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Dechlorination of 1,4-dichlorobenzene on unsupported nickel phosphides synthesized *in situ*: effect of Ni/P ratio on the catalyst activity

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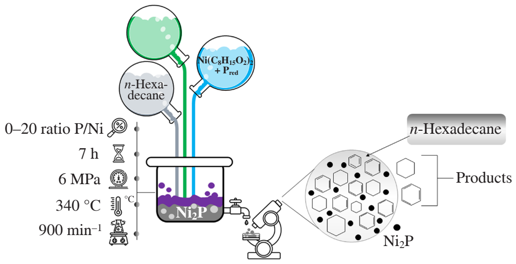
The synthesis of nickel phosphides was conducted *in situ* during the hydrodechlorination reaction of 1,4-dichlorobenzene using either red phosphorus or triphenylphosphine as a starting reactant to produce the phosphides. At Ni/P ratio of 1 : 0.5, the most active nickel phosphide phase, Ni_2P, was observed. An increase in phosphorus loading resulted in reducing the degree of dechlorination.



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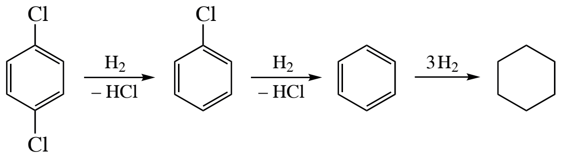
Over the past two decades, transition metal phosphides have been the subject of extensive research in the context of hydrogenolysis processes, including hydrodeoxygenation,[1,2] hydrodesulfurization,[3] hydrodeazotization[4] and dechlorination.[5–10] In comparison with palladium and platinum catalysts, nickel phosphides represent a promising option for hydrogenolysis processes due to their cost-effectiveness and enhanced resistance to deactivation compared with the metallic nickel. This is ascribed to the minimal charge transfer from the nickel atom to the phosphorus atom and the ligand effect, which encompasses the screening of nickel atoms by phosphorus atoms.[8–12] Consequently, a reduction in the interaction between nickel and hydrogen chloride is evident when comparing nickel phosphide dechlorination with that of metallic nickel catalysts. This is corroborated by the phase composition analysis of the aforementioned dechlorination process. Even if not all nickel atoms are bonded to phosphorus atoms, the shielding effect of phosphorus on the surface reduces the proportion of nickel atoms that are available for interaction with hydrogen chloride.

The catalytic activity observed in hydrogenolysis reactions involving transition metal phosphides is found to be significantly affected by the phase composition of the phosphides in question. The phases Ni_3P, $Ni_{12}P_5$, Ni_2P, Ni_5P_4, NiP and NiP_2 are known to occur in nickel phosphides.[13] In the context of dechlorination, phosphide catalysts, predominantly represented by the Ni_2P phase, have been the subject of the most extensive investigation.[6,11,12,14–17] However, there is a paucity of literature devoted to the catalysis of dechlorination in the presence of Ni_3P. It has been demonstrated that the Ni_3P/SiO_2 catalyst exhibits superior activity and stability in the dechlorination of chlorobenzene in comparison with the Ni/SiO_2 catalyst. A juxtaposition of the catalytic activity of different phases of nickel phosphide in dechlorination would undoubtedly prove insightful. The study conducted[11] to investigate the dechlorination of chlorobenzene on catalysts comprising Ni_2P/SiO_2, Ni_3P/SiO_2, and $Ni_{12}P_5/SiO_2$ revealed that all catalysts demonstrated chlorobenzene conversion in excess of 95% after 30 h of operation, exhibiting minimal variation in activity. However, Ni_2P/SiO_2 and $Ni_{12}P_5/SiO_2$ are distinguished by an induction period in which they exhibit low activity, particularly during the initial hours of the reaction. This is due to the blocking of the catalyst surface by excess of phosphorus, a phenomenon that is typical of phases with high phosphorus content (Ni_2P, $Ni_{12}P_5$, NiP, NiP_2). As the reaction progresses, the surplus phosphorus is gradually removed from the surface, leading to an increase in catalytic activity.

