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I : 镍卟啉加氢脱镍催化剂的研究

Study on the HDM Catalysts for Ni Removal of Ni-TPP

II :  $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$  的制备、表征及其光催化性能研究

Preparation, Characterization of  $\text{LaNi}_{1-x}\text{Cu}_x\text{O}_3$

Photocatalyst and its Photocatalytic Activity for Water

Splitting

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## 摘要

原油重质化的逐渐加剧产生了两方面的影响。一是渣油产量增加，使得渣油加氢处理技术越来越受到关注；二是渣油中的金属镍和钒杂质含量随之提升，这对于整个加氢处理过程有很多不利的影响。因此，研究镍、钒的脱除机理和方法包括相关催化剂对渣油深加工意义重大。

本文主要研究内容和获得的重要结果如下。

(1) 开发一种制备加氢脱金属催化剂的方法，即以氯化铝、碱式碳酸镍和钼酸铵为原料，尿素和碳酸铵为添加剂，通过一步控制组分析出法制备MoNi-Al<sub>2</sub>O<sub>3</sub> HDM催化剂。此方法由于无需过滤和洗涤，缩短了制备时间和降低过程成本。研究表明，制备的催化剂具有较好的孔隙率，且Ni、Mo等活性组分分散均匀。

以溶解在液体石蜡中的模型化合物镍卟啉(Ni-TPP)为评价对象，对所制备的MoNi-Al<sub>2</sub>O<sub>3</sub>催化剂进行活性评价，并与浸渍法制备的相同组分催化剂进行对比。实验结果表明，一步法制备的MoNi-Al<sub>2</sub>O<sub>3</sub>催化剂对于镍卟啉的脱镍反应(以下简称HDM)具有优异的活性。

(2) 选用不同的制备方法如水热和溶胶凝胶法及不同的添加剂制备NiW非负载型HDM催化剂，运用XRD、BET、TPR和XPS等手段对催化剂进行表征，结果表明：(a) 无论是采用水热合成法还是溶胶凝胶法制备NiW非负载型加氢脱金属(HDM)催化剂时，若加入合适的添加剂，则其HDM活性显著提高，尤其以加入尿素效果最佳。(b) 无添加剂所制NiW催化剂的孔隙性质较差，当加入添加剂后，孔隙性质明显改善，尤其以添加尿素最为显著。(c) 尿素不仅可以络合金属离子，而且还具有燃烧和助燃作用。这些作用提高了金属组分的分散性，同时促进催化剂的还原硫化，从而提高其HDM活性。

(3) 研究不同预处理方法(还原或硫化)对NiW非负载型催化剂物化性质及HDM活性的影响。选用NiW非负载型催化剂作为研究对象是因为：①此类催化剂不存在载体的影响，金属组分间相互作用较为简单，其作用机理容易了解；②此类催化剂有可能提供较多的活性中心数目。利用BET、XRD、

TPR、H<sub>2</sub>-TPD、XPS 和 TEM 等手段，对上述系列催化剂分别进行表征，以建立不同预处理方法与催化剂还原（硫化）程度及活性相结构与催化性能之间的关系，探讨其内在规律。结果表明：

(a) 无论是硫化态催化剂还是还原态催化剂，在合适的 W/Ni 比条件下，都能得到较高的 HDM 活性，脱镍转化率高于 99.0%。对于硫化态催化剂，合适的 W/Ni 比较大，范围为 0.25-0.35，而还原态催化剂合适的 W/Ni 比为 0.1-0.25。可见，高活性还原态催化剂需要更多的 Ni 组分。

(b) 对于硫化态 NiW 非负型催化剂，XRD 和 TEM 图显示其存在诸多相关物种（相），如 Ni、Ni<sub>3</sub>S<sub>2</sub>、NiO<sub>x</sub>、WS<sub>2</sub>、WO<sub>x</sub>、WO<sub>3</sub> 和 NiWO<sub>4</sub> 等，这些物相体量分布可以通过变动 W/Ni 比和硫化条件（强度）来控制。

