磷化镍/介孔 TiO_2 催化剂的制备及其催化加氢脱硫性能

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摘要: 以介孔 TiO_2 (m- TiO_2) 为载体, 采用程序升温还原法制备了 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂, 考察了不同起始 Ni/P 摩尔比及活性组分负载量对该催化剂结构及其催化加氢脱硫 (HDS) 性能的影响。结果表明, 当 Ni/P 摩尔比为 1.25 时, 活性组分以 Ni_2P 为主, 催化剂的最佳 Ni 负载量为 10%。采用 X 射线衍射、低温 N_2 吸附-脱附、场发射扫描电镜和程序升温还原等技术表征了 m- TiO_2 及其它不同载体负载的 Ni_2P 催化剂。结果表明, 高结晶度 m- TiO_2 载体使 Ni 和 P 物种的还原温度大幅度降低, 在 450~600 °C 还原制得的 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂的结构参数基本一致, 比表面积均为 90 m^2/g 左右, 具有很高的热稳定性和对二苯并噻吩的 HDS 催化性能。在相同的反应条件下, m- TiO_2 负载的 Ni_2P 催化剂 HDS 性能最好, 各载体负载的 Ni_2P 催化剂活性大小顺序为 $\text{Ni}_2\text{P}/\text{m-TiO}_2 > \text{Ni}_2\text{P}/\text{SiO}_2 > \text{Ni}_2\text{P}/\text{P25}$ 。

关键词: 介孔; 二氧化钛; 磷化镍; 加氢脱硫; 二苯并噻吩

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Preparation of Nickel Phosphide/Mesoporous- TiO_2 Catalyst and Its Hydrodesulfurization Performance

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Abstract: Using mesoporous TiO_2 (m- TiO_2) as the support, novel nickel phosphide/m- TiO_2 catalysts ($\text{Ni}_2\text{P}/\text{m-TiO}_2$) were prepared by a temperature-programmed reduction method. The influence of the Ni/P molar ratio and the amount of active component on the catalyst structure and the hydrodesulfurization (HDS) performance was investigated. The results indicated that the reduction of precursor with Ni/P = 1.25 yielded mainly Ni_2P , and the optimum loading of Ni was 10%. The influence of m- TiO_2 on the preparation and HDS performance of nickel phosphide catalysts was also evaluated by X-ray diffraction, N_2 physisorption, field-emission scanning electron microscopy, and temperature-programmed reduction. The results showed that m- TiO_2 with high crystallinity could dramatically decrease the reduction temperatures of Ni and P species. When the reduction temperatures were between 450 and 600 °C, the textures of the $\text{Ni}_2\text{P}/\text{m-TiO}_2$ catalysts were very similar and the specific surface areas were about 90 m^2/g . The effects of the support on the dibenzothiophene HDS performance of the nickel phosphide catalysts were also investigated. The results showed that the order of dibenzothiophene conversion was $\text{Ni}_2\text{P}/\text{m-TiO}_2 > \text{Ni}_2\text{P}/\text{SiO}_2 > \text{Ni}_2\text{P}/\text{P25}$.

Key words: mesoporous; titania; nickel phosphide; hydrodesulfurization; dibenzothiophene

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过渡金属磷化物是一种具备独特物理化学特性的新型材料,在催化、电子和电磁等许多领域受到了广泛的关注^[1~4]。研究发现,过渡金属磷化物具有良好的油品加氢脱硫 (HDS) 和加氢脱氮性能,其中以 Ni_2P 的催化性能最佳,表现出与贵金属相当的高催化活性^[1,5],在石油加工领域具有巨大的应用潜力。

然而,常规非负载型 Ni_2P 催化剂的比表面积很小 ($< 10 \text{ m}^2/\text{g}$),催化活性不能充分发挥^[6],将 Ni_2P 负载在高比表面积的载体上是目前提高其总体活性的主要方法之一。常用的载体有 Al_2O_3 ^[7], SiO_2 ^[5], SBA-15^[8], 超稳 Y 型分子筛^[9], 活性炭^[10] 和 MCM-41^[11] 等。载体的表面性质和结构对负载的过渡金属磷化物的制备和催化性能有很大的影响^[12]。 $\gamma\text{-Al}_2\text{O}_3$ 是典型的加氢催化剂载体,但由于 $\gamma\text{-Al}_2\text{O}_3$ 和磷之间存在强相互作用,在载体表面形成磷铝酸盐^[13],从而阻碍磷化物的形成,因而不宜用作 Ni_2P 催化剂的载体。 SiO_2 是传统的大比表面积稳定的催化剂载体,负载于其上的 Ni_2P 催化剂在 HDS 反应中表现出较高的活性和选择性^[14],因而成为目前负载磷化镍最常用的载体基材。 TiO_2 作为新一代催化剂载体引起了广泛关注,和惰性载体相比,它能促进电子转移^[15],获得较低价态的钼,因而在 HDS 过程中表现出较高的催化活性和选择性^[16,17]。Wang 等^[18]发现 TiO_2 能够有效地提高 Ni_2P 催化剂的性能, Li 等^[19,20]发现 TiO_2 与 Ni_2P 的复合物较未负载的 Ni_2P 具有更多的活性中心和低酸性的特点。然而常规的 TiO_2 比表面积较小,一般在 $50 \text{ m}^2/\text{g}$ 以下^[21,22],且热稳定性较低, 550°C 会出现金红石相^[23]。在目前程序升温还原法制备 Ni_2P 催化剂^[24]过程中,常规 TiO_2 难以在高温下保持自身的结构,出现转晶和结构坍塌现象。因此,比表面积小和热稳定性差成为 TiO_2 用作 Ni_2P 催化剂载体的瓶颈。

