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Article

Effect of H₂S pre-treatment on structure and activity of Ni₂P/SiO₂ catalyst for hydrodechlorination of chlorobenzene

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ABSTRACT

The effect of 10% H₂S/H₂ treatment on the structure of Ni₂P/SiO₂ and its activity for the hydrodechlorination of chlorobenzene was investigated using X-ray diffraction, inductively coupled plasma atomic emission spectroscopy, X-ray photoelectron spectroscopy, CO chemisorption, H₂ temperature-programmed desorption, NH₃ temperature-programmed desorption, and activity tests. The H₂S/H₂ treatment did not change the Ni₂P phase or crystallite size even at temperatures as high as 873 K. However, S species were incorporated in the surface of the Ni₂P crystallites to form surface phosphosulfide (NiP_xS_y) species, which blocked the Ni sites and induced their further electron-deficiency. H₂S/H₂ treatment also led to an increase of spilt-over hydrogen species. The treated Ni₂P/SiO₂ catalyst had higher turnover frequencies in the hydrodechlorination of chlorobenzene than the untreated catalyst. This was ascribed to the increased electron-deficiency of Ni site and a greater amount of spilt-over hydrogen species.

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1. Introduction

Catalytic hydrodechlorination (HDC) has become an attractive process for the disposal of waste chlorinated compounds because it operates at low temperature and pressure and allows easier and/or safer post-treatment of the resulting stream. Noble metals [1–6], Ni [7–9], molybdenum carbide [10], sulfurized Ni-Mo/Al₂O₃ [11], and nickel phosphides [12–14] have been studied as HDC catalysts. It has been found that the structural and electronic properties of such catalysts remarkably influence their performance. HDC is structurally sensitive over Ni and Pd catalysts, and a higher HDC turnover frequency (TOF) is associated with larger supported metal particles [5,7]. There are differing opinions on the role of the electronic properties. Babu et al. [2–4] have proposed that Pdⁿ⁺ species favor increased activity and stability of supported Pd

catalysts because the adsorption of chlorine on Pdⁿ⁺ is weak in comparison with that on Pd⁰. We have proposed that the superior HDC activity and stability of nickel phosphide to those of metallic Ni are attributable to the electron deficiency of nickel in nickel phosphides [12,13]. However, it has also been reported that electron-deficient nickel species are not favorable for HDC [9], whereas electron-enriched nickel species promote HDC [15].

Transition metal phosphides have attracted much attention as novel catalytic materials over the last decade [16–21]. Among these, Ni₂P has been particularly focused on, especially for hydrotreating processes. The effect of S on the properties of Ni₂P has been explored. After use in hydrosulfurization (HDS) or treatment by H₂S/H₂, S species are incorporated into the surface of Ni₂P particles and form a surface phosphosulfide (NiP_xS_y) phase, while the Ni₂P phase is not destroyed [16–20].

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Because S has higher electronegativity than P and Ni, it withdraws electrons from Ni and lowers the electron density of the Ni sites in Ni_2P [18,20]. Additionally, in some cases, real processed wastes contain organosulphur compounds. Such organosulphur compounds and their hydrogenation product H_2S can severely poison metal catalysts [22–26]. Investigation of the influence of S on the HDC reactivity of Ni_2P will provide information about the electron effect and the resistance of Ni_2P to S during HDC. No similar investigations have been reported so far.

In the present work, selecting the HDC of chlorobenzene as a model reaction, we have investigated the effect of H_2S on the structure and activity of $\text{Ni}_2\text{P}/\text{SiO}_2$ and discussed the relationship between them. For comparison, Ni/SiO_2 was also prepared and tested for HDC.

