水蒸气处理对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂催化氯苯加氢脱氯反应的促进作用

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摘要: 在 303, 514 和 543 K 下用 0.8% H_2O -99.2% H_2 对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂进行了水蒸气处理, 利用 N_2 吸附-脱附、X 射线衍射、电感耦合等离子体发射光谱、 H_2 程序升温脱附及原位漫反射红外光谱等技术对水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的结构进行了表征, 并在常压固定床反应器上评价了其催化氯苯加氢脱氯活性。结果表明, 经水蒸气处理后, $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的物相及元素组成、 Ni_2P 晶粒大小、比表面积及孔结构没有明显改变。与未处理和 303 K 处理的 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂不同, 513 和 543 K 处理的催化剂表面暴露的 Ni 中心数量减少, 表面 P-OH 基团数量增多。在 513 K, 氯苯空速 3.75 ml/(g·h) 及 H_2 和氯苯的摩尔比为 9.0 的反应条件下, 经不同温度水蒸气处理的 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂上氯苯初始转化率高于 93.8%, 约是未预处理催化剂的 17 倍。这可能与金属 Ni 中心和表面 P-OH 基团的协同作用有关。

关键词: 磷化镍; 加氢脱氯; 水蒸气处理; 酸性

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Promotion Effect of Steam Treatment on Activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ for Hydrodechlorination of Chlorobenzene

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Abstract: $\text{Ni}_2\text{P}/\text{SiO}_2$ was pretreated with a 0.8% H_2O -99.2% H_2 flow at 303, 514, and 543 K. The $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after treatment were characterized by N_2 adsorption-desorption, X-ray diffraction, inductively coupled plasma atomic emission spectrometry, H_2 temperature-programmed desorption, and in situ diffuse reflection infrared Fourier transform spectroscopy, and their activities in the hydrodechlorination of chlorobenzene (CB) were tested in a fix-bed reactor. There was no difference in BET specific surface area, pore structure, the Ni_2P crystallite size, the Ni content, and the Ni/P ratio for the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after treatment. The treatment at 303 K did not decrease the density of exposed Ni sites on $\text{Ni}_2\text{P}/\text{SiO}_2$, while the treatment at 514 and 543 K led to the decrease of exposed Ni sites and the increase of the P-OH groups on $\text{Ni}_2\text{P}/\text{SiO}_2$. Under the conditions of 513 K, the CB space velocity of 3.75 ml/(g·h), and the H_2 /CB molar ratio of 9.0, the initial CB conversions on the treated $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts exceeded 93.8%, which was much higher than that (5.6%) on the untreated one. The promotion effect of steam treatment on the activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ may be related to a synergism between the Ni sites and the P-OH groups.

Key words: nickel phosphide; hydrodechlorination; steam treatment; acidity

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催化加氢脱氯是消除有机氯污染物的有效方法之一。所用催化剂主要为金属 Ni^[1,2] 及贵金属^[3~5]。

然而, 在加氢脱氯反应过程中生成 HCl , 它不仅抑制金属催化剂对 H_2 的吸附活化, 还会诱导金属晶粒烧结^[6]. 研究表明^[7,8], 氯作为电子接受体与金属产生相互作用, 降低金属位的电子云密度有利于减弱其与氯的相互作用, 从而提高金属的抗氯中毒性能. Seshu Babu 等^[9]研究发现, 缺电子 Pd 物种的加氢脱氯活性及稳定性高于 Pd^0 . 本课题组首次将磷化镍催化剂用于氯苯加氢脱氯反应中^[10-12], 发现其活性及稳定性明显高于金属 Ni 催化剂. 这与其中镍位缺电子性及催化剂表面有大量溢流氢有关. 然而, 与贵金属催化剂相比, 磷化镍催化剂加氢脱氯反应温度较高, 并且在反应初期通常存在诱导期. 因此, 需提高磷化镍催化剂在较低温度条件下的活性及缩短反应诱导期. 最近, 我们发现水蒸气处理可以缩短 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂加氢脱氯反应诱导期, 明显提高了催化剂较低温度时的加氢脱氯活性. 在 513 K、氯苯空速 3.75 $\text{ml}/(\text{g}\cdot\text{h})$ 及 H_2 和氯苯摩尔比为 9.0 的反应条件下, 水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂上氯苯转化率由 5.6% 增加至 93.8% 以上. 至今, 尚未见水蒸气处理对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 结构及催化性能影响的研究报道.

