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硕 士 学 位 论 文

**NiMo/Al₂O₃催化剂及载体性质与加氢脱硫
活性的定量关系模型**

**Quantitative relationship model between catalyst/support
properties and hydrodesulfurization activity over
NiMo/Al₂O₃**

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摘 要

随着汽柴油消耗量的逐年增长,尾气排放引起严重的环境问题。为此,需要进一步提高油品的质量。目前,加氢脱硫(HDS)技术是工艺成熟且极为有效的脱硫技术,而 HDS 催化剂是技术核心。影响 HDS 催化剂活性的因素颇多,研制一种新的催化剂或对原有催化剂进行改进往往需要消耗大量的人力、时间和资金成本。而通过建立数学模型的方法,可以有目的性地对催化剂进行改进,优化工艺参数,提高 HDS 催化剂的使用效率,节约时间和成本。因此,本文提出了一种能够定量描述催化剂或载体性质变量与 HDS 催化活性关系的数学模型。对于非相互独立的性质变量,模型可以正确了解某一变量对催化剂活性的影响规律。此外,模型具有良好的应用拓展性。

首先,通过乙酸溶液水热法合成一系列不同织构性质和酸性的 Al_2O_3 并浸渍得到相应的系列 $\text{NiMo}/\text{Al}_2\text{O}_3$ 催化剂。采用多种谱学技术进行表征,结果表明,催化剂的织构性质和酸性变化规律与载体的一致,载体性质会影响催化剂的还原性和活性组分的分散度。然后,在催化反应转化率对于表观速率系数关系式的基础上,提出载体“性质指数”的概念(它是各个性质变量的超几何平均量),建立二苯并噻吩(DBT) HDS 反应转化率与催化剂载体性质(比表面积、孔径和表面酸量)呈现定量关系的数学模型,具体方程为

$$\begin{aligned} X_M &= 1 - \exp(-4.319g^{2.84}) \\ &= 1 - \exp(-4.319 \cdot S_r^{1.824} \cdot D_r^{0.674} \cdot b_r^{0.346}) \end{aligned}$$

其中,模型对实验数据拟合的平均相对偏差为 1.43%,预测精度为 2.21%。对模型参数进行分析表明,载体性质对催化剂 HDS 活性的影响程度高低次序为:比表面积>孔径>载体酸性。进一步给出了载体各个性质变量对于催化剂活性升降贡献率的分析方法。其中, HDS 转化率 X_M 与性质指数 g 成单增函数关系。

其次,通过改变金属负载量得到一系列不同性质的 $\text{NiMo}/\text{Al}_2\text{O}_3$ 催化剂。表征结果表明,金属负载量会影响金属在载体上的分散性、还原性和活性相的分散度等性质,故可将金属负载量视为一类性质变量。通过考虑 HDS 催化剂 NiO 负

载量、MoO₃ 负载量和活性 MoS₂ 晶簇表面有效 Mo 原子分散度三个性质变量，运用“动态超几何平均”的方法将模型中载体的性质指数转换成催化剂的性质指数，对实验数据进行拟合，得到 HDS 转化率与催化剂性质的关系式模型为

$$X_M = 1 - \exp(-1.95 \cdot N_r^{1.45-2.83N_r} \cdot M_r^{1.35-2.06M_r} \cdot f_r^{0.65})$$

实验数据拟合的平均相对偏差仅为 1.13%，说明修正后的模型是适宜的。其中，催化剂 HDS 活性对助剂 NiO 含量的敏感程度大于活性金属组分 MoO₃ 含量。在本实验范围内，选用 12 wt.% 的 MoO₃ 和 3 wt.% NiO 的金属负载量制备催化剂最佳。修正的模型不仅可以表达单向影响关系，还可应用于变量范围较宽时，存在最佳值的情况。

最后，对模型进行拓展应用。针对非性质变量但与性质相关的活性影响因素进行考察。通过调变焙烧温度获得一系列不同性质的催化剂。其中，焙烧温度过高会使催化剂的比表面积、孔容明显降低，孔径增加，活性组分的还原性和分散性降低。将系列焙烧温度实验数据作为广义的性质变量代入模型，得到催化剂焙烧温度与 HDS 转化率的关系式为

$$X_M = 1 - \exp(-0.19 \cdot T_r^{5.43-17.1T_r})$$

模型拟合的平均相对偏差为 2.68%，拟合曲线与实验数据具有较高的重合度，说明模型的变量可以拓展到影响催化剂性质的制备条件如焙烧温度上。

进一步，同时考虑焙烧温度和金属负载量对催化剂 HDS 活性的影响，即将焙烧温度、NiO 负载量和 MoO₃ 负载量作为研究变量，分段选取不同的变量区间范围进行研究，其与 HDS 转化率的关系模型为