2. Experimental

2.1. Preparation of catalysts

$\text{Ni}_2\text{P}/\text{SiO}_2$, Ni/SiO_2 , and PO_x/SiO_2 were prepared using the methods described in the literature [27]. $\text{Ni}_2\text{P}/\text{SiO}_2$ and Ni/SiO_2 were treated with 10% $\text{H}_2\text{S}/\text{H}_2$ using the following procedure. First, the SiO_2 supported nickel phosphate precursor was reduced in H_2 from 293 to 923 K at a heating rate of 1 K/min and then maintained at 923 K for 3 h. Second, the prepared $\text{Ni}_2\text{P}/\text{SiO}_2$ (0.8 g) was decreased to 573 or 873 K in an H_2 flow and then treated with a 10% $\text{H}_2\text{S}/\text{H}_2$ flow (60 ml/min) for 1 h. The $\text{Ni}_2\text{P}/\text{SiO}_2$ sample treated at 573 K is labeled $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$, and loosely adsorbed H_2S was removed at the same temperature using a H_2 flow. The $\text{Ni}_2\text{P}/\text{SiO}_2$ sample treated at 873 K and cooled to 573 K in the $\text{H}_2\text{S}/\text{H}_2$ flow was labeled $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$ and was swept with H_2 at 573 K to remove the loosely adsorbed H_2S . To reduce its surface S content, the $\text{Ni}_2\text{P}/\text{SiO}_2$ sample treated at 873 K was also cooled to 573 K in a H_2 flow and was labeled $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$. This was feasible because the surface phosphosulfide phase decomposes at high temperature in the absence of H_2S [28]. $\text{Ni}/\text{SiO}_2\text{-S573}$ represents the Ni/SiO_2 catalyst treated at 573 K with the same procedure as that for $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$. To avoid drastic oxidation, the prepared catalysts were passivated with a 0.5% O_2/N_2 flow for 6 h at room temperature before exposure to air.

2.2. Characterization of catalysts

X-ray diffraction (XRD) patterns were obtained on a Rigaku D/max 2500 V/PC powder diffractometer operated at 40 kV and 200 mA using monochromatized $\text{Cu-K}\alpha$ radiation. The average size of the Ni_2P crystallites was calculated using the Scherrer equation. Elemental analysis was conducted using an inductively coupled plasma atomic emission spectrometer (ICP-MS; Varian VISTA-MPX). Samples for ICP-MS were dissolved with aqua regia. X-ray photoelectron spectroscopy (XPS) was performed using a PHI-1600 ESCA instrument with $\text{Mg K}\alpha$ radiation (1253.6 eV). Binding energies were determined using C 1s (284.6 eV) as the reference.

The amount of active sites was measured by CO chemisorp-

tion using a laboratory-made instrument. The sample without H_2S treatment was re-reduced in H_2 (99.999%) at 673 K for 1 h. The catalyst treated with H_2S was prepared in situ from the re-reduced sample. The re-reduced sample was flushed with He (99.999%, 80 ml/min) at 673 K for 1 h, while the H_2S treated sample was flushed with the He stream at 573 K for 1 h. The samples were then cooled to 303 K under the He stream. After the thermal conductivity detector (TCD) signal became stable, CO pulses were injected until the effluent area of consecutive pulses was constant.

H_2 temperature-programmed desorption ($\text{H}_2\text{-TPD}$) was carried out using a laboratory-made instrument. The passivated sample (150 mg) was placed in a quartz reactor (4 mm in diameter) and reduced with a H_2 flow (60 ml/min) at 723 K for 1 h, and then allowed to cool to 303 K. The catalyst treated with H_2S was prepared in situ from the re-reduced sample. After H_2 adsorption for 30 min at 303 K, the sample was swept with a N_2 flow (20 ml/min) until the TCD signal was stable. $\text{H}_2\text{-TPD}$ was carried out at a heating rate of 15 K/min. The desorbed H_2 was detected using a TCD detector.

$\text{NH}_3\text{-TPD}$ was performed using the same apparatus. The passivated sample (70 mg) was reduced with a H_2 flow (40 ml/min) at 723 K for 1 h and then cooled to 383 K. The catalyst treated with H_2S was prepared in situ from the re-reduced sample. After NH_3 adsorption at 383 K for 30 min, the sample was flushed with He (60 ml/min) to remove the physically adsorbed NH_3 . The chemisorbed NH_3 was desorbed by increasing the temperature at a rate of 10 K/min and detected using a TCD.