采用程序升温还原法 (H_2 -TPR) 制备 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂^[13]. 以 $\text{NH}_4\text{H}_2\text{PO}_4$ 水溶液浸渍 SiO_2 载体, 晾干后经 393 K 干燥 12 h 和 773 K 焙烧 4 h 后制得 PO_x/SiO_2 样品. 采用 H_2 -TPR 法在石英管反应器中制备 0.8 克 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂, 然后在 303, 513 或 543 K 通入 0.8% H_2O -99.2% H_2 混合气 (100 ml/min) 进行水蒸气处理 1 h, 所得催化剂记为 $\text{Ni}_2\text{P}/\text{SiO}_2$ - T , 其中 T 为预处理温度 (K).

氢气程序升温脱附 (H_2 -TPD) 表征采用自组装装置, 测试程序同文献^[13], 测试样品均原位制备且未经钝化. 用于 N_2 吸附-脱附及 X 射线衍射 (XRD) 测试的催化剂在常温下用 0.5% O_2 -99.5% N_2 钝化 6 h. N_2 吸附-脱附曲线采用 Quantachrome NOVA-2000 型吸附仪测定, 吸附温度为 77 K, 采用 BET 方程计算催化剂比表面 (A_{BET}), 采用 BJH 方法由脱附曲线数据计算平均孔径及孔体积. XRD 测试采用德国布鲁克 AXS 有限公司 D8 Focus 型多晶粉末衍射仪, $\text{Cu } K_\alpha$ ($\lambda = 0.15406 \text{ nm}$) 辐射线. 催化剂中 Ni 和 P 的含量采用 Varian VISTA-MPX 电感耦合等离子体发射光谱仪测定. 原位漫反射红外光谱 (In situ

DRIFTS) 研究在 Thermo 公司 NICOLET 6700 型傅里叶变换红外光谱仪上进行, 采用 P/NOO30-102 原位池.

氯苯加氢脱氯反应性能评价采用常压石英管固定床反应器 (内径 12 mm), 反应条件为: 513 K, 氯苯空速 3.75 $\text{ml}/(\text{g}\cdot\text{h})$, H_2 /氯苯摩尔比 9.0. 以无水乙醇吸收反应产物, 吸收液采用北京分析仪器厂 SP-3420 型气相色谱仪分析, OV-101 毛细管柱, FID 检测器.

图 1 为水蒸气预处理对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂上氯苯加氢脱氯反应 1 h 初始活性的影响. 未处理的 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂上氯苯转化率为 5.6%, 而 $\text{Ni}_2\text{P}/\text{SiO}_2$ -303, $\text{Ni}_2\text{P}/\text{SiO}_2$ -513 和 $\text{Ni}_2\text{P}/\text{SiO}_2$ -543 催化剂上氯苯转化率分别为 93.8%, 95.4% 和 95.3%.

图 1 不同温度水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的氯苯加氢脱氯活性

Fig. 1. Hydrodechlorination activities of $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after steam treatment at different temperatures.

另外, 还考察了反应过程中引入水蒸气对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂加氢脱氯活性的影响, 结果见图 2. 可以看出, 在未引入水蒸气反应的 24 h 内, 氯苯转化率由 5.6% 缓慢增至 7.8%. 向 H_2 中引入 0.8% 水蒸气后, 氯苯转化率在随后 4 h 内由 7.9% 增加至 67.6%, 并在之后的 7 h 内稳定在 70% 左右. 前期研究表明^[12], $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂在使用过程中存在诱导期: 在 573 K 条件下, 第 1 h 氯苯转化率为 14.8%, 至 10 h 时升至 93% 以上. Tavoularis 等^[1]对氯苯加氢脱氯反应的热力学计算表明, 在常压、273~573 K 条件下该反应的热力学平衡常数大于 1.6×10^6 , 表明在热力学上于 513 K 氯苯可以完全转化. 因此, 水处理提高了 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂上氯苯加氢脱氯性能, 并缩短了反应诱导期.

图2 反应过程中加入水蒸气对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂加氢脱氯活性的影响

Fig. 2. Effect of adding steam during reaction on hydrodechlorination activity of $\text{Ni}_2\text{P}/\text{SiO}_2$.