$$X_M = 1 - \exp(-0.27 \cdot T_r^{-5.82} \cdot N_r^{1.78} \cdot M_r^{0.59})$$

模型拟合的平均相对偏差为 3.81%。根据拟合结果，分段选取不同的变量区间范围进行研究，得到的结果与单独研究结果一致。

关键词：加氢脱硫；模型；载体性质；金属负载量；焙烧温度；NiMo/Al₂O₃ 催化剂

Abstract

Due to the increase in oil consumption, exhaust emission has become a serious problem of environmental. Producing ultra-low-sulfur diesel fuel is necessary in order to prevent air pollution. It is well known that hydrodesulfurization (HDS) is an effective desulfurization technology in industrial process. Therefore, it is very important to improve the performance of the current HDS catalysts. However, it would be consume a lot of resources (human, time, financial) to develop a new catalyst or improve the original catalyst. Therefore, it is necessary to propose a model approach to increase the HDS activities by controlling the main physicochemical properties of the catalysts and optimizing the process parameters. Mathematical modeling is an efficient and lowcost method which can lay the foundation for HDS catalysts technological service platform. Hence, this thesis proposed and developed a mathematical model that could be used to quantitatively analyze the effect of different variables on the HDS activity. Otherwise, the model benefits to understand the influence rule of a certain variable on HDS performance in the case as those variables are dependent on each other. The results indicate that the model has a good expansibility.

Firstly, a series of Al_2O_3 with different textural properties and acidity were obtained by hydrothermal method with acetic acid solution. The $\text{NiMo}/\text{Al}_2\text{O}_3$ catalyst which prepared by wet co-impregnation method has been shown that the textural properties and acidity are strongly dependent on the support. In addition, the support properties can influence the reducibility and the dispersion of active phase. Accordingly, a quantitative relationship model between the support properties (surface area, average pore size and surface acidity) and the conversion of dibenzothiophene (DBT) HDS was established by building the correlation between “property index” and apparent rate coefficient. So we get the equation as follows:

$$\begin{aligned} X_M &= 1 - \exp(-4.319g^{2.84}) \\ &= 1 - \exp(-4.319 \cdot S_r^{1.824} \cdot D_r^{0.674} \cdot b_r^{0.346}) \end{aligned}$$

It shows that the total average relative deviation for the proposed model is 1.43% and the prediction deviation is 2.21%. The effects of the property variables on the catalyst activity follow the order as surface area > average pore size > surface acidity properties of the supports. Moreover, an analysis method for the contribution rate of the property variables to the catalytic activity was provided and ΔX_M will be determined by Δg .

Next, a series of NiMo/Al₂O₃ catalysts with different metal loading were prepared to revise the model. The metal loading can influence the reducibility and the dispersion of the catalysts. NiO loading, MoO₃ loading and the MoS₂ dispersion of the catalysts will be considered and a “dynamic super geometric average” was applied to replace describe catalyst property index. So we get a quantitative relationship equation between the catalyst properties and the HDS conversion as follows:

$$X_M = 1 - \exp(-1.95 \cdot N_r^{1.45-2.83N_r} \cdot M_r^{1.35-2.06M_r} \cdot f_r^{0.65})$$

The average relative deviation is only 1.13 %. The results indicate that NiO loading has a higher influence degree than MoO₃ loading on the HDS activity. The optimum MoO₃ loading and NiO loading are 12 wt. % and 3 wt. % respectively. The revised model suggests that this approach also can be worked for wide range of variables.

Finally, a series of NiMo/Al₂O₃ catalysts with different calcination temperature were prepared in order to research the selectivity of model variables and expand the application of the model. High calcination temperature will cause a great loss of specific surface area, pore volume and increases average pore size. Moreover, with the calcination temperature increasing, the reducibility and dispersion of the active components decrease. The calcination temperature is regarded as a property variable, so an equation between calcination temperature and the HDS conversion can be obtained as follows:

$$X_M = 1 - \exp(-0.19 \cdot T_r^{5.43-17.1T_r})$$

The average relative deviation is 2.68 % and the fitting curve is good match with experimental results. The results indicate that the model variables can extend to preparation conditions of catalysts. In addition, the optimum calcination temperature is 450~500 °C according to the fitting results.

Moreover, the model was verified by different type of variables. The NiO loading, MoO₃ loading and calcination temperature of the catalysts will be considered within a certain range. We can obtain

$$X_M = 1 - \exp(-0.27 \cdot T_r^{-5.82} \cdot N_r^{1.78} \cdot M_r^{0.59})$$

The average relative deviation is 2.68 %. The results are consistent with the research of separate variable.

Keywords: hydrodesulfurization; model; support property; metal loading; calcination temperature; NiMo/Al₂O₃ catalyst.

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