS active structure and the HDS performance.

This thesis provides new insight into the NiMoS model, revealing that there is a sulfur dynamic equilibrium between the NiMoS edge and the gas phase. The results indicated the presence of reducible non-stoichiometric sulfur species S_x (composed of S^{2-} , S_2^{2-} and S^0) on the catalyst surface, which would fully cover on the NiMoS edge sites before being reduced and removed, severely degrading the HDS activity by suppressing the formation of coordinatively unsaturated sites (CUS). Further research indicates that in a hydrogen atmosphere and at an appropriate temperature, S_x can be reduced into H_2S , H_2S_2 , S_2 , S_3 , etc. During the reduction of S_x , the S–S bonds on the NiMoS edge can be cleaved by hydrogen to form SH groups and release H_2S through

the further hydrogenation, accompanied by a significant increase in CUS on the NiMoS edge, resulting in an enhancement of adsorption of CO, pyridine and thiophene, which leads to an outstanding HDS activity. During the HDS reaction, the sulfur-containing reactant is hydrogenated by capturing the H atoms from –SH groups, while its S atom is transferred to the vacancy on the NiMoS edge, and then, the NiMoS structure is restored to its initial state after the S atom hydrotreated and removed. These results reveal the reversibility of sulfidation–reduction reaction for S_x on the NiMoS edge, and that is what we call ‘sulfur dynamic balance’.

During the HDS reaction process, S_x is in a dynamic balance, and the equilibrium is actually reactive atmosphere and temperature-dependent. The effect of S_x on HDS activity and the dependence of S_x on H_2S partial pressure over NiMo-based catalysts have been systematically investigated; the results indicate that the relationship reasonably follows thermodynamic equilibrium. S_x over the NiMoS/ Al_2O_3 catalyst shows a higher H_2S partial pressure sensitivity than that over the unsupported NiMoS catalyst, and a larger enthalpy change of the reduction reaction has been observed for the former catalyst. To sum up, this work makes an effort to elucidate the effect of S_x on the NiMoS structure and to quantitatively study the relationship among H_2S partial pressure, S_x content and HDS activity. It is expected that these results will be used to deepen the understanding of HDS reaction over Ni(Co) promoted MoS_2 catalysts, as well as to guide the research on ultra-deep HDS of fuel oils.

On the other hand, to the best of our knowledge, reports on Ni(Co) promoted MoS_2 catalysts with a defined nanostructure are still limited. Nevertheless, NiMoS catalysts are widely used for the HDS of petroleum fractions, so it is of interest to develop Ni(Co) promoted MoS_2 nanomaterials as potential catalysts for industrial deep HDS processes. Herein, the present work shows a systematic investigation of the synthesis of NiMoS nanomaterials and their catalytic activity.

As a result, uniform 3D NiMoS nanoflowers with self-assembled nanosheets were successfully synthesized via a simple hydrothermal growth method using cheap and nontoxic elemental sulfur as sulfur source. The elemental sulfur and hydrazine monohydrate, hydrothermal temperature and hydrothermal time play important roles

in the preparation of NiMoS nanoflowers. The structure and morphology of the nanomaterials were characterized by SEM, TEM, XRD, Raman and XPS analyses, revealing that the NiMoS nanoflowers were composed of ultrathin nanosheets with a thickness of approximately 6–12 nm. In particular, these flower-like hierarchical structures provide sufficient pore space between the neighboring nanosheets, which will facilitate rapid diffusion of large molecules. The HRTEM results indicate that the curve/short MoS₂ slabs on the nanosheets possess the characteristics of dislocations, distortions and discontinuity, which suggests a defect-rich structure, resulting in the exposure of additional Ni–Mo–S edge sites. The obtained NiMoS nanoflower exhibited an excellent activity for thiophene HDS and 4,6-dimethyl-dibenzothiophene deep HDS due to their high density of active sites. The outstanding HDS performance suggests that these NiMoS composites with a unique flower-like nanostructure could be useful as promising catalysts for the deep desulfurization of fuel oils.

Keywords: hydrodesulfurization; non-stoichiometric sulfur; sulfur equilibrium; SH groups; NiMoS; nanoflower

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