为研究水蒸气预处理对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂结构的影响, 图3给出了水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的 XRD 谱。可以看出, 除了无定形 SiO_2 外, 各样品均只出现 Ni_2P 物相。基于 $\text{Ni}_2\text{P}(111)$ 晶面的衍射峰, 由谢乐公式算得各催化剂中 Ni_2P 晶粒大小相差不大 (见表1)。另外, 由表1可知, 水蒸气预处理对

图3 水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的 XRD 谱

Fig. 3. XRD patterns of $\text{Ni}_2\text{P}/\text{SiO}_2$ before (1) and after steam treatment at 513 K (2) and 543 K (3).

表1 水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的结构参数

Table 1 Structural parameters of $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after steam treatment

Sample	Ni content (wt%)	Ni/P molar ratio	$A_{\text{BET}}/(\text{m}^2/\text{g})$	$V_p/(\text{cm}^3/\text{g})$	d_p/nm	Ni_2P crystallite size ^a (nm)
$\text{Ni}_2\text{P}/\text{SiO}_2$	12.7	4.5	294	0.41	5.6	12.6
$\text{Ni}_2\text{P}/\text{SiO}_2\text{-513}$	13.7	4.6	292	0.40	4.9	13.5
$\text{Ni}_2\text{P}/\text{SiO}_2\text{-543}$	13.7	4.6	297	0.43	5.7	13.8

^aCalculated based on the reflection of $\text{Ni}_2\text{P}(111)$.

$\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂比表面积、孔结构、Ni 含量及体相 Ni/P 比影响很小。

图4为水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的 H_2 -TPD 谱。通常认为, 在 673 K 以下的脱附峰为吸附在金属表面氢物种的脱附, 而 673 K 以上的对应于溢流氢^[14]。由图可见, 未处理的 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂在 473 K 左右有一个明显的脱附峰, 在 303 K 经水蒸气处理后, 该峰面积略有增加, 但经 514 和 543 K 水蒸气处理后又明显降低, 表明催化剂表面暴露的镍位减少, 这与在较高温度下水处理过程中氧与镍相互作用阻碍了氢吸附有关。还可以看出, 水蒸气处理使得样品在 673 K 左右的脱附峰增大, 并且在 673~973 K 也具有较大的溢流氢脱附量。这可能与 Ni_2P 颗粒表面形成较多的 P-OH 基团有关。

图4 水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂的 H_2 -TPD 谱

Fig. 4. H_2 -TPD profiles of $\text{Ni}_2\text{P}/\text{SiO}_2$ before (1) and after steam treatment at 303 K (2), 513 K (3), and 543 K (4).

研究表明^[15], 催化剂表面羟基具有促进溢流氢形成及稳定氢物种的作用。Liu 等^[16]研究发现, 在 $\text{Ni}_2\text{P}(001)$ 催化剂上进行水煤气变换反应时, O 主要和 P 相互作用形成 P-O 键, 从而会形成 P-OH 基团。为了证明水蒸气处理导致 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂表面形成 P-OH 基团, 采用原位 DRIFTS 对水蒸气处理过程中 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂表面结构进行了表征。钝化后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂在 723 K 用 H_2 还原 1.0 h 后降至 514 或 543 K, 采集谱图作为背景; 然后, 通入 0.8% H_2O -99.2% H_2 对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂进行水蒸气处理 1.0 h, 期间连续采集谱图。图5为 543 K 下 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂水蒸气处理过程中原位 DRIFTS 谱。由图可见, 处理 4 min 后即在 3740 和 3665 cm^{-1} 附近出现了分别归属于 Si-OH 和 P-OH 基团中羟

图 5 在 543 K 下 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂水蒸气处理过程中的原位漫反射红外光谱

Fig. 5. In situ DRIFTS spectra of $\text{Ni}_2\text{P}/\text{SiO}_2$ during steam treatment at 543 K.