本课题组从钛酸盐出发^[25],采用离子交换并于 500°C 热处理得到比表面积大于 $100 \text{ m}^2/\text{g}$ 、孔径均一、结晶度高的锐钛矿型介孔 TiO_2 ,经 600°C 焙烧后,其比表面积为 $59 \text{ m}^2/\text{g}$ ^[26],当焙烧温度升至 900°C 时仍然能够保持完整的锐钛矿结构^[27]。以介孔

TiO_2 (m- TiO_2) 为载体制得的催化剂在对硝基苯酚加氢^[28]、CO 氧化^[26,29]、酯化^[30]和还原产氢^[31,32]等体系中均表现出良好的性能,具有广泛的应用前景。

因此,本文以上述介孔 TiO_2 为载体,采用程序升温还原法制备磷化镍/m- TiO_2 催化剂。借助 X 射线衍射 (XRD)、低温 N_2 吸附-脱附、场发射扫描电镜 (FESEM) 及程序升温还原 (H_2 -TPR) 等手段表征了载体及催化剂结构和性质,通过二苯并噻吩/十氢萘模拟柴油体系评价了催化剂的 HDS 催化性能。

1 实验部分

1.1 样品的制备

按一定 Ni/P 摩尔比在硝酸镍 (恒信化学试剂有限公司) 水溶液中加入磷酸氢二铵溶液 (西陇化工厂),得到黄色沉淀;滴加少量硝酸 (中试化工总公司),待沉淀完全溶解后,加入介孔氧化钛 (按文献^[25]制备),搅拌加热蒸去过量水分,于 120°C 烘干,然后在空气气氛中于 500°C 焙烧 2 h 制得催化剂前驱体。

将催化剂前驱体在 200°C 用 100 ml/min 的 N_2 处理 2 h,然后切换成 150 ml/min 的 H_2 ,以 3°C/min 升至指定温度保持 2 h,待冷却至室温后,切换成 60 ml/min 的 N_2 钝化 1 h,即得磷化镍/m- TiO_2 催化剂,标记为 $\text{Ni}_2\text{P/m-TiO}_2$ 。以商业二氧化钛 (P25, Degussa 公司,比表面积 $50 \text{ m}^2/\text{g}$,锐钛矿和金红石含量比约为 4:1) 和氧化硅 (Degussa 公司) 为载体,制备条件基本同上,还原温度为 650°C ,分别制得 $\text{Ni}_2\text{P/P25}$ 和 $\text{Ni}_2\text{P/SiO}_2$ 催化剂。

1.2 样品的表征

样品的物相结构采用德国 Bruker 公司的 D8 Advance 型 X 射线衍射仪检测, $\text{Cu K}\alpha$ 辐射源,管电流 30 mA ,管电压 40 kV ,扫描范围 $2\theta = 5^\circ \sim 60^\circ$,扫描步长 0.05° ,扫描速率 0.2 s/step 。 H_2 -TPR 实验在天津先权工贸发展有限公司 TP-5000 型多用吸附仪上进行,检测前催化剂前驱体先用 20 ml/min 的 N_2 于 200°C 预处理 2 h,然后降至室温,在 20 ml/min 的 $10\% \text{ H}_2$ - $90\% \text{ N}_2$ 混合气中,以 10°C/min 程序升温

到预定温度, TCD 检测耗氢量. 样品的织构性质采用美国 Micromeritics 公司 TristarII 3020M 型比表面孔隙吸附仪测定, 通过 BET 方程和 BJH 模型分别计算比表面积及孔体积和孔径. 样品的微结构形貌采用 Hitachi S-4800 型场发射扫描电镜观测, 操作电压为 5 kV.

1.3 样品的评价

在微型固定床反应器(自制, 装置结构流程参见文献[33])上进行加氢脱硫实验, 其中反应管内径为 9.4 mm, 长 500 mm. 将上述催化剂在 12 MPa 下压片成型, 破碎筛分, 选取 20~40 目的催化剂 0.333 g, 用 1.5 g 相同目数石英砂稀释后置于反应器恒温段内, 于 400 °C 用 60 ml/min 的 H_2 处理 2 h, 去除表面的钝化层. 以 0.5% 二苯并噻吩/十氢萘模拟柴油反应液, 将温度调至设定值, 压力 2.0 MPa, 氢气流速 40 ml/min, 体积空速 $12\ h^{-1}$. 预反应 4 h 稳定后开始采集第一个产物, 之后每隔 1 h 采集一次. 反应产物采用山东鲁南瑞虹化工仪器有限公司 SP-2000A 型气相色谱仪进行分析, 石英毛细管色谱柱 (0.32 mm $\times$ 30 m), 固定相为 PEG-20M, FID 检测器.