2.3. Activity test of catalysts

The HDC reaction was performed in an atmospheric fixed-bed quartz reactor (i.d. = 12 mm). The precursor was supported on quartz cotton and a layer of quartz particles was placed on the catalyst bed. The catalyst was then prepared in situ as described in Section 2.1, after which its temperature was decreased to 573 K. The feed stream was switched to a mixture of chlorobenzene and H_2 . The space velocity of chlorobenzene was 10.6 ml/(g_{cat}·h) and the H_2 /chlorobenzene molar ratio was 3. To avoid loss due to volatilization, the reaction products were absorbed with anhydrous ethanol in an ice-water bath and were subsequently analyzed using a gas chromatograph equipped with a hydrogen flame ionization detector and an OV-101 capillary column.

The chlorobenzene conversion (X) and TOF (s^{-1}) for HDC were calculated as $X = (1 - n/n_0) \cdot 100\%$ and $\text{TOF} = n_0 \cdot X \cdot 10^6 / (m \cdot D \cdot T)$, respectively, where n_0 and n denote the moles of chlorobenzene in the feed and product, respectively, and m , D , and T denote catalyst mass (g), CO uptake ($\mu\text{mol/g}$), and reaction time (s), respectively.

3. Results and discussion

3.1. XRD

Figure 1 shows the XRD patterns of the $\text{Ni}_2\text{P}/\text{SiO}_2$ and

Fig. 1. XRD patterns of different samples. (1) Ni/SiO₂; (2) Ni/SiO₂-S573; (3) Ni₂P/SiO₂; (4) Ni₂P/SiO₂-S573; (5) Ni₂P/SiO₂-S873; (6) Ni₂P/SiO₂-S873(H₂); (7) Used Ni₂P/SiO₂-S873.

Ni/SiO₂ catalysts before and after H₂S/H₂ treatment. Only peaks due to metallic Ni (PDF card 65-0380) are visible for Ni/SiO₂. For Ni/SiO₂-S573, peaks due to Ni₃S₂ (PDF card 44-1418) and NiS (PDF card 12-0041) are observed, whereas those due to metallic Ni are not obvious. This indicates that the metallic Ni was sulfurized to Ni₃S₂ and NiS during H₂S/H₂ treatment at 573 K. In the fresh and treated Ni₂P/SiO₂, only Ni₂P phase (PDF card 03-0953) was detected. Further, the Ni₂P crystallite size of the treated Ni₂P/SiO₂ was similar to that of the as-prepared one (Table 1). Clearly, Ni₂P/SiO₂ had much higher resistance to S poisoning than Ni/SiO₂. This is consistent with the literature [16,17]. In addition, the Ni₂P crystallite size of the used Ni₂P/SiO₂-S873 was similar to that of the as-prepared sample. As indicated in previous work [29], the Ni₂P crystallite size and the HDC activity of Ni₂P/SiO₂ did not obviously change after reaction for 130 h. Therefore, the Ni₂P crystallites had strong anti-sintering properties during the HDC process. This is very different from Ni catalysts, in which chlorine induces crystallite sintering through the formation of NiCl₂ and leads to irreversible catalyst deactivation [30].

3.2. ICP-AES

Table 1 shows the contents of Ni, P, and S in the Ni₂P/SiO₂ catalysts before and after H₂S/H₂ treatment. The fresh and treated catalysts had similar Ni/P ratios (1.7–1.8). In the treated Ni₂P/SiO₂ catalysts, the mass contents of S ranged from 0.20% to 0.52%, and S/Ni ratios were from 0.025 to 0.06. Such low S contents are similar to those reported in the literature [16–19,31]. For instance, the S/Ni ratio of used 24.4 wt%

Table 2

XPS data of the catalyst samples.