基伸缩振动的吸收峰^[17]。此外,在 2956, 2872, 2767, 2390 及 2166 cm^{-1} 附近出现吸附峰,并随时间的增加吸收峰强度增大,可能对应于位于不同环境且形成氢键的 P-O-H 伸缩振动^[18,19]。在 514 K 对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂进行水蒸气处理也发现相同的现象。因此,在 514 或 543 K 水处理过程中, $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂表面形成了 P-OH 基团。Lee 等^[17]和 Duan 等^[20]的吡啶吸附 FT-IR 结果发现,在 $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{MCM-41}$ 及 PO_x/SiO_2 催化剂表面形成的 P-OH 基团为 Brönsted 中心。我们也对水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂进行了原位吡啶吸附 DRIFTS 研究。结果表明,水蒸气处理前后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂均出现吡啶与 B 酸形成吡啶离子的特征吸收峰 (1450 cm^{-1})。结合图 5 可以认为,水蒸气处理使 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂表面形成了新的 P-OH 基团。

综上所述,水蒸气处理后 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂表面 Ni 中心数量减少, P-OH 基团数量增多,而且明显提高了 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂加氢脱氯活性。由此可以推测,水蒸气对 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂活性的促进作用与表面 P-OH 基团增多有关, P-OH 基团可能提供了用于加氢脱氯的氢物种。Tøpsoe 等^[21]和 Ryymin 等^[22]认为,硫化物催化剂表面 SH 基团作为 Brönsted 酸

中心可以提供用于加氢的氢物种。Welters 等^[23]研究发现,单独 Brönsted 酸中心可催化噻吩加氢脱硫反应。研究表明^[13,17], PO_x/SiO_2 样品表面含有大量具有 Brönsted 酸性的 P-OH 基团。我们对 PO_x/SiO_2 的氯苯加氢脱氯性能进行了评价,发现其并没有加氢脱氯活性,说明单独的 P-OH 基团不具有加氢脱氯活性,加氢脱氯反应还需金属中心存在。因此,我们初步认为,加氢脱氯反应过程中 $\text{Ni}_2\text{P}/\text{SiO}_2$ 催化剂表面 Ni 中心和 P-OH 基团之间可能存在协同作用。前者具有吸附解离氢及吸附活化氯苯分子的作用,而具有酸性的 P-OH 基团可以提供质子氢与活化的氯苯反应生成苯及 HCl。

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Catalytic hydrodechlorination (HDC) has become an economically viable alternative since it operates at low temperature and pressure and allows easier and/or safer post-treatment of the resulting stream. Ni [1,2] and noble-metal [3–5] catalysts have been widely used for HDC. However, catalyst poisoning by the HCl by-product is a serious problem. HCl can react with the metal to form a metal chloride, inducing a decrease in the electron density, restructuring of the metal, and sintering of metal particles [6]. Since chlorine is known to act as an electron acceptor with respect to transition metals [7,8], the adsorption of chlorine on a metal can be weakened by reducing the electronic density of the metal atom. Seshu Babu et al. [9] have found that Pd^{n+} species are more active than Pd^0 in HDC. Our previous studies [10–12] have shown that $\text{Ni}_2\text{P}/\text{SiO}_2$ has much higher activity and stability than Ni/SiO_2 . This is attributed to the specific physicochemical properties of Ni_2P (such as electron-deficient Ni sites) and a large spill-over of hydrogen species on $\text{Ni}_2\text{P}/\text{SiO}_2$. However, compared with noble-metal catalysts, $\text{Ni}_2\text{P}/\text{SiO}_2$ needs higher reaction temperatures, and there is an induction period during HDC. It is important to find ways of increasing the activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ at low temperatures. Recently, we found that steam treatment significantly increased the activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ in the HDC of chlorobenzene. Under conditions of 513 K, a chlorobenzene space velocity of 3.75 ml/(g·h), and an H_2 /chlorobenzene molar ratio of 9.0, the initial chlorobenzene conversion increased from 5.6% to above 93.8% after treatment of the $\text{Ni}_2\text{P}/\text{SiO}_2$ with steam. To our knowledge, there have been no previous reports on the influence of steam treatment on the properties of $\text{Ni}_2\text{P}/\text{SiO}_2$.

$\text{Ni}_2\text{P}/\text{SiO}_2$ was prepared by the H_2 temperature-programmed reduction (H_2 -TPR) method according to previous reports [13]. A PO_x/SiO_2 sample was prepared by impregnating silica with an aqueous solution of $\text{NH}_4\text{H}_2\text{PO}_4$, followed by drying at 393 K for 12 h and calcination at 773 K for 4 h. $\text{Ni}_2\text{P}/\text{SiO}_2$ (0.8 g) prepared in a fixed-bed quartz reactor was treated with 0.8% H_2O -99.2% H_2 (100 ml/min) at 303, 513, or 543 K for 1 h. The resulting samples are denoted by $\text{Ni}_2\text{P}/\text{SiO}_2$ - T , where T is the treatment temperature (K).

