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燃烧法一步合成NiMo-Al₂O₃加氢脱硫催化
剂及预硫化动力学的研究

Study on the one-pot combustion synthesis of NiMo-Al₂O₃
catalysts for hydrodesulfurization and the Kinetics of
presulfiding

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摘 要

随着高品质石油产品需求量的逐年增加,石油馏分加氢脱硫(HDS)工业装置产能随之扩大,导致 HDS 催化剂的用量越来越大。另一方面,环保法规日益严苛,要求石油产品硫含量越来越低,因而开发具有制备周期短、生产成本低、催化性能好等特点的 HDS 催化剂合成方法显得尤为重要。本文以氯化铝为铝源,钼和镍为活性金属组分,以淀粉为燃烧剂,采用燃烧法一步合成 NiMo-Al₂O₃ 加氢脱硫催化剂。利用 BET、XRD、SEM、TEM、H₂-TPR、TPD、TG-DSC、XPS、元素分析等方法对催化剂的物相结构及物理化学性质进行表征,并与 HDS 催化性能进行关联,系统研究催化剂制备-物化性质-催化活性三者之间的关系。

首先,考察了活性金属组分 Ni 与 Mo 及络合剂柠檬酸对燃烧法一步合成 NiMo-Al₂O₃ 催化剂的影响,并与传统浸渍法所制备的催化剂进行比较。Ni 的添加有效促进 Mo 物种的还原,利于 Ni-Mo-S 活性相的生成。柠檬酸的添加显著提高催化活性,且以共络合的方式加入效果更好。采用该方法制备的催化剂,其载体氧化铝的平均粒径在 30 nm 左右,且具有适宜的孔隙结构,催化剂具有适中的硫化还原能力,Ni、Mo 物种的分散性明显高于浸渍法所制催化剂,硫化后 MoS₂ 晶片长度和堆垛层数明显较小,因而具有较高的整体 HDS 活性。

其次,系统研究了淀粉的添加对燃烧反应、催化剂物理化学性质、Ni-Mo-S 结构及 HDS 活性的影响。淀粉的添加明显提高燃烧反应的摩尔焓变,增加催化剂载体的孔隙率,且通过削弱 Mo、Ni 与载体氧化铝之间的相互作用提高催化剂的硫化还原能力。然而,过量的淀粉容易使得燃烧过程中产生过多的摩尔焓及过高的火焰温度,并最终导致活性 Mo 物种颗粒聚集,分散度下降。当淀粉添加量(以 (C₆H₁₀O₅):2Al 摩尔比计量)从 0 增加至 2.5 时,Ni-Mo-S 活性相 II 型结构的比例增加,使得催化剂二苯并噻吩(DBT) HDS 的平均转化频率(TOF)升高,同时总活性位数目亦增多;但继续增大淀粉的添加量将使总活性位数目开始减小而 TOF 却不再提高。催化剂 TOF 的升高以及表面活性位的增加能够显著提高其加氢能力,进而提高 DBT 加氢脱硫的催化活性。因此,NiMoAl-2.5 催化剂具有最佳的催化性能。

最后，本文还考察了预硫化温度和预硫化时间对 NiMo/Al₂O₃ 催化剂加氢脱硫性能的影响。根据已有的相关知识和经验，建立了如下预硫化动力学模型。即

$$\ln[-\ln(1-x_A)] = \ln k'_{20} + n_2 \ln t - E_2 / T - k'_{10} t^{n_1} e^{(E_1 - E_2) / T}$$

对实验数据的拟合分析结果表明：(1)模型参数合理，平均相对偏差为 2.8 %，模型计算结果与实验结果较为符合。(2)晶粒生长活化能 37.5 kJ·mol⁻¹，大于硫化反应活化能 25.5 kJ·mol⁻¹，晶粒生长所需温度高于硫化反应进行的温度。(3)模型假设(如晶粒大小与硫化度)符合实际情况，表征结果证明实验测定值与模型假设预测值基本一致。

关键词：加氢脱硫；燃烧合成；淀粉；NiMo 催化剂；预硫化动力学。

Abstract

With the increasing demand for high quality petroleum products, the producing ability of hydrodesulfurization (HDS) apparatus for petroleum fractions in refinery is also expanding accordingly, which lead to a heavy use of HDS catalysts. On the other hand, due to increasingly stringent regulations for environmental protection purpose, the prescriptive value of the sulfur content in fuel oil becomes lower and lower. Thereby, it appears especially important to develop the synthetic method of HDS catalyst, which has the advantages of facile, cost-effective, short fabrication period and high catalytic performance. Mesoporous NiMo-Al₂O₃ catalysts for HDS were prepared by efficient and simple one-pot combustion synthesis method using aluminum chloride as start material, nickel and molybdenum as active components, and starch as fuel. The catalysts were characterized by means of BET, XRD, SEM, TEM, H₂-TPR, TPD, TG-DSC, XPS and elemental analysis. The structure and physicochemical property of the catalysts have been studied, and then related to the HDS catalytic performance, so as to discuss the relations among preparation, physicochemical property and catalytic performance.