Sample	Binding energy (eV)	
	Ni 2p _{3/2}	P 2p _{3/2}
Ni ₂ P/SiO ₂	853.5, 856.8	134.2, 129.5
Ni ₂ P/SiO ₂ -S573	853.9, 856.8	134.1, 129.6
Ni ₂ P/SiO ₂ -S873	853.9, 856.9	134.5, 129.7
Ni ₂ P/SiO ₂ -S873(H ₂)	853.7, 856.6	134.3, 129.4
Ni/SiO ₂	852.4, 856.8	—
Ni/SiO ₂ -S573	852.8, 855.8	—

Ni₂P/SiO₂ was 0.03 after HDS for 300 h [17], while that of Ni₂P/SiO₂ treated at 650 K in a H₂S/H₂ flow was only 0.008 [31].

Ni₂P/SiO₂-S873 had a similar S/Ni ratio to that of Ni₂P/SiO₂-S573, indicating that the treatment temperature had no remarkable influence on the interaction between S and Ni₂P. However, the S/Ni ratio of Ni₂P/SiO₂-S873(H₂) was lower than that of Ni₂P/SiO₂-S873. This is ascribed to the desorption of H₂S and/or –HS in the absence of H₂S, which had a weaker interaction with the Ni₂P surface. In addition, the S/Ni ratio in the used Ni₂P/SiO₂-S873 decreased, indicative of a loss of sulfur during HDC. Nelson and coworkers [28] have suggested that there are three states of adsorbed S species on the Ni₂P (001) surface, H₂S, –HS, and –S. The relative stability follows the order: adsorbed H₂S < adsorbed –SH < adsorbed –S. In the absence of H₂S, some reversible S species (such as H₂S and/or –HS) left the surface of Ni₂P.

3.3. XPS

Table 2 shows the electronic binding energies (BEs) of Ni 2p_{3/2} and P 2p_{3/2} in the fresh and treated catalysts. For Ni/SiO₂, the BEs of 852.4 and 856.8 eV are ascribed to Ni⁰ and Ni²⁺, respectively. The formation of Ni²⁺ was due to the oxidation of nickel species during passivation. For Ni/SiO₂-S573, the BE of 852.8 eV is designated to the Ni²⁺ species in NiS and Ni₃S₂, while that of 855.8 eV is also related to the oxidation of Ni species during passivation. For the fresh and treated Ni₂P/SiO₂ catalysts, the BEs of 856.6–856.9 and 134.1–134.5 eV are respectively assigned to Ni²⁺ and P⁵⁺ species in the passivation layer [20,32]. The P species with BEs of 129.4–129.7 eV and Ni with BEs of 853.5–853.9 eV belong to Ni₂P. The Ni₂P/SiO₂ catalysts that had been treated with H₂S/H₂ had higher Ni 2p_{3/2} BEs than those of the fresh catalysts. Therefore, the existence of S lowered the electron density of Ni in Ni₂P. This is consistent with the formation of a surface phosphosulfide phase on the Ni₂P particles [16–19,28].

Table 1

Properties of Ni₂P/SiO₂ subjected to H₂S pretreatment under different conditions.

Catalyst	Bulk composition	CO uptake (μmol/g)	Ni ₂ P crystallite size (nm)	Chlorobenzene conversion (%) (TOF, s ⁻¹)	
				At the 1st hour	At the 15th hour
Ni ₂ P/SiO ₂	Ni ₂ P _{1.19}	21	10.7	14.8 (0.20)	95.9 (1.3)
Ni ₂ P/SiO ₂ -S573	Ni ₂ P _{1.16} S _{0.11}	5	10.9	4.2 (0.24)	88.6 (5.1)
Ni ₂ P/SiO ₂ -S873	Ni ₂ P _{1.14} S _{0.12}	4	9.9	3.7 (0.27)	80.0 (5.8)
Ni ₂ P/SiO ₂ -S873(H ₂)	Ni ₂ P _{1.16} S _{0.05}	9	9.5	7.4 (0.24)	97.5 (3.1)
used Ni ₂ P/SiO ₂ -S873	Ni ₂ P _{1.11} S _{0.08}	—	10.2	—	—