2 结果与讨论

2.1 磷化镍结构表征

图 1 是 Ni 负载量为 20%, 还原温度为 650 °C 时不同起始 Ni/P 摩尔比制备的 $Ni_2P/m-TiO_2$ 催化剂的 XRD 谱. 由图可见, 样品在 $2\theta = 40.7^\circ$, 44.6° 和 47.3° 处出现衍射峰, 对应于 Ni_2P 相 (PDF 03-0953),

图 1 不同起始 Ni/P 摩尔比制得的 $Ni_2P/m-TiO_2$ 催化剂的 XRD 谱

Fig. 1. XRD patterns of $Ni_2P/m-TiO_2$ obtained from various initial Ni/P molar ratios. Ni loading: 20%; reduction temperature: 650 °C.

另外, $2\theta = 48.9^\circ$ 处衍射峰对应于 $Ni_{12}P_5$ 相 (PDF 22-1190). 可以看出, 当 Ni/P 摩尔比为 0.5, 1 和 1.25 时, 催化剂中物相主要为 Ni_2P ; 至 2 时催化剂中 Ni_2P 衍射峰降低, 同时出现 $Ni_{12}P_5$ 相, 这与 P 在还原过程中生成 PH_3 挥发损失有关^[34]. Wang 等^[11]研究发现 $Ni_{12}P_5$ 相催化活性低于 Ni_2P 相, 李冬燕等^[35]研究了金红石型 TiO_2 负载 Ni_2P 催化剂, 发现起始 Ni/P 摩尔比从 1/3 到 1/2, XRD 衍射峰强度却有所增加. 原因可能是在 Ni 含量恒定时, 大大过量的 P 有助于生成的 Ni_2P 晶体生长. 而本文样品中 P 相对较少, 随着 Ni/P 摩尔比的增大, 富余的 P 越来越少, 劣化了 Ni_2P 的生长环境, 因此 Ni_2P 衍射峰强度逐渐降低.

图 2 是在 Ni/P 摩尔比为 1.25, 还原温度为 650 °C 条件下制备的不同 Ni 负载量 $Ni_2P/m-TiO_2$ 催化剂的 XRD 谱. 由图可见, 当 Ni 负载量 5% 时, 样品中未出现 Ni_2P 衍射峰, 表明 Ni_2P 较好地分散在载体表面; 至 10% 时, $Ni_2P/m-TiO_2$ 催化剂出现微弱的 Ni_2P 衍射峰, 且随着 Ni 负载量进一步增加而越来越明显. 根据 $Ni_2P(201)$ 晶面 ($2\theta = 44.6^\circ$) 衍射峰由 Scherrer 公式算得 Ni 负载量为 15% 和 20% 时催化剂表面 Ni_2P 晶粒粒径分别为 18.4 和 26.1 nm. 这表明随着 Ni 负载量增加, 活性组分 Ni_2P 晶粒长大, 在载体上分散性变差.

图 2 不同 Ni 负载量的 $Ni_2P/m-TiO_2$ 催化剂的 XRD 谱

Fig. 2. XRD patterns of $Ni_2P/m-TiO_2$ with various Ni loadings. Initial Ni/P molar ratio: 1.25; reduction temperature: 650 °C.

图 3 是 Ni 负载量为 10%, 还原温度为 650 °C, 不同起始 Ni/P 摩尔比制备的催化剂上 HDS 反应性能. 可以看出, 当 Ni/P 摩尔比为 1 及 1.25 时, 催化

图3 Ni/P 摩尔比对 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂上 HDS 反应性能的影响

Fig. 3. Influence of initial Ni/P molar ratios on dibenzothiophene (DBT) HDS performance of $\text{Ni}_2\text{P}/\text{m-TiO}_2$ catalyst. Ni loading: 10%; reduction temperature: 650 °C; reaction temperature: 340 °C.

剂活性最佳, 二苯并噻吩转化率为 92% 左右, 至 Ni/P 比值为 2 时又降到 47%。可见 Ni/P 摩尔比对所制催化剂性能有显著影响: 当 Ni/P 比较低时, 活性组分以 Ni_2P 相为主, Ni_2P 催化剂上 HDS 反应性能随着 Ni/P 比提高而增加; 当 Ni/P 比进一步增大时, 活性组分中出现 Ni_{12}P_5 , 催化剂的 HDS 性能下降。负载在 SiO_2 ^[5]、活性炭^[10]和 MCM-41^[11]上的磷化镍均以 Ni_2P 活性最高, TiO_2 作为载体也不例外。因此在催化剂制备过程中 Ni/P 摩尔比应略小于理论值 2, 以保证活性组分结构为 Ni_2P 相, 因此本文认为采用 Ni/P 为 1.25 较为合适。

图 4 是 Ni/P 摩尔比为 1.25, 还原温度为 650 °C 条件下制得的催化剂中不同 Ni_2P 负载量对 HDS 反应性能的影响。可以看出, 当 Ni 负载量为 5% 时, DBT 转化率仅有 21%, 至 10% 和 15% 时, DBT 转化率基本相当, 达到 72% 左右, 而当 Ni 负载量为 20% 时, DBT 转化率降至 62%。结合 XRD 结果认为, 催化剂中活性组分负载量和分散度都会影响其 HDS 性能: 当活性组分负载量较低时, 因活性位数量较少而造成催化剂性能较低; 而当 Ni_2P 含量过高时, Ni_2P 晶粒长大, 在介孔 TiO_2 载体上分散性变差, 导致催化剂的 HDS 反应性能降低。可见, 催化剂中适宜 Ni_2P 负载量 (以 Ni 计) 约为 10%。

2.2 催化剂低温还原活性

图 5 是不同载体负载的磷化镍催化剂前驱体

图4 Ni 负载量对 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂上 HDS 反应性能的影响

Fig. 4. Influence of Ni loadings on DBT HDS performance of $\text{Ni}_2\text{P}/\text{m-TiO}_2$ catalyst. Ni/P molar ratio: 1.25; reduction temperature: 650 °C; reaction temperature: 340 °C.