First, the effect of active components (Ni and Mo) and complexing agent (citric acid) on one-pot combustion synthesis of NiMo-Al₂O₃ catalysts for HDS have been investigated, and the as-prepared catalysts also have been compared to the NiMo/Al₂O₃ catalysts prepared by impregnation method. The addition of Ni promotes efficiently the reduction of Mo species, which is beneficial to form Ni-Mo-S active phase. The addition of citric acid improves significantly the catalytic activity of HDS catalysts, and the better effect can be got using the co-complexation. The alumina supports show appropriate specific surface area, small nano-sized (about 30 nm) spherical particles. The as-prepared NiMo-Al₂O₃ catalysts show suitable reducibility and sulfidation degree and high dispersions of Ni and Mo species, short length and low stacking layer number of MoS₂ slabs, which lead to a higher HDS performance.

Secondly, the effect of starch addition on the precursor combustion reaction, physicochemical properties, Ni-Mo-S phase and intrinsic hydrodesulfurization activity of the NiMo-Al₂O₃ catalysts has been studied scientifically. The results show that the increase in starch addition markedly enhances the molar enthalpy of the combustion reaction, developing the porosity of the catalysts, and improves the reducibility and sulfidability by reducing the interaction of Mo and Ni with the Al₂O₃ supports. However, the excessive molar enthalpy and adiabatic flame temperature of the combustion process in which excess starch has been used as fuel will lead to the high agglomeration of Mo particles, resulting in high MoS₂ stacking and low MoS₂ dispersion. Moreover, the proportion of Type II as well as the total population of the (TypeI+II) active sites increases as the starch addition increases up to 2.5 [(C₆H₁₀O₅):2Al], leading to an increase in the turnover frequency (TOF) for the catalysts; However, the total population of the (TypeI+II) active sites decreases with a further increase in the addition of starch. The increase in total population of Ni-Mo-S active sites significantly improves hydrogenation ability and HDS performance of the catalysts. As a result, the specific activities of HDS over NiMoAl-x catalysts peak at a starch addition ratio (x) of 2.5.

Last, the effect of presulfiding temperature and presulfiding duration on HDS performance of the NiMo/Al₂O₃ catalysts have been investigated. According to existing knowledge and experiences, the kinetic model of presulfiding has been established, as follows:

$$\ln[-\ln(1-x_A)] = \ln k'_{20} + n_2 \ln t - E_2 / T - k'_{10} t^{n_1} e^{(E_1 - E_1 / T)}$$

Fitting analysis results of the experimental data show that: (1) The model parameter is reasonable, the average relative deviation is only 2.8 %, and model calculations are in good agreement with the experimental results. (2) The activation energy of grain growth is about 37.5 kJ·mol⁻¹, while the activation energy of sulfidation is 25.5 kJ·mol⁻¹, the temperature as grain growth required is higher than sulfidation temperature. (3) The model assumption (e.g. grain size and sulfidation degree) is in agreement with the facts, the characterization results prove that the model prediction

matches the experimental values well.

Keywords: hydrodesulfurization; combustion synthesis; starch; NiMo catalyst; kinetics of presulfiding.

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第一章 绪论

1.1 课题研究背景

随着全球经济的较快发展,世界各国对轻质石油燃油如柴油和汽油的需求量与日俱增,目前国内的柴油和汽油需求量已超过国内生产总量^[1, 2]。石油燃油中含有芳烃、含硫化合物及含氮化合物。含硫、含氮化合物和芳烃含量的增加,不但降低柴油的十六烷值,而且导致大气中有害气体及颗粒物(PM)排放量增加^[3, 4]。石油燃油的大量使用使得机动车尾气与工业制造的排放量越来越大。含硫化合物是石油中的主要非烃组分,其含量随原油产地的不同呈现很大差别,通常含硫量低于 0.4%,这些含硫化合物包括了简单的硫醇、硫醚及复杂的多硫化合物(如噻吩类和二苯并噻吩等)以及未知的大分子硫化物。在燃烧的过程中这些含硫成分会与氧气反应生成硫氧化物(SO_x),主要是二氧化硫(SO₂)和三氧化硫(SO₃),其中又以 SO₂ 占比最高,约为 90%。这些硫氧化物是造成环境污染的罪魁祸首,是一种无色有刺激性气味的气体,会对人体的呼吸器官产生伤害,对植物也会引起很强的毒性,且易导致酸雨的形成,腐蚀建筑物及各种金属器件,破坏臭氧层等。另一方面,SO_x 能够显著促进汽车尾气中 NO_x 和颗粒物(PM)的排放,且易使得汽车尾气转化器中的贵金属催化剂中毒,从而导致污染物的排放增加。

在环境问题日益严峻的情况下,人们对环境质量的要求也越来越高,对石油燃料的质量要求日益严格,世界各国均制定了严格的燃油标准。欧洲于 2000 年实施欧 III 清洁燃油配方,规定油品中硫含量不大于 150 μg·g⁻¹,而 2005 年实施欧 IV 配方,要求硫含量降至 50 μg·g⁻¹,北京已于 2005 年实施国 III 标准(相当于欧 III),2008 年实施国 IV 标准(相当于欧 IV),这一标准要求硫含量小于 50 μg·g⁻¹。此外,在雾霾天气的压力之下,国家开始加快油品升级的脚步,要求自 2013 年起全国车用汽油需置换至 IV 标准,过渡期至年底 12 月 31 日;而从 2013 年 7 月起国内流通的国标柴油需全部升级到国 III 标准。在当前环保要求日益苛刻、节能要求迫切的形势下,石油馏分脱硫技术已成为含硫原油加工的关键工艺技术,且该技术的发展已成为多方关注的焦点。

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