3.4. CO uptake

Table 1 shows the CO uptakes of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after $\text{H}_2\text{S}/\text{H}_2$ treatment. Compared to the as-prepared catalyst, the treated $\text{Ni}_2\text{P}/\text{SiO}_2$ had much lower uptake of CO, which is ascribed to the blockage of Ni sites by S species. $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$ had similar CO uptake to $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$, while $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$ had lower CO uptake than $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$. The higher S/Ni ratio led to the lower CO uptake. Thus, the incorporation of S in the surface of the Ni_2P particles not only lowered the electron density of Ni but also blocked CO adsorption. This is ascribed to the formation of surface phosphosulfide phase, consistent with the results reported by Lee et al. [18] and Layman et al. [20].

3.5. H_2 -TPD

Figure 2 shows the H_2 -TPD profiles of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after the $\text{H}_2\text{S}/\text{H}_2$ treatment. Usually, H species desorbed below 673 K are ascribed to those adsorbed on the metal sites, while those desorbed above 673 K are attributed to spilt-over hydrogen species [12]. Compared with the fresh $\text{Ni}_2\text{P}/\text{SiO}_2$, the $\text{Ni}_2\text{P}/\text{SiO}_2$ treated with $\text{H}_2\text{S}/\text{H}_2$ exhibited less desorption of H_2 below 673 K and more H_2 desorption above 673 K. Because H_2S preferentially dissociates on the Ni sites and Ni-P bridges in Ni_2P where H_2 adsorbs, the amount of H_2 that desorbed from the treated $\text{Ni}_2\text{P}/\text{SiO}_2$ below 673 K was lower than that from the fresh catalyst. Moreover, from the XPS and H_2 -TPD results, the decrease of Ni electron density due to S adsorption may also have facilitated the desorption of H_2 from Ni sites. This is consistent with a report by Kiskinova and Goodman [33]. Interestingly, the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts treated with $\text{H}_2\text{S}/\text{H}_2$ had greater amounts of spilt-over hydrogen species than the fresh catalysts. This increase may be related to the interaction between H_2S and phosphate on silica. As reported in previous work [27], the greater amount of spilt-over species on $\text{Ni}_2\text{P}/\text{SiO}_2$ compared with that on Ni/SiO_2 is ascribed to the P-OH groups on the silica. We have also found that steam treatment can create new P-OH groups on $\text{Ni}_2\text{P}/\text{SiO}_2$ [14]. By analogy, new P-OH groups and even P-SH groups might be

Fig. 2. H_2 -TPD profiles of $\text{Ni}_2\text{P}/\text{SiO}_2$ samples treated by different procedures. (1) $\text{Ni}_2\text{P}/\text{SiO}_2$; (2) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$; (3) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$; (4) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$.

Fig. 3. H_2 -TPD profiles of different samples. (1) $\text{PO}_x/\text{SiO}_2\text{-S873}(\text{H}_2)$; (2) $\text{PO}_x/\text{SiO}_2\text{-S573}$; (3) PO_x/SiO_2 . $\text{PO}_x/\text{SiO}_2\text{-S573}$ indicates PO_x/SiO_2 treated with $\text{H}_2\text{S}/\text{H}_2$ at 573 K, and $\text{PO}_x/\text{SiO}_2\text{-S873}(\text{H}_2)$ indicates PO_x/SiO_2 treated with $\text{H}_2\text{S}/\text{H}_2$ at 873 K and cooled in a H_2 flow.

formed during the $\text{H}_2\text{S}/\text{H}_2$ treatment and act as reservoir of spilt-over hydrogen. Indeed, hydroxyl groups can facilitate hydrogen spillover [34], and supported hydrogen can store hydrogen [35]. To test this speculation, the PO_x/SiO_2 samples were characterized by H_2 -TPD before and after $\text{H}_2\text{S}/\text{H}_2$ treatment (Fig. 3). Indeed, the PO_x/SiO_2 treated with $\text{H}_2\text{S}/\text{H}_2$ was found to have a greater amount of desorbed H_2 , especially when treated at higher temperature.