(Ni 负载量为 10%, Ni/P 摩尔比为 1.25) 的 H_2 -TPR 谱。由图可见, 以介孔 TiO_2 为载体时, 样品在 450 和 540 °C 出现还原峰, 分别对应于 Ni 物种和 P 物种的还原, 并且两者的还原几乎同时发生。在 H_2 -TPR 过程中, 由于 Ni 物种优先还原, 生成的 Ni 首先吸附 H_2 并解离成活性氢, 后者促进了 P 物种还原, 进一步反应生成 Ni_2P ^[36]。这与 XRD 结果较为一致, 如图 6 所示, 还原温度为 500 °C 制备的 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂表面已经开始出现 Ni_2P 相, 至 650 °C 时样品中 Ni_2P 的衍射峰强度增加。鲁墨弘等^[37]以 TiCl_4 水解生成无定形 TiO_2 为前驱体, 制备

图5 不同载体负载的 Ni_2P 催化剂前驱体的 H_2 -TPR 谱

Fig. 5. H_2 -TPR profiles of precursors of Ni_2P catalysts with various supports. Ni loading: 10%; initial Ni/P molar ratio: 1.25.

图 6 不同还原温度制备的 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 样品的 XRD 谱

Fig. 6. XRD patterns of $\text{Ni}_2\text{P}/\text{m-TiO}_2$ reduced at 500 and 650 °C. Ni loading: 10%; initial Ni/P molar ratio: 1.25.

了 Ni_2P 催化剂, 发现当还原温度超过 300 °C 时, NiO 和 TiO_2 会生成难以还原的 NiTiO_3 . 本课题组前期研究表明^[38], 无定形 TiO_2 比结晶 TiO_2 有更高的反应活性, 本文采用相对惰性的高结晶度介孔 TiO_2 为载体, 充分发挥了 TiO_2 的促电子转移, 提高 HDS 活性的作用; 另一方面, 结晶 TiO_2 抑制了 Ni-TiO_3 的生成, 使 Ni、P 物种的还原温度大幅度降低. 以混合晶型的 P25 为载体时, TPR 测试所得前驱体表明, 相对于 SiO_2 等惰性载体, 结晶 TiO_2 可促进磷镍化合物形成, 结合图 6 可认为, 在 P25 表面上首先形成了 Ni_{12}P_5 .

2.3 催化剂的热稳定性

H_2 -TPR 结果表明, 介孔 TiO_2 作为载体有助于活性组分 Ni_2P 在较低温度下生成, 有必要进一步考察其在低温下的结构稳定性及其催化 HDS 反应性能. 表 1 列出了还原温度 450~650 °C 制备的 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 及介孔 TiO_2 载体的结构性质. 可以看

表 1 各样品的比表面积、孔体积及平均孔径

Table 1 Surface area, pore volume, and pore size of various samples

Catalyst	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_{\text{pore}}/(\text{m}^3/\text{g})$	$d_{\text{pore}}/\text{nm}$
m- TiO_2	132.5	0.34	8.6
$\text{Ni}_2\text{P}/\text{SiO}_2(650)$	141.0	0.50	10.0
$\text{Ni}_2\text{P}/\text{P25}(650)$	42.1	0.12	9.6
$\text{Ni}_2\text{P}/\text{m-TiO}_2(450)$	91.8	0.23	7.9
$\text{Ni}_2\text{P}/\text{m-TiO}_2(500)$	91.3	0.24	8.4
$\text{Ni}_2\text{P}/\text{m-TiO}_2(550)$	89.8	0.24	8.3
$\text{Ni}_2\text{P}/\text{m-TiO}_2(600)$	87.8	0.23	8.3
$\text{Ni}_2\text{P}/\text{m-TiO}_2(650)$	60.3	0.22	11.9

出, 介孔 TiO_2 的比表面积为 132.5 m^2/g , 孔体积及平均孔径等参数都适合用作催化剂载体, 克服了常规 TiO_2 的比表面积小, 作为载体的协同作用难以发挥的问题. 按照 Ni/P 摩尔比 1.25, 负载 10% 活性组分之后, 所得的前驱体比表面积、孔体积及平均孔径均有所下降, 这主要是由于活性组分分散在 TiO_2 的介孔孔道中所致. 当还原温度为 450~600 °C 时, 所得 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂样品的结构参数基本一致, 比表面积均为 90 m^2/g 左右. 当还原温度升高至 650 °C 时, $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂的结构有所坍塌, 但是其比表面积仍然保持在 60 m^2/g 以上, 明显高于 $\text{Ni}_2\text{P}/\text{P25}$ 催化剂. XRD 结果表明, 介孔 TiO_2 载体晶相为锐钛矿型, 表明 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂具有较高的热稳定性.