在低的 W/Ni 比条件下，主要存在五种物相 Ni<sub>3</sub>S<sub>2</sub>、NiO<sub>x</sub>、WO<sub>x</sub>、WS<sub>2</sub> 和 WO<sub>3</sub>，并且这些物相的量应当在合适的比例范围内，才能获得高的 HDM 活性。当 W/Ni 比过低时，后面三种物相过少，将使总体 HDM 活性降低；当 W/Ni 比过大时，催化剂难以硫化，也使活性减弱。

(c) 对于还原态 NiW 非负型催化剂，原位 XRD 图及相关研究结果显示存在诸多相关物种，如 Ni<sup>0</sup>、Ni<sub>x</sub>O<sub>y</sub>、WO<sub>y</sub>、NiWO<sub>4</sub> 和 WO<sub>3</sub> 等，这些物相体量分布可以通过变动 W/Ni 比和还原条件（强度）来控制。

还原态 NiW 双组分催化剂，也显示了较高的 HDM 活性，说明非硫化的催化剂也有内在活性。从原位 XRD 及 H<sub>2</sub>-TPD 结果推测可知，H<sub>2</sub> 在 Ni<sup>0</sup> 或者 Ni<sub>x</sub>O<sub>y</sub> 上吸附形成解离的活泼氢原子，然后氢原子迁移到酸性位 WO<sub>y</sub>，这与 HDS 催化剂的遥控模型类似。

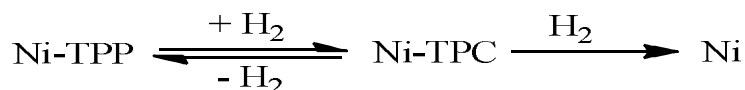
在低的 W/Ni 比条件下，Ni<sup>0</sup> 位点较多，H<sub>2</sub>-TPD 第一脱附峰面积较大，且随着 W 含量逐渐提高，WO<sub>3</sub> 点位也增多，使溢流氢数量增大。对于高 W/Ni 比或单 W 催化剂，Ni<sup>0</sup> 数量很小或者不存在，所以难以检测到第一脱附峰。

(4) 加氢脱金属催化反应的动力学研究一直是人们关注的热点之一，这方面的研究不仅在理论上具有重要的意义，而且对相应工艺条件的优化也具有参考价值。因此，进一步考察经不同预处理方法获得的 NiW 非负载型催化剂的 HDM 活性与反应条件如反应温度和反应时间，以期对反应历程有所了解。

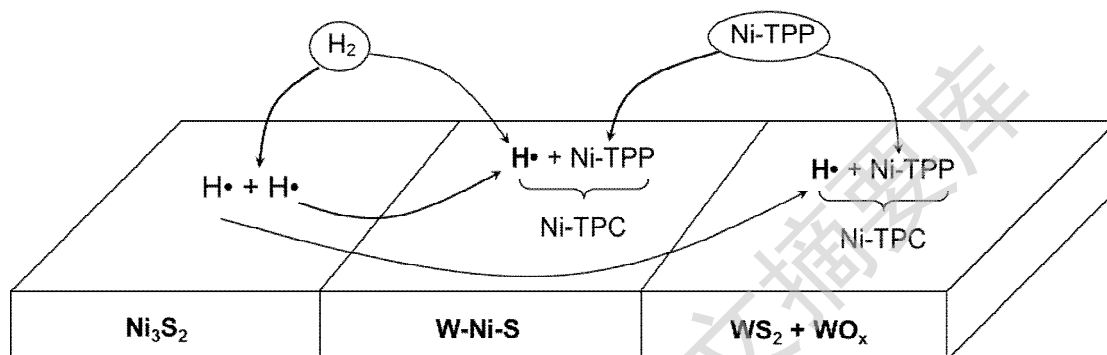
对溶解在液体石蜡中的卟啉镍模型化合物进行 HDM 反应，结果表明，延长反应时间和提高反应温度将会促进卟啉镍的加氢反应，有效地提高脱镍率。