3.6. NH_3 -TPD

Figure 4 shows the NH_3 -TPD profiles of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after $\text{H}_2\text{S}/\text{H}_2$ treatment. The $\text{H}_2\text{S}/\text{H}_2$ treatment reduced the acid amount of $\text{Ni}_2\text{P}/\text{SiO}_2$. $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$ had slightly more acid sites than $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$, which had similar amounts. The acidity of $\text{Ni}_2\text{P}/\text{SiO}_2$ is attributed to the Ni site and the P-OH group, which are Lewis and Brönsted acid sites, respectively [27]. It is reasonable that the combination of S and Ni may reduce the number of Lewis acid sites, while the formed -SH and -OH groups contribute to the number of Brönsted acid sites. The decrease in acidity of the H_2S treated $\text{Ni}_2\text{P}/\text{SiO}_2$ compared with that of the untreated

Fig. 4. NH_3 -TPD profiles of $\text{Ni}_2\text{P}/\text{SiO}_2$ samples treated by different procedures. (1) $\text{Ni}_2\text{P}/\text{SiO}_2$; (2) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$; (3) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$; (4) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$.

Fig. 5. Chlorobenzene conversion on different catalysts with time on stream. (1) $\text{Ni}_2\text{P}/\text{SiO}_2$; (2) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$; (3) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$; (4) $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$; (5) Ni/SiO_2 ; (6) $\text{Ni}/\text{SiO}_2\text{-S573}$.

catalyst may be mainly related to the decrease in the number of exposed Ni sites.

3.7. Catalyst activity

Figure 5 shows the activity of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after $\text{H}_2\text{S}/\text{H}_2$ treatment. Induction periods were observed for both the as-prepared and treated $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts. The initial chlorobenzene conversion over $\text{Ni}_2\text{P}/\text{SiO}_2$ was 14.8%, while those over $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$, $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$, and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$ were 4.2%, 3.7%, and 7.4%, respectively. As indicated in previous work [14], the existence of an induction period may be related to the blocking of active sites by surplus P, which hinders the activation of chlorobenzene and the adsorption of hydrogen species on the Ni_2P . An induction period also occurred for the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts treated with $\text{H}_2\text{S}/\text{H}_2$, which may also be related to the blockage of the surface Ni sites by S species. Surface reconstruction as well as S loss may have taken place during the induction period, and the activity subsequently increased. As indicated by the XRD and ICP-AES results, the Ni_2P phase did not change, and a loss of S took place, which would have led to reconstruction of the surface of the Ni_2P crystallites. Although $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$ had lower CO uptake than $\text{Ni}_2\text{P}/\text{SiO}_2$, it had a higher TOF (Table 1). This led to the $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}(\text{H}_2)$ exhibiting a similar chlorobenzene conversion to that of $\text{Ni}_2\text{P}/\text{SiO}_2$ after the induction period. Because $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$ exhibited much lower CO uptake than $\text{Ni}_2\text{P}/\text{SiO}_2$, they gave lower chlorobenzene conversion despite having higher TOF (Table 1). The chlorobenzene conversion over $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S573}$ and $\text{Ni}_2\text{P}/\text{SiO}_2\text{-S873}$ remained about 84%, as many as that over $\text{Ni}_2\text{P}/\text{SiO}_2$. Obviously, the conversion was determined by both TOF and CO uptake.