图 7 是前驱体及 500 和 650 °C 还原温度处理的 $\text{Ni}_2\text{P}/\text{m-TiO}_2$ 催化剂的 FESEM 照片. 可以看出, 载体 TiO_2 具有丰富的介孔孔道, 然而较难观测到前驱体物种, 这可能是由于它均匀分散于介孔 TiO_2 上所致. 分别经 500 或 650 °C 氢气还原处理后, 催化剂表面均形成很多白色球状 Ni_2P 团簇, 均匀地分散在介孔 TiO_2 上, 且 Ni_2P 团簇并没有随温度升高而出现增大的趋势.

图 7 各样品的 FESEM 照片

Fig. 7. FESEM images of various samples. (a) m- TiO_2 ; (b) $\text{Ni}_2\text{P}/\text{m-TiO}_2(500)$; (c) $\text{Ni}_2\text{P}/\text{m-TiO}_2(650)$.

图 8 是 Ni₂P/m-TiO₂ 催化剂对 DBT 的 HDS 反应性能. 由图可见, 经 450~650 °C 不同温度还原获得的 Ni₂P/m-TiO₂ 催化剂上 DBT 转化率均在 70%~80% 之间, 450 和 650 °C 还原制备的催化剂上 DBT 转化率略低, 这可能是由于还原温度较低时形成 Ni₂P 的量较少, 因而催化剂上 HDS 性能稍有下降; 而当还原温度较高时, Ni₂P 晶粒变大或催化剂的结构发生坍塌, 导致催化剂的活性位数量减少, 从而造成催化剂性能下降. 而以 P25 为载体, 还原温度为 500 °C 制备的 Ni₂P/P25 催化剂上 DBT 转化率只有 26%, 这可能是由于催化剂比表面积较小及在表面形成了 Ni₁₂P₅ 所致.

图 8 不同温度还原的 Ni₂P 催化剂上二苯并噻吩的 HDS 反应性能

Fig. 8. Influence of various reduction temperatures on DBT HDS performance of Ni₂P catalysts. Ni loading: 10%; initial Ni/P molar ratio: 1.25; reaction temperature: 320 °C.

2.4 不同载体负载的 Ni₂P 催化剂的 HDS 反应性能比较

图 9 是不同载体负载的 Ni₂P 催化剂上 HDS 反应性能比较, 催化剂中 Ni 负载量均为 10%, Ni/P 摩尔比为 1.25, 还原温度为 650 °C. 可以看出, 尽管 Ni₂P/m-TiO₂ 的比表面积小于 Ni₂P/SiO₂ (表 1), 但其催化性能最高, 各催化剂活性大小顺序为 Ni₂P/m-TiO₂ > Ni₂P/SiO₂ > Ni₂P/P25. 由此可见, TiO₂ 载体有利于 Ni₂P 催化剂上 HDS 反应的进行. 鲁墨弘等^[37]研究表明, 由于表面 Ti 物种上电子向 Ni₂P 转移, 使得 TiO₂ 表面钝化层中 Ni 和 P 物种的峰向低结合能方向移动, 提高了 Ni₂P 催化剂上 HDS 反应性能. 同时介孔 TiO₂ 的高比表面积有利于获得较多的活性位, 进一步提高了 Ni₂P 催化剂性能.

图 9 不同载体负载的 Ni₂P 催化剂上 HDS 反应性能的比较

Fig. 9. Comparison of DBT HDS performance of nickel phosphides on various supports. Ni loading: 10%; initial Ni/P molar ratio: 1.25; reduction temperature: 650 °C.

3 结论

以介孔 TiO₂ 为载体, 采用程序升温还原法制备了磷化镍/介孔 TiO₂ 催化剂. 高结晶度介孔 TiO₂ 载体使 Ni 和 P 物种的还原温度大幅度降低, 促进了 Ni₂P 的形成. 当还原温度为 450~600 °C 时, 所得 Ni₂P/m-TiO₂ 催化剂有很好的热稳定性和 HDS 性能. 不同载体负载 Ni₂P 催化剂的 HDS 反应结果表明, 介孔 TiO₂ 负载的 Ni₂P 催化剂的 HDS 性能最高.

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英 译 文

English Text

Transition-metal phosphides are new types of materials. They have special physical and chemical properties and have been widely studied in a range of research fields [1–4]. Transition-metal phosphides are effective in the hydrodesulfurization (HDS) and hydrodenitrogenation of petroleum. The catalytic properties of Ni₂P are better than those of noble metals [1,5]. Ni₂P has similar properties to those of noble metals and is promising for oil-processing applications.