H_2 temperature-programmed desorption (H_2 -TPD) was carried out on a laboratory-made instrument, and the procedure was the same as that used in previous work [13]. $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2$ - T samples were prepared in situ.

Before the N_2 adsorption and X-ray diffraction (XRD) characterizations, $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2$ - T were passivated with 0.5% O_2 -99.5% N_2 at room temperature for 6 h. The XRD patterns were obtained on a Bruker AXS D8 Focus powder diffractometer operated at 40 kV and 40 mA using $\text{Cu-K}\alpha$ radiation ($\lambda = 0.15406$ nm). N_2 adsorption-desorption isotherms were obtained on a Quantachrome NOVA-2000 apparatus at 77 K. The Brunauer-Emmett-Teller (BET) equation was used to calculate the specific surface area (A_{BET}). The Barrett-Joyner-Halenda (BJH) method was used to calculate the average pore diameter (d_p) and pore volume (V_p) from the desorption branch of the isotherm. The Ni and P contents in the catalysts were determined using an inductively coupled plasma atomic emission spectrometer (ICP-AES, Varian VISTA-MPX). In-situ diffuse reflection infrared Fourier-transform spectroscopy (DRIFTS) was carried out on a Thermo NICOLET 6700 spectrometer equipped with a diffuse-reflectance accessory and an in-situ P/NOO30-102 chamber.

Catalyst activity was tested using an atmospheric fixed-bed quartz reactor (i.d. = 12 mm), in which the $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2$ - T catalysts were all prepared in situ. The reaction conditions were 513 K, a chlorobenzene space velocity of 3.75 ml/(g·h), and an H_2 /chlorobenzene molar ratio of 9.0. The products were analyzed on a 3420 gas chromatograph equipped with a hydrogen flame-ionization detector and an OV-101 capillary column.

Figure 1 shows the initial chlorobenzene conversions on $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2$ - T . $\text{Ni}_2\text{P}/\text{SiO}_2$ gave a chlorobenzene conversion of 5.6%, whereas $\text{Ni}_2\text{P}/\text{SiO}_2$ -303, $\text{Ni}_2\text{P}/\text{SiO}_2$ -513, and $\text{Ni}_2\text{P}/\text{SiO}_2$ -543 gave conversions of 93.8%, 95.4%, and 95.3%, respectively.

Figure 2 shows the effect of adding H_2O during the reaction on the activity of $\text{Ni}_2\text{P}/\text{SiO}_2$. The conversion slowly increased from 5.6% at the first hour to 7.8% at the 24th hour on $\text{Ni}_2\text{P}/\text{SiO}_2$. After the 24th hour, 0.8% H_2O was introduced into the H_2 stream. The conversion increased to above 67.9% during the following 4 h. Previous work [12] has shown that there is an induction period for the HDC of chlorobenzene on $\text{Ni}_2\text{P}/\text{SiO}_2$. At 573 K, the chlorobenzene conversion increased from 14.8% at the first hour to above 93% at 10 h [12]. Tavoularis et al. [1] have calculated equilibrium constants between 273 and 573 K for the HDC of chlorobenzene, and they exceed 1.6×10^6 . The equilibrium constants are so high that chlorobenzene can be completely converted to benzene at 513 and 573 K. Thus, steam treatment enhanced the activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ and shortened the induction period for the HDC of chlorobenzene.

To account for the effect of steam treatment on the properties of $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2$ - T were characterized using XRD, N_2 adsorption, ICP-AES, H_2 -TPD, and in situ DRIFTS. Figure 3 shows the XRD patterns of

$\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}T$. Apart from amorphous SiO_2 , only the Ni_2P phase was detected in $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}T$, and the Ni_2P crystallite sizes in $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}T$ were similar (about 13 nm, see Table 1). Table 1 also shows that $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}T$ had similar A_{BET} values, d_p , V_p , Ni contents, and Ni/P molar ratios. Thus, steam treatment at 303–543 K did not obviously affect the textural properties, the Ni_2P phase, and the Ni_2P crystallite size and composition in $\text{Ni}_2\text{P}/\text{SiO}_2$.