The activity of Ni/SiO_2 and $\text{Ni}/\text{SiO}_2\text{-S573}$ is also shown in Fig. 5 for comparison. The initial chlorobenzene conversion was 30.8% for Ni/SiO_2 and 15.2% for $\text{Ni}/\text{SiO}_2\text{-S573}$. The conversion over Ni/SiO_2 first increased and then decreased with time on stream, while that over $\text{Ni}/\text{SiO}_2\text{-S573}$ decreased. Clearly, $\text{H}_2\text{S}/\text{H}_2$ treatment had a greater negative effect on the activity of Ni/SiO_2 than on that of $\text{Ni}_2\text{P}/\text{SiO}_2$. $\text{H}_2\text{S}/\text{H}_2$ treatment did

not influence the bulk phase of Ni_2P in $\text{Ni}_2\text{P}/\text{SiO}_2$, and S was only incorporated in the surface of the Ni_2P to form a surface phosphosulfide phase. However, the metallic Ni in Ni/SiO_2 was converted to Ni_3S_2 and NiS after treatment with $\text{H}_2\text{S}/\text{H}_2$. The metallic character of Ni_3S_2 and NiS should be much lower than that of metallic Ni. Thus, $\text{Ni}/\text{SiO}_2\text{-S573}$ had lower activity for H_2 activation as well as for the HDC of chlorobenzene than Ni/SiO_2 .

The TOFs of the $\text{Ni}_2\text{P}/\text{SiO}_2$ catalysts before and after H_2S treatment are shown in Table 1. Interestingly, the treated $\text{Ni}_2\text{P}/\text{SiO}_2$ had higher TOFs than the fresh catalyst, especially at steady state (after reaction for 10 h). It is known that chlorine acts as an electron acceptor with respect to transition metals [1,36]. Interaction between Cl and a metal site leads to the formation of a M-Cl (M = metal site) species, which reduces the electron density of the metal site and depresses its catalytic activity [37,38]. According to the Sabatier principle [39], a good catalyst is characterized by a low activation energy and weak bonding with intermediates, that is, good bonding with reactants and moderate bonding with products [40]. Reasonably, reducing the interaction between HCl and metal sites may improve the catalyst activity. Moderately decreasing the electron density of the metal sites may be a route to achieve this aim. As circumstantial evidence, theoretical calculations indicate that the electron-deficient W weakens the binding with sulfur [41], while sulfur is also electronegative and acts as an electron acceptor. Indeed, Prasada and coworkers [2,3] have proposed that the Pd^{n+} species in Pd/ZrO_2 , Pd/TiO_2 , and Pd/CeO_2 are resistant to deactivation because of the weak adsorption of chlorine on Pd^{n+} . They [4] also found that addition of Fe promotes the formation of active Pd^{n+} species at the interface of Pd-O-Fe in $\text{Pd-Fe}/\text{Al}_2\text{O}_3$, and $\text{Pd-Fe}/\text{Al}_2\text{O}_3$ shows higher activity and stability than $\text{Pd}/\text{Al}_2\text{O}_3$ for the HDC of chlorobenzene. In addition, metal sites bearing positive charge may act as Lewis sites and activate reactants by forming adducts, where electrons are transferred from Cl to the metal sites. For the HDC of CCl_4 , Gómez-Sainero et al. [42] have proposed a dual active site ($\text{Pd}^{n+}\text{-Pd}^0$), where CCl_4 is adsorbed and activated on Pd^{n+} by abstraction of the slightly nucleophilic chloride anion (Cl^-) forming intermediate complex $[\text{Cl-Pd}^0 \rightarrow \text{CCl}_3]^+$. Small platinum particles on $\text{Pt}/\gamma\text{-Al}_2\text{O}_3$, which possess low coordination number and electron-deficient character, favor the complete dechlorination of CCl_4 [43]. Due to the ligand effect of P, the Ni site in Ni_2P bears a small positive charge ($\text{Ni}^{\delta+}$). The $\text{Ni}^{\delta+}$ site may act as a Lewis site to adsorb and activate molecular chlorobenzene through electron transfer from chlorine to $\text{Ni}^{\delta+}$. In the case of the $\text{Ni}_2\text{P}/\text{SiO}_2$ treated with $\text{H}_2\text{S}/\text{H}_2$, the incorporated S increases the positive charge of the $\text{Ni}^{\delta+}$ site (Table 2), which may further promote the activation of molecular chlorobenzene. Although some of the S is lost during the reaction, the role of S should be in effect. The activated molecular chlorobenzene is attracted by hydrogen adsorbed on the $\text{Ni}^{\delta+}$ site, provided by the P-OH and/or -SH groups on the Ni_2P particles or the spilt-over hydrogen, to form HCl and benzene. In fact, the P-OH and/or -SH groups give rise to Brønsted acidity. Tøpsoe et al. [44] have suggested that the -SH group may be the source of hydrogen during the catalytic cycle. Thus, in comparison with the untreated $\text{Ni}_2\text{P}/\text{SiO}_2$, the treated $\text{Ni}_2\text{P}/\text{SiO}_2$ had a lower