The phase composition of the catalyst is dependent upon the ratio of nickel to phosphorus in the precursors and the synthesis conditions employed.[8,17] In the synthesis of nickel phosphides, water-soluble nickel salts and ammonium hydrophosphates or phosphoric acid are the most commonly used precursors.[5–7,11,12,14,17] The resulting phosphates are converted into phosphides during reduction. In particular, triphenylphosphine and nickel carboxylates have been proposed as water- and oil-soluble precursors for the synthesis of unsupported nickel phosphides.[1] The use of unsupported phosphide catalysts may be of interest in dechlorination and other reactions of hydrogenolysis of complex mixtures. These mixtures may include products of pyrolysis of chlorine-containing polymers, hydroconversion of polymers and their mixtures with oil fractions, bio-oil and other raw materials. The hydrogenation of these materials on traditional supported catalysts may be associated with coking of the carrier and its destruction caused by the interaction with hydrogen chloride. Only two works,[18,19] which synthesized nickel phosphides by the hydrothermal method and examined their performance in the dechlorination of trichloroethylene, have focused on unsupported phosphide catalysts for dechlorination.

In the selection of phosphorus precursors, it is important to consider the high cost (and toxicity) of some compounds, which represents a significant challenge in the development of industrial catalysis on phosphides compared to sulfides. It is therefore of interest to investigate the possibility of synthesizing phosphides



Scheme 1

using an affordable, non-toxic and environmentally friendly precursor, namely red phosphorus. In the present study, an investigation has been conducted into the influence of the Ni/P ratio in the *in situ* synthesis in the reaction medium of unsupported nickel phosphides on their phase composition and catalytic activity in the dechlorination of 1,4-dichlorobenzene. The use of triphenylphosphine and red phosphorus as phosphidation agents was considered to be a more promising approach from both an environmental and a technological standpoint (see details in Online Supplementary Materials).

1,4-Dichlorobenzene undergoes hydrodechlorination to yield chlorine-free products, namely benzene and cyclohexane (Scheme 1).

The dechlorination rate was calculated as follows (using dechlorination as an example):

$$\text{Dechlorination rate} = \frac{W_0 - (W_1 n_1 + W_2 n_2)}{W_0},$$

where W_0 represents the fraction of chlorine in the feedstock, W_1 is the fraction of unconverted substrate in the product mixture, n_1 is the fraction of chlorine in the substrate, W_2 is the fraction of chlorine-containing product and n_2 is the fraction of chlorine in the product.

The phase composition of the catalysts synthesized at varying Ni/P ratios was initially evaluated *via* X-ray power diffraction (XRD) analysis (Figure 1) (see details in Online Supplementary Materials). In the absence of phosphorus in the system, only phases of nickel chloride and its hydrates of different compositions were identified. However, in the presence of chlorine-containing compounds in the reaction medium, the formation of metallic nickel and nickel oxides was not observed [Figure 1(*a*)]. But upon introduction of red phosphorus at Ni/P ratio of 1/1, the Ni_2P phase was found [Figure 1(*b*)] alongside the phases of nickel chloride and its hydrate. An increase in the phosphorus content in the system during the synthesis of the catalyst (Ni/P = 1/6) resulted in a decrease in the intensity of the signals associated with the nickel chloride phase and an increase in those corresponding to the Ni_2P phase. Additionally, the sample exhibited the presence of a nickel pyrophosphate phase. At Ni/P ratio of 1/20 [Figure 1(*e*)], the signals of the Ni_2P phase are accompanied by those of the nickel chloride and pyrophosphate phases. The $Ni_{12}P_5$ and Ni_3P phases were not identified in any of the samples. The introduction of triphenylphosphine into the system, like in the case of adding red phosphorus, causes the formation of Ni_2P as the main phase [Figure 1(*f*)].

In the absence of the catalyst, 1,4-dichlorobenzene undergoes dechlorination to a limited extent. At 340 °C and 6 MPa pressure, the degree of dechlorination is 10%. The introduction of nickel particles, formed *in situ* from nickel 2-ethylhexanoate, into the system results in an increase in the dechlorination degree of 1,4-dichlorobenzene up to 14% (Figure 2). Conversely, addition of a phosphorus source (triphenylphosphine or red phosphorus) along with nickel 2-ethylhexanoate causes a significant increase in the conversion of 1,4-dichlorobenzene, accompanied by the formation of a notable amount of benzene, indicating complete dechlorination of the substrate.