(a) 对于硫化态催化剂，通过分析、综合先前和本文的研究试验结果，初步提出如下反应历程和活性相模型。

反应历程：

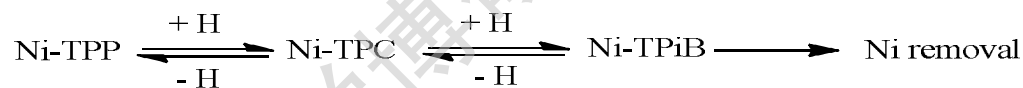


对应的活性相模型（多相共存）可简示为：

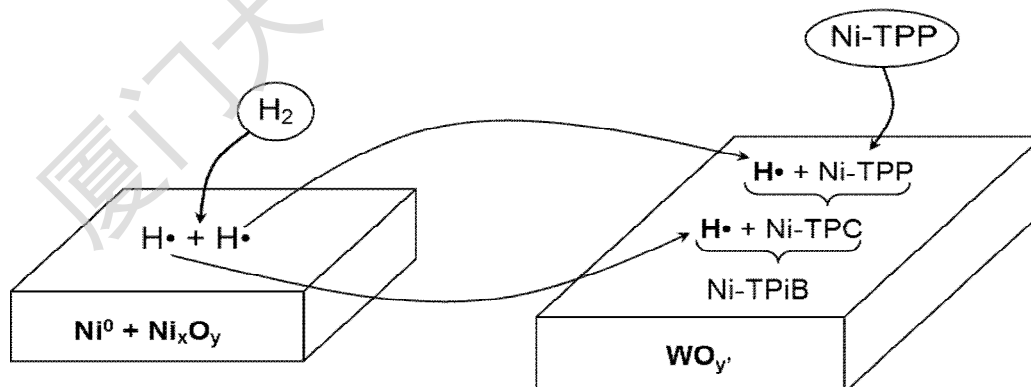


(b) 对于还原态催化剂，通过系统研究，初步提出如下反应历程和活性相模型。

反应历程：



对应的活性相模型（氢溢流）：



关键词：金属卟啉，镍卟啉化合物，加氢脱金属，MoNi-Al<sub>2</sub>O<sub>3</sub> 催化剂，NiW 非负载催化剂，还原/硫化处理，活性相模型

## Abstract

With the vast deposits of heavy crude oils in several parts of the world, it will have a significant impact on two aspects. One is the increasing amount of residua, which makes the hydrotreating process receive more and more attentions; the other is the abundant and undesirable metal Ni and V, which will produce much adverse influences on the hydrotreating process. These trends have emphasized the tremendous importance of the research on the removal of metals.

The predominant research content and result obtained from experiment are summarized as follows:

(1) A new approach has been developed for the first time to prepare HDM catalyst. Videlicet, a series of NiMo-Al<sub>2</sub>O<sub>3</sub> catalysts are prepared by one-pot method with controlled precipitation of AlCl<sub>3</sub>·6H<sub>2</sub>O, (NH<sub>4</sub>)<sub>6</sub>Mo<sub>7</sub>O<sub>24</sub>·4H<sub>2</sub>O and NiCO<sub>3</sub>·2Ni(OH)<sub>2</sub>·4H<sub>2</sub>O using urea and ammonium carbonate as additives. This method shortens synthetic process and lowers costs due to free of filtering and washing. The characterization results show that the effective hydrotreating catalyst prepared by optimum urea additive has high porosity and well dispersed nickel and molybdenum oxide particles.

The HDM of Ni-TPP dissolved in liquid paraffin was used as a model reaction for estimating the activity of the above prepared catalyst samples. For comparison, the reference catalyst with same components were prepared by wet-impregnation method. The results show hydrotreating catalysts prepared by one-pot method had high HDM performance.

(2) Different preparation method (such as hydrothermal method and sol-gel method) and various additives was chose to synthesize NiW unsupported catalysts, and the resultant catalysts were characterized by XRD、BET、TPR and XPS. The results show that (a) All additives used in hydrothermal or sol-gel enhance the activity of NiW unsupported catalysts in HDM of Ni-TPP, especially urea additive most effective. (b) unsupported catalysts prepared with additive had well porosity, especially urea additive most best, whereas NiW catalysts prepared without additive



had bad porosity, (c) Urea employed as additive not only chelate metal Ni and W ion, increase the combustion rate and undergo a decomposition process (endothermic reaction) that could contribute to the reduction of the combustion temperature, but also can improve well-dispersed Ni- and W-oxo species and facilitate the formation of reduced and sulfided catalyst, ultimately enhance HDM activity.