amount of exposed Ni (Table 1), whereas the decreased electron density of its Ni sites may have favored the activation of chlorobenzene. Moreover, the treated Ni₂P/SiO₂ had a greater amount of spilt-over hydrogen species. There are many evidences for the promoting effect of spilt-over hydrogen on HDC [37]. In a recent work [14], we found a promotion effect of steam treatment on the activity of Ni₂P/SiO₂, which may be related to a synergism between the Ni sites and the P–OH groups. The lower electron density of the Ni site and larger amount of spilt-over hydrogen led to the treated Ni₂P/SiO₂ exhibiting a higher TOF in comparison with that of the untreated one.

4. Conclusions

H₂S/H₂ treatment did not influence the Ni₂P phase and particle size of Ni₂P/SiO₂, while a small amount of S was incorporated into the surface of the Ni₂P particles. The incorporated S withdrew electrons from Ni and blocked Ni sites. This reduced the electron density of Ni, the number of exposed Ni sites, and the number of acid sites, while the amount of spilt-over hydrogen on Ni₂P/SiO₂ increased after treatment. Because the treated Ni₂P/SiO₂ catalysts had a lower surface density of exposed Ni sites, they exhibited lower chlorobenzene conversions than the untreated catalysts. However, the treated catalysts had higher TOFs than the untreated catalysts, which may be attributed to their lower Ni site electron densities and larger amounts of spilt-over hydrogen.

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Graphical Abstract

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Effect of H₂S pre-treatment on structure and activity of Ni₂P/SiO₂ catalyst for hydrodechlorination of chlorobenzene

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H₂S/H₂ treatment improved the turnover frequency of hydrodechlorination on Ni₂P/SiO₂. This is ascribed to an increased electron deficiency of Ni sites and a greater amount of spilt-over hydrogen species.

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H₂S预处理对Ni₂P/SiO₂催化剂结构及氯苯加氢脱氯性能的影响

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摘要: 采用10% H₂S/H₂对Ni₂P/SiO₂催化剂进行预处理, 利用X射线衍射、电感耦合等离子发射光谱、X射线光电子能谱、CO化学吸附、H₂程序升温脱附、NH₃程序升温脱附及活性评价等方法研究了H₂S预处理对催化剂结构和氯苯加氢脱氯反应性能的影响. 结果表明, 即使在873 K进行H₂S预处理, Ni₂P/SiO₂催化剂体相结构及Ni₂P晶粒大小没有发生变化, 但导致Ni₂P晶粒表面形成了磷硫镍相(NiP₃S₂), 同时使表面溢流氢数量增加. 硫物种的存在不仅阻塞了部分镍中心, 使催化剂表面镍中心密度降低, 也导致镍中心的缺电子性进一步增加. 经H₂S预处理后Ni₂P/SiO₂催化剂上氯苯加氢脱氯反应的转化频率(TOF)明显提高, 这可能与催化剂表面Ni物种的缺电子性增强及溢流氢数量增多有关.

关键词: 磷化镍; 硫化氢; 电子结构; 溢流氢; 氯苯; 加氢脱氯

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