The diminished activity of the nickel particles can be attributed to their rapid deactivation, which is evidenced by the

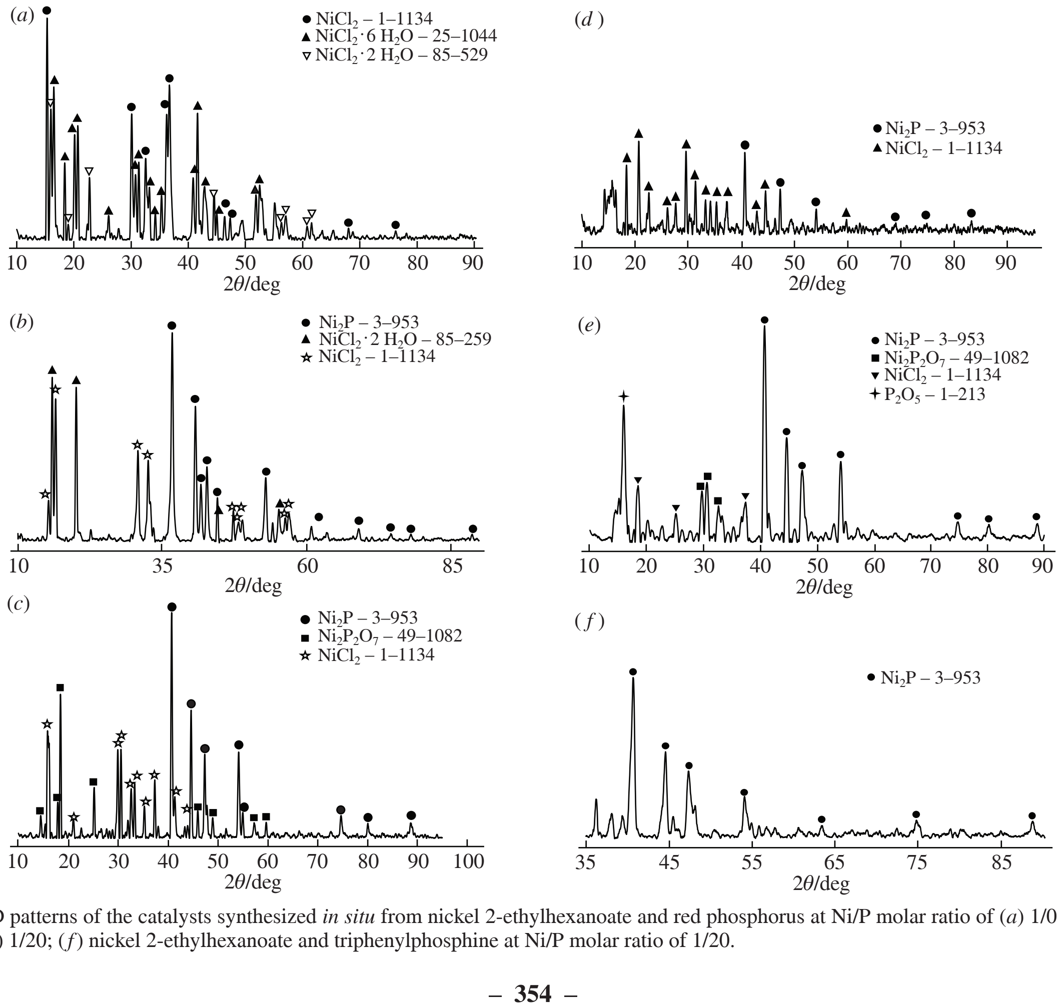


Figure 1 XRD patterns of the catalysts synthesized *in situ* from nickel 2-ethylhexanoate and red phosphorus at Ni/P molar ratio of (*a*) 1/0, (*b*) 1/1, (*c*) 1/6, (*d*) 1/10 and (*e*) 1/20; (*f*) nickel 2-ethylhexanoate and triphenylphosphine at Ni/P molar ratio of 1/20.