(3) The effect of the pretreatment conditions such as sulfuration and reduction on the structure properties of the NiW unsupported catalysts and the HDM activity were investigated. Choosing NiW unsupported catalysts as model study is just to ① simplify the catalytic system without the influence of metal-support interaction and ② have much possible active site. BET, XRD, TPR, H<sub>2</sub>-TPD, XPS and TEM characterizations were studied with a view to establishing the relationship between active structure and catalytic performance of these pretreated catalysts

(a) The catalysts were studied in the variable W/Ni ratio. Reaction of the unsupported NiW catalyst pretreated in reduction or sulfidation conditions with Ni-TPP at 220 °C in the presence of H<sub>2</sub> obtained high HDM activity, respectively, at different W/Ni ratio. Sulfided catalysts with the W/Ni ratio of 0.25-0.35 can give the HDM activity of 99.0% or above, whereas the suitable W/Ni ratio in reduced catalysts is 0.1-0.25, suggesting more Ni component is needed in reduced catalysts.

(b) For sulfided NiW unsupported catalysts, XRD and TEM results show that there are some relevant species such as Ni, Ni<sub>3</sub>S<sub>2</sub>, NiO<sub>x</sub>, WO<sub>x</sub>, WS<sub>2</sub>, WO<sub>3</sub> and NiWO<sub>4</sub>, and the relative speciation of these phases can be controlled by parameters as the W/Ni ratio and sulfidation condition.

At low W/Ni ratio, Ni<sub>3</sub>S<sub>2</sub>, NiO<sub>x</sub>, WO<sub>x</sub>, WS<sub>2</sub> and NiWO<sub>4</sub> are coexisted in catalysts. The high HDM activity can be obtained only when the amount of these species is in an appropriate ratio. When W/Ni ratio is too low, the HDM activity is reduced due to the lower amount of WO<sub>x</sub>, WS<sub>2</sub> and NiWO<sub>4</sub>. When W/Ni ratio is too high, the NiW catalyst is difficult to sulfide, which also make the activity drop.

(c) For reduced NiW unsupported catalysts, in situ XRD result show that there are some relevant species such as Ni<sup>0</sup>, Ni<sub>x</sub>O<sub>y</sub>, WO<sub>y</sub>, NiWO<sub>4</sub> and WO<sub>3</sub>, and these species can be adjusted by the variable W/Ni ratio and reduction condition.

Reduced catalysts also show quite a measurable activity in HDM of Ni-TPP. Hence, it may be assumed that non-sulfided catalysts show some intrinsic HDM

activity. According to the outcome of in-situ XRD and H<sub>2</sub>-TPD experiments, it is suggested that H<sub>2</sub> dissociates on the Metal Ni<sup>0</sup> or oxide Ni<sub>x</sub>O<sub>y</sub> into highly reactive hydrogen species (H·), which then spills over onto the Bronsted site or Lewis site of oxide WO<sub>y</sub>. This process is similar to Remote-Control model of HDS catalyst.

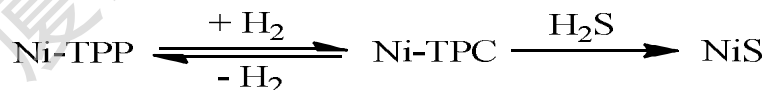
The amount of H<sub>2</sub> adsorbed both in the low and high temperature stage increases with the increasing of W content and reaches a maximum, then decreases and even disappears at W/Ni atomic ratio of 0.75 or above. For the catalyst with high W/Ni ratio or single W, the concentration of Ni<sup>0</sup> is so little or none that it is hard to detect the hydrogen desorbed on the catalysts.

(4) The theory of the kinetics of HDM is focused on by researcher and developed with the experimentally supported assumptions, such insights may provide the basis for a better optimizing of the reaction condition in direct demetallation and hydrogenation routes in HDM. Issues explore are elucidation of the HDM reaction mechanism of Ni-TPP in the presence of sulfided or reduced catalyst and the influence of reaction condition such as reaction temperature, reaction time, H<sub>2</sub> partial pressure and catalyst weight on the HDM kinetics.