Normally, Ni₂P catalysts have small specific surface areas (< 10 m²/g) and cannot fully exert their catalytic properties [6]. One method for improving the catalytic properties of Ni₂P is to load it onto a support with a high specific surface area. Commonly used supports include Al₂O₃ [7], SiO₂ [5], SBA-15 [8], ultra-stable zeolite-Y [9], absorbite [10], and MCM-41 [11]. The surface properties and structure of the support have a significant influence on the synthesis and catalytic properties of transition-metal phosphides [12]. γ -Al₂O₃ is a typical hydrogenation catalyst support, but it is not a suitable support for phosphates because γ -Al₂O₃ interacts strongly with P to form phosphoaluminate [13]. SiO₂ is a traditional stable catalyst support, and shows high selectivity and catalytic activity after loading with Ni₂P. SiO₂ has been chosen as the support for Ni₂P in many studies [14]. A new support, TiO₂, is better than inert supports for facilitating electron transfer [15]. Low-oxidation-state molybdenum is formed and HDS catalyst selectivity and activity are improved [16,17]. Wang et al. [18] found that TiO₂ improves the catalytic properties of Ni₂P catalysts. Ni₂P/TiO₂ composites have large numbers of active centers and low acidity [19,20]. Typically, TiO₂ has a low specific surface area, usually less than 50 m²/g [21,22], and rutile is formed at 550 °C [23]. Normally, TiO₂ cannot keep its structure, and phase transitions and structural deterioration occur when temperature-programmed reduction (TPR) methods are used to prepare Ni₂P catalysts [24]. The low specific surface area and thermostability are therefore obstacles in catalyst prepara-

tion.

He et al. [25] used ion-exchange with titanate as the precursor and calcination at 500 °C to prepare highly crystalline mesoporous TiO₂ (m-TiO₂) with a specific surface area of 100 m²/g and uniform pores. The as-prepared TiO₂ had high thermostability, and after calcination at 600 °C the specific surface area was still 59 m²/g [26]. The anatase structure was fully maintained after calcination at 900 °C [27]. We used the as-prepared TiO₂ as a support for Ni₂P, and the catalyst showed good properties in the hydrogenation of *p*-nitrophenol [28], CO oxidation [26,29], esterification [30], and reductive hydrogen production [31,32], proving that the catalyst has a wide range of applications.

In this study we use the above method to prepare m-TiO₂ as the support and TPR method to prepare Ni₂P/mesoporous TiO₂ catalyst. The support was characterized by X-ray diffraction (XRD), N₂ adsorption-desorption, field-emission scanning electron microscopy (FESEM), and TPR. The HDS properties were evaluated using a dibenzothiophene (DBT)/decahydronaphthalene system to simulate diesel.

1 Experimental

1.1 Sample preparation

The preparation of the Ni₂P catalyst consisted of two steps: preparation of the support, and reduction. In the first step, (NH₄)₂HPO₄ (Xi Long Chemical Plant) solution was added dropwise to a Ni(NO₃)₂·6H₂O (Heng Xin Chemical Reagent Co., Ltd.) solution in a given molar ratio, and a small amount of HNO₃ (Zhong Shi Chemical Corporation) was added dropwise to the solution until the yellow precipitate formed was dissolved. m-TiO₂ (prepared as in Ref. [25]) was then added to the solution, and the solution was stirred. Heating at 120 °C and calcination at 500 °C for 2 h gave the support precursor. In the second step, the precursor was treated in a N₂ atmosphere (flow rate 100 ml/min) at 200 °C for 2 h and then in a H₂ atmosphere (flow rate 150 ml/min) at 3 °C/min, and kept at a given temperature for 2 h. After cooling to room temperature, the catalyst was inactivated in a N₂ atmosphere for 1 h (flow rate 60 ml/min); the as-prepared catalyst was designated by Ni₂P/m-TiO₂. P25 (Degussa, specific surface area 50 m²/g, anatase:rutile = 4:1) and SiO₂ (Degussa) loaded with Ni₂P using the same method were used as references, and the reduction temperature was set at 650 °C, based on the literature; they were designated by Ni₂P/P25 and Ni₂P/SiO₂.

1.2 Characterization

XRD was performed using a D8 Advance diffractometer (Bruker, Germany; Cu K_α, tube current 30 mA, tube potential 40 kV, 5°–60°, 0.05°/step, 0.2 s/step). H₂-TPR was per-

formed using a TP-5000 instrument (Tianjing Xianquan Co., Ltd.). The precursor was treated under a N₂ atmosphere (flow rate 20 ml/min, 200 °C) for 2 h and cooled to room temperature. A 10% H₂-90% N₂ mixture was heated to a given temperature at a rate of 10 °C/min; the gas flow rate was 20 ml/min. A thermal conductivity cell was used to measure H₂ consumption. The specific surface area and pore distribution of the precursor were characterized using a TristarII 3020M (Micromeritics). The specific surface area and pore volume were measured using the Brunauer-Emmett-Teller (BET) and Barrett-Joyner-Halenda (BJH) methods. The surface structure was characterized by FESEM (Hitachi S-4800, 5 kV).

1.3 Activity evaluation

The HDS properties were evaluated in a mini fixed-bed reactor (self-made, see Ref. [33]). The length of the pipe was 500 mm, and the internal diameter was 9.4 mm. The catalyst was shaped under a pressure of 12 MPa and then shattered. After screening, 20–40 mesh was chosen. The catalyst (0.333 g) was diluted with quartz-sand (1.5 g) of the same mesh, loaded into the reactor, and treated under a H₂ atmosphere (flow rate 60 ml/min, 400 °C) for 2 h to remove the surface passivation layer; 0.5% dibenzothiophene (DBT, Acros Organics)/decahydronaphthalene (Siopharm Chemical Reagent Co., Ltd.) was used to simulate diesel oil. The pressure was 2.0 MPa, the H₂ flow rate was 40 ml/min, and the air speed was 12 h⁻¹. After pre-reaction for 4 h, the resulting product was collected every hour. A SP-2000A gas chromatograph (fixed phase: PEG-20M, 0.32 mm × 30 m, flame ionization detector; Shandong Lunan Ruihong Chemical Apparatus Co., Ltd.) was used.