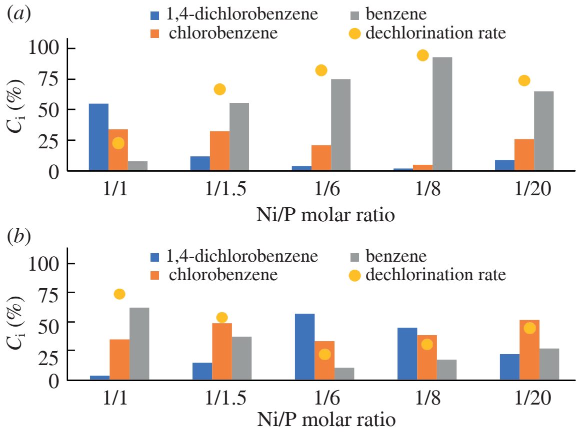


Figure 2 Effect of Ni/P molar ratio on product mixture composition and degree of dechlorination during synthesis of catalyst from (*a*) triphenylphosphine and (*b*) red phosphorus.

formation of $NiCl_2$ (as illustrated in Figure 1). In a hydrogen environment, the reduction of nickel chloride to metallic Ni occurs with the formation of larger crystallites of nickel, which has the effect of reducing the dispersion and activity of the catalyst.[20] In phosphides, the nickel atom exhibits a partial positive charge, which decreases in the series: $Ni_2P > Ni_{12}P_5 > Ni_3P$.[21] The presence of a partial positive charge on the nickel atom renders the interaction between chlorine and nickel weaker, thereby facilitating the desorption of chlorine from the surface of catalytic particles.[8–12] Furthermore, phosphorus atoms on the surface of the catalytic particles create an ‘ensemble effect’, *i.e.*, steric hindrance for chlorine adsorption on nickel atoms.[11] Therefore, it can be concluded that the higher the positive charge on the nickel atom, the more stable this catalyst will be to deactivation and the higher its activity in dechlorination.

The phosphide particles obtained from red phosphorus in terms of activity are comparable to those synthesized from triphenylphosphine. The introduction of red phosphorus into the system in Ni/P ratio of 1/1 has been observed to contribute to enhancing the dechlorination degree up to 73%. Hence, red phosphorus can be be considered as a promising phosphidising agent for the *in situ* synthesis of nickel phosphides and a replacement of the expensive phenyl- and alkylphosphines.

The use of triphenylphosphine as a phosphorus source results in the formation of the most active catalyst at Ni/P ratio of 1/8 [Figure 2(*a*)]. Additionally, the products exhibit minimal 1,4-dichlorobenzene content. The introduction of red phosphorus [Figure 2(*b*)] into the system at Ni/P ratios of 1/1 and 1/1.5 results in the formation of the most active catalyst. At higher Ni/P ratios, the dechlorination degree exhibits a decline in both systems. The Ni/P ratio of 1/1 is sufficient for the formation of the Ni_2P phase during the synthesis of the catalyst from red phosphorus (see Figure 1). Further increase in the indicated ratio does not result in the formation of a pure Ni_2P phase. Instead, the samples still contain phases of nickel chloride and pyrophosphate.[22] Thus, it is considered inexpedient to increase the Ni/P ratio above 1/1.5, which leads to a decrease in catalytic activity, probably due to the presence of an induction period necessary to remove excess phosphorus from the catalyst surface.

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Online Supplementary Materials

Supplementary data associated with this article can be found in the online version at doi: 10.71267/mencom.7662.