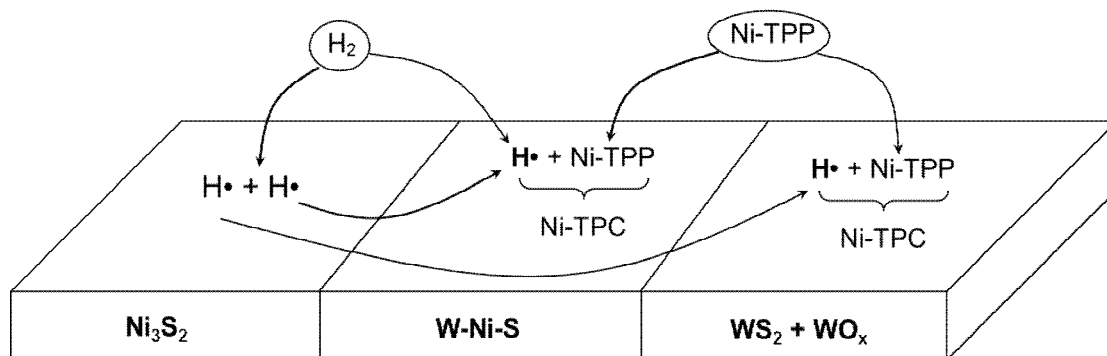
HDM of Ni-TPP results show that long reaction time, increased catalyst weight, high reaction temperature and elevated H<sub>2</sub> partial pressure will greatly promote the hydrogenation of Ni-TPP and effectively enhance the removal of Ni.

(a) For sulfide catalyst, from the previous studies and our experimental results, we preliminary propose the intrinsic HDM kinetics and model of active species.

HDM kinetics:

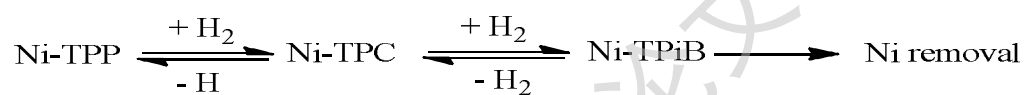


Model of active species (multiphase coexist):

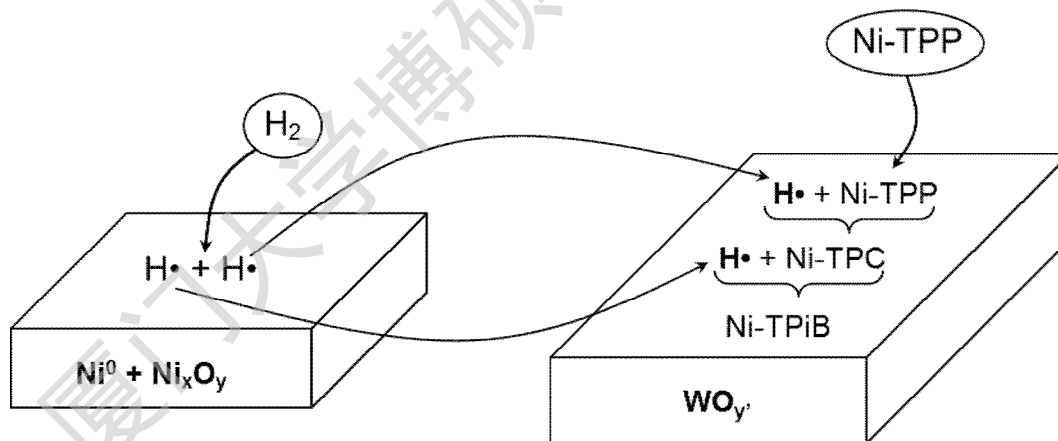


(b) For the reduced catalyst, based on the systematic studies, we preliminary propose the intrinsic HDM kinetics and model of active species.

HDM kinetics:



Model of active species (multiphase coexist):



**Keywords:** Metal porphyrin, Nickel porphyrin, Hydrodemetallation (HDM),  $\text{MoNi-Al}_2\text{O}_3$  catalyst, NiW unsupported catalyst, Reduction/Sulfidation pretreatment, Model of active species

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