2 Results and discussion

2.1 Nickel phosphide structure

Figure 1 shows the XRD patterns of Ni₂P/m-TiO₂ obtained from various initial Ni/P molar ratios at an initial loading of 20% Ni and a reduction temperature of 650 °C. At 2θ = 40.7°, 44.6°, and 47.3°, obvious diffraction peaks were found. These were Ni₂P diffraction peaks (PDF 03-0953). This indicates that different Ni/P molar ratios in the precursor can result in different crystal phases of the catalyst. When the molar ratios were 0.5, 1, and 1.25, the active ingredient was Ni₂P, but when the molar ratio reached 2, the peak of the Ni₂P phase declined and the Ni₁₂P₅ phase emerged. This is the result of the reduction of P to volatile PH₃ [34]. Wang et al. [11] reported that the catalytic activity of Ni₁₂P₅ is lower than that of Ni₂P. Li et al. [35] found that the Ni₂P XRD peaks increased with increasing initial molar ratio of Ni/P from 1/3 to 1/2. Keeping the Ni content constant and varying the

amount of P favors the formation of Ni_2P crystals. In this paper, with increasing Ni/P molar ratio, the excess of P decreases, so the conditions for formation of the Ni_2P phase become less favorable, and the intensities of the Ni_2P diffraction peaks decrease. The following results show that the reduction temperature of Ni_2P decreased on the support consisting of m- TiO_2 precursor, and the low temperature decreased P leakage. Increasing the molar ratio of Ni/P and the formation of inert Ni_{12}P_5 can therefore be avoided.

Figure 2 shows the XRD patterns of $\text{Ni}_2\text{P}/\text{m-TiO}_2$ with various Ni loadings at an initial Ni/P molar ratio of 1.25 and a reduction temperature of 650 °C. The figure shows that when the Ni loading reached 5%, no Ni_2P peak was found, indicating good distribution of Ni_2P on the support. However, when the Ni loading reached 10%, a small Ni_2P peak emerged. With further increase in the Ni loading, the diffraction peak of $\text{Ni}_2\text{P}/\text{m-TiO}_2$ became more obvious. Based on the reflex crystal face of $\text{Ni}_2\text{P}(201)$ ($2\theta = 44.6^\circ$), using the Scherrer equation, we calculated that for Ni loadings of 15% and 20%, the particle diameters of Ni_2P on the catalyst surface were 18.4 and 26.1 nm, respectively, indicating that as the Ni loading increased, the particle diameter of the active ingredient, Ni_2P , increased and the dispersity decreased.

Figure 3 shows the effects of catalysts prepared at different Ni/P ratios on HDS performance (reaction temperature 340 °C) for a Ni loading of 10% and a reduction temperature of 650 °C. As shown in Fig. 3, the optimum HDS activity is obtained when the Ni/P ratios are 1 and 1.25; the conversion rate reaches about 92%. When the Ni/P ratio rises to 2, the HDS performance of the catalyst drops to 47%. These results show that the Ni/P ratio has a significant effect on the HDS performance. When the ratio is low, the active component is largely Ni_2P , and the HDS performance of the corresponding catalyst improves as the ratio increases. When the ratio is further increased to 2, Ni_{12}P_5 is present in the components, leading to a decrease in HDS performance. When nickel phosphide is loaded on SiO_2 [5], absorbite [10], or MCM-41 [11], the optimum HDS activity is obtained because the active components largely consist of Ni_2P . The TiO_2 support is not an exception. In conclusion, the Ni/P ratio should be slightly lower than 2, the theoretical value that guarantees that the main constitute of the active component is Ni_2P . In this study, the optimum ratio of Ni/P was found to be 1.25.

Figure 4 shows the influence of Ni_2P loading on $\text{Ni}_2\text{P}/\text{m-TiO}_2$ catalysts and their HDS properties at a Ni/P ratio of 1.25, a reduction temperature of 650 °C, and a reaction temperature of 340 °C. When the Ni loading was 5%, the DBT conversion was only 21%, and when the loadings reached 10% and 15%, the DBT conversions were 72%. When the Ni loading reached 20%, the conversion decreased to 62%. Combined with the XRD analysis, these results suggest that the loading content and dispersion both have an

effect on the HDS properties. The HDS properties decrease as a result of the lack of catalytic activity centers when the Ni_2P content is low, and as a result of poor Ni_2P dispersion on the support at high contents. The best Ni_2P loading is 10% by Ni content.