References

1 M. A. Golubeva and A. L. Maximov, *Appl. Catal., A*, 2021, **628**, 118401; https://doi.org/10.1016/j.apcata.2021.118401.
2 Z. Yu, K. Yao, Y. Wang, Y. Yao, Z. Sun, Y. Liu, C. Shi, W. Wang and A. Wang, *Catal. Today*, 2021, **371**, 179; https://doi.org/10.1016/j.cattod.2020.06.006.
3 R. Wang and K. J. Smith, *Appl. Catal., A*, 2009, **361**, 18; https://doi.org/10.1016/j.apcata.2009.03.037.
4 J. L. Wagner, E. Jones, A. Sartbaeva, S. A. Davis, L. Torrente-Murciano, C. J. Chuck and V. P. Ting, *Dalton Trans.*, 2018, **47**, 1189; https://doi.org/10.1039/C7DT03318D.
5 J. Chen, D. Ci, R. Wang and J. Zhang, *Appl. Surf. Sci.*, 2008, **255**, 3300; https://doi.org/10.1016/j.apsusc.2008.09.035.
6 J. A. Cecilia, I. Jiménez-Morales, A. Infantes-Molina, E. Rodríguez-Castellón and A. Jiménez-López, *J. Mol. Catal. A: Chem.*, 2013, **368–369**, 78; https://doi.org/10.1016/j.molcata.2012.11.017.
7 X. Liu, J. Chen and J. Zhang, *Catal. Commun.*, 2007, **8**, 1905; https://doi.org/10.1016/j.catcom.2007.03.008.
8 G. Yun, Q. Guan and W. Li, *RSC Adv.*, 2017, **7**, 8677; https://doi.org/10.1039/C7RA00250E.
9 E. G. Dzhabarov, N. N. Petrukhina and E. M. Zakharyan, *Mendeleev Commun.*, 2023, **33**, 839; https://doi.org/10.1016/j.mencom.2023.10.033.
10 T. I. Gorbunova, D. O. Egorova, V. I. Saloutin and O. N. Chupakhin, *Russ. Chem. Rev.*, 2024, **93**, RCR5138; https://doi.org/10.59761/RCR5138.
11 X. Liu, J. Chen and J. Zhang, *Ind. Eng. Chem. Res.*, 2008, **47**, 5362; https://doi.org/10.1021/ie7017542.
12 J. Chen, D. Ci, Q. Yang and K. Li, *Appl. Surf. Sci.*, 2014, **320**, 643; https://doi.org/10.1016/j.apsusc.2014.09.127.
13 Y. Liu, A. J. McCue and D. Li, *ACS Catal.*, 2021, **11**, 9102; https://doi.org/10.1021/acscatal.1c01718.
14 J. Chen, T. Guo, K. Li and L. Sun, *Catal. Sci. Technol.*, 2015, **5**, 2670; https://doi.org/10.1039/C5CY00044K.
15 J. Chen, Y. Chen, Q. Yang, K. Li and C. C. Yao, *Catal. Commun.*, 2010, **11**, 571; https://doi.org/10.1016/j.catcom.2009.12.022.16.
16 S. Gutiérrez-Rubio, A. Berenguer, J. Přech, M. Opanasenko, C. Ochoa-Hernández, P. Pizarro, J. Čejka, D P. Serrano, J. M. Coronado and I. Moreno, *Catal. Today*, 2020, **345**, 48; https://doi.org/10.1016/j.cattod.2019.11.015.
17 C. V. M. Inocêncio, P. M. de Souza, R. C. Rabelo-Neto, V. T. da Silva and F. B. Noronha, *Catal. Today*, 2021, **381**, 133; https://doi.org/10.1016/j.cattod.2020.07.077.
18 G. Yuan, J. Bai, S. Lu, L. Ren, B. Gao, J. Mei, Y. Ma, X. Chen and L. Zhang, *ChemistrySelect*, 2019, **4**, 950; https://doi.org/10.1002/slct.201803443.
19 H. Xu, S. Lu and L. Ren, *Int. J. Hydrogen Energy*, 2017, **42**, 18383; https://doi.org/10.1016/j.ijhydene.2017.04.133.
20 B. Veriansyah, H.-M. Choi, Y.-W. Lee, J. W. Kang, J.-D. Kim and J. Kim, *Environ. Sci. Health, Part A*, 2009, **44**, 1538; https://doi.org/10.1080/10934520903263421.
21 Z. Yu, K. Yao, Y. Wang, Y. Yao, Z. Sun, Y. Liu, C. Shi, W. Wang and A. Wang, *Catal. Today*, 2021, **371**, 179; https://doi.org/10.1016/j.cattod.2020.06.006.
22 J. Chen, S. Zhou, X. Liu and J. Zhang, *Catal. Lett.*, 2008, **122**, 167; https://doi.org/10.1007/s10562-007-9363-7.

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