Figure 4 shows the H_2 -TPD profiles of $\text{Ni}_2\text{P}/\text{SiO}_2$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}T$. Usually, the hydrogen species desorbed below 673 K are ascribed to those adsorbed on the metal sites, and those desorbed above 673 K are attributed to the spilt-over hydrogen species [14]. Below 673 K, there was a peak (at about 473 K) with a shoulder at higher temperature in the profile of $\text{Ni}_2\text{P}/\text{SiO}_2$. $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}303$ had a peak at 473 K of similar area to that of $\text{Ni}_2\text{P}/\text{SiO}_2$. However, the area of this peak decreased significantly for $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}513$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-}543$, indicating a decrease in the number of exposed Ni sites. This may be related to interactions between Ni and O, which prevent H_2 adsorption. After treatment, the shoulder peak at about 673 K and the H_2 desorption amount between 673 and 973 K increased. This is probably related to the involvement of hydrogen species in P–OH groups.

It has been proposed that hydroxyl groups can promote hydrogen spill-over and stabilize spilt-over hydrogen species on the catalyst surface [15]. Liu et al. [16] have found that during water-gas-shift reactions on a $\text{Ni}_2\text{P}(001)$ catalyst, oxygen mainly interacts with the P on the Ni–P sites to form oxy-phosphide species. It is reasonable to suppose that the combination of P and O contributes to the formation of P–OH groups. In-situ DRIFTS was used to prove the formation of P–OH groups during the steam treatment. First, the passivated $\text{Ni}_2\text{P}/\text{SiO}_2$ was reduced at 723 K for 1.0 h. After the reduction, when the catalyst temperature had decreased to 514 or 543 K, a background spectrum was recorded. Then a 0.8% H_2O –99.2% H_2 flow was introduced into an in-situ cell to treat the $\text{Ni}_2\text{P}/\text{SiO}_2$, and the DRIFT spectrum was continuously recorded. Figure 5 shows the DRIFT spectra of $\text{Ni}_2\text{P}/\text{SiO}_2$ treated at 543 K. After 4 min, bands were observed at about 3740 and 3665 cm^{-1} ; these were attributed to hy-

droxyl vibrations of SiO–H and PO–H groups [17], respectively. In addition, bands at about 2956, 2872, 2767, 2390, and 2166 cm^{-1} were visible and became stronger along with time; these are related to the stretching mode of P–O–H groups forming hydrogen bonds [18,19]. Similar results were observed when $\text{Ni}_2\text{P}/\text{SiO}_2$ was treated at 514 K (not shown). Thus, P–OH groups were formed on $\text{Ni}_2\text{P}/\text{SiO}_2$ during the steam treatment. Using FT-IR analysis with pyridine as the probe molecule, Lee et al. [17] and Duan et al. [20] have detected Brønsted acid sites on $\text{Ni}_2\text{P}/\text{SiO}_2$, $\text{Ni}_2\text{P}/\text{MCM-41}$, and PO_x/SiO_2 . Here, DRIFTS analysis with a pyridine probe molecule was used to characterize the acidity of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after steam treatment. In all the spectra (not shown here), a band at 1540 cm^{-1} was visible, corresponding to the pyridinium ring vibration modes on the P–OH groups. These results further indicate the formation of new P–OH groups on $\text{Ni}_2\text{P}/\text{SiO}_2$ during the steam treatment.

The H_2 -TPD and in-situ DRIFTS results indicate that the steam treatment led to a decrease in the number of Ni sites and an increase in the number of P–OH groups on $\text{Ni}_2\text{P}/\text{SiO}_2$. The steam treatment also promoted the HDC activity of $\text{Ni}_2\text{P}/\text{SiO}_2$. It is speculated that this promoting effect may be related to the increase in the number of P–OH groups which could provide hydrogen species. Topsøe et al. [21] and Ryymin et al. [22] have suggested that the SH^- groups on sulfided catalysts can provide the hydrogen species for hydrogenation. Welters et al. [23] have found that Brønsted acid sites on their own can catalyze the hydrodesulfidation of thiophene. It has been reported that PO_x/SiO_2 possesses a large number of surface P–OH groups [13,17]. However, PO_x/SiO_2 had no any activity in the HDC of chlorobenzene. This means that a metal site is essential for activating the chlorobenzene molecule. We suggest that there may be a synergism between the Ni sites and P–OH groups for HDC. The Ni sites can adsorb and activate H_2 and chlorobenzene molecules, and the P–OH groups provide the hydrogen species to attack the activated chlorobenzene molecule to form benzene and HCl.

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