2.2 Reduction activity of the catalyst at low temperatures

Figure 5 shows the H_2 -TPR profiles of the nickel phosphide precursor (Ni loading 10% and molar ratio of Ni/P 1.25) doped on various supports. As the figure shows, the reduction temperatures of the precursor loaded on m- TiO_2 are 450 and 540 °C. The low-temperature peak corresponds to reduction of Ni, and the second peak corresponds to the reduction of P. The reduction of Ni and P occur almost simultaneously. In the TPR process, Ni is reduced first. The generated Ni adsorbs H_2 , which is dissociated to active hydrogen, and this promotes the reduction of P, and further reaction to Ni_2P [36]. XRD analysis supports this view, and the $\text{Ni}_2\text{P}/\text{m-TiO}_2$ surface begins to appear at a Ni_2P reduction temperature of 500 °C. As the reduction temperature increases to 650 °C, the intensity of the Ni_2P diffraction is enhanced (Fig. 6). Lu et al. [37] hydrolyzed TiCl_4 to obtain amorphous TiO_2 , which acts as a precursor for the preparation of Ni_2P . It was discovered that when the reduction temperature exceeded 300 °C, NiO and TiO_2 reacted to give NiTiO_3 , which is difficult to be reduced. As the TPR profiles show, the sharp and narrow reduction peaks of NiTiO_3 and NiO both emerge at around 700 °C. Our group's previous research [38] indicates that amorphous TiO_2 is more reactive than crystalline TiO_2 . In this research, we chose amorphous TiO_2 of high crystallinity as the support. It can promote electron transfer and enhance HDS activity. Crystalline TiO_2 can restrain the generation of NiTiO_3 , and this in turn significantly decreases the reduction temperatures of Ni and P. TPR testing of a precursor based on P25 indicated that, compared with inert carriers such as SiO_2 , crystalline TiO_2 can promote the generation of nickel-phosphorus compounds. Based on the XRD analysis of $\text{Ni}_2\text{P}/\text{P25}$ preparation at a reduction temperature of 500 °C, we conclude that Ni_{12}P_5 is first generated on the P25 surface.

2.3 Thermostability of catalyst

TPR studies showed that the TiO_2 support contributed to the formation of Ni_2P at low temperature, it is necessary to investigate the structural stability and HDS properties at low temperatures. Table 1 shows the structure of the $\text{Ni}_2\text{P}/\text{m-TiO}_2$ catalyst and TiO_2 support at reduction temperatures of 450–650 °C. The specific surface area of m- TiO_2 is 132.5 m^2/g , and the pore volume and average pore size of the

support are suitable for a catalyst support. The m-TiO₂ support overcomes the shortcomings of other catalyst supports with low specific surface areas and synergistic reactions between the active ingredient and the support. For a Ni/P molar ratio of 1.25 and an active ingredient loading of 10%, the specific surface area, pore volume, and average pore diameter of the obtained catalyst decreased as a result of diffusion of the active ingredient into the mesopores of the support. When the reduction temperature was 450–600 °C, the specific surface area was 90 m²/g. When the temperature reached 650 °C, the structure collapsed, but the specific surface area was still more than 60 m²/g, which is larger than that of the Ni₂P/P25 catalyst. XRD shows that the crystal phase is anatase, indicating that the Ni₂P/m-TiO₂ catalyst has high thermostability.

Figure 7 shows the FESEM images of the precursor treated at various reduction temperatures. The images show that the TiO₂ support has a large number of mesopores, but it is difficult to see the average mesopore distribution in the precursor. Treatment under a H₂ atmosphere at 500 or 650 °C increases the amount of Ni₂P clusters, seen in the images as white balls, on the catalyst surface. These clusters are evenly distributed on the m-TiO₂. The cluster size does not increase with increasing treatment temperature.

Figure 8 shows the effects of HDS reduction temperature on the catalytic activity of obtained Ni₂P/m-TiO₂ compared with that of P25-supported catalyst. It can be seen that the DBT conversion is between 70% and 80% for different temperatures between 450 and 650 °C. For the catalysts prepared at 450 and 650 °C, the DBT conversion rates are slightly lower. This is because when the reduction temperature is low, less Ni₂P is formed, reducing the number of active catalytic sites, and this contributes to the decrease in the performance of the HDS catalyst. However, for the Ni₂P/P25 catalyst prepared at a reduction temperature of 500 °C, the

DBT conversion rate is only 26%. This is attributed to the smaller surface area and the possibility of Ni₁₂P₅ formation on the surface.

2.4 Comparison of performance of different supports loaded with Ni₂P

Figure 9 shows a comparison of the HDS performance of nickel phosphide on various supports at Ni loading of 10%, initial Ni/P molar ratio of 1.25, and reduction temperature of 650 °C. Although the specific surface area of Ni₂P/m-TiO₂ is smaller than that of Ni₂P/SiO₂ (Table 1), the HDS properties are best for the m-TiO₂ support. The order of the HDS performance on different supports is Ni₂P/m-TiO₂ > Ni₂P/SiO₂ > Ni₂P/P25. This indicates that Ni₂P supported on TiO₂ can enhance the HDS ability. X-ray photoelectron spectroscopy studies by Lu et al. [37] showed that peaks of Ni and P on the TiO₂ passivation layer shift towards lower binding energies due to the moving of electrons on Ti surface to Ni₂P, which enhances the HDS activity of the Ni₂P catalyst.

3 Conclusions

A novel Ni₂P/m-TiO₂ catalyst was prepared by the TPR method. The m-TiO₂ with high crystallinity could significantly decrease the reduction temperatures of Ni and P species, and promote the formation of Ni₂P. When the reduction temperature was between 450 and 600 °C, the Ni₂P/m-TiO₂ had good thermal stability and HDS performance. The effects of the supports on HDS performance showed that TiO₂ can enhance the HDS performance, and m-TiO₂ gave the best performance.

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