Synthesis of palladium phosphides for aqueous phase hydrodechlorination: Kinetic study and deactivation resistance

Zhijie Wu [a],*, Tao Pan [a], Yan Chai [b], Shaohui Ge [c], Yana Ju [c], Tianshu Li [c], Kai Liu [c], Ling Lan [c], Alex C.K. Yip [d],*, Minghui Zhang [b],*

[a] State Key Laboratory of Heavy Oil Processing and the Key Laboratory of Catalysis of CNPC, China University of Petroleum, Beijing 102249, China
[b] Key Laboratory of Advanced Energy Materials Chemistry (Ministry of Education), College of Chemistry, Nankai University, Tianjin 300071, China
[c] Petrochemical Research Institute, PetroChina Company Limited, E318, A42 Block, China Petroleum Innovation Base, Changping, Beijing 100195, China
[d] Department of Chemical and Process Engineering, University of Canterbury, Christchurch, New Zealand

ABSTRACT

We report the synthesis of noble metal phosphides by a temperature-programmed reduction method for aqueous phase hydrodechlorination (HDC) of 4-chlorophenol (4-CP). $Pd_3P_{0.95}/SiO_2$, Rh_2P/SiO_2 and PtP_2/SiO_2 catalysts were prepared and showed higher 4-CP HDC rates than their corresponding noble metal catalysts. $Pd_3P_{0.95}/SiO_2$ sample exhibited a higher HDC rate than the other phosphide catalysts and Pd/SiO_2 catalysts. The XPS spectra show the surface interaction reactions of the Pd and P species that occur via the electron transfer from Pd to P. $Pd_3P_{0.95}/SiO_2$ was synthesized with different phosphide particle size (1.1–13.5 nm based on hydrogen chemisorptions) via changing the metal loading from 1 to 10 wt%. The 4-CP HDC reaction is sensitive to the size of the Pd and $Pd_3P_{0.95}$ particles, and the optimum sizes for Pd/SiO_2 and $Pd_3P_{0.95}/SiO_2$ were ∼8 and ∼5 nm, respectively. The effects of the initial 4-CP and Cl^- ion concentration and the S to Pd_{surf} (surface active Pd metal sites determined by hydrogen chemisorptions) ratio on the 4-CP HDC activity were examined for both catalysts. The Langmuir-Hinshelwood kinetic model that was developed considering the surface reaction as the rate-determining step suggests P has an enhancing effect on sorption in the 4-CP HDC reaction and an inhibiting effect on chloride sorption for $Pd_3P_{0.95}/SiO_2$. Moreover, $Pd_3P_{0.95}/SiO_2$ possesses better sulfide resistance than Pd/SiO_2 because P can prevent the conversion of Pd metallic sites into inactive Pd_4S compounds with a sulfide treatment. As a result, $Pd_3P_{0.95}/SiO_2$ shows better HDC stability than those of Pd/SiO_2 catalysts.

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1. Introduction

The removal of organochlorinated pollutants is a pressing problem in water treatment because of their toxicity and tightened environmental policies [1,2]. Among all chlorinated organic compounds, chlorophenols (CPs, typically 50–500 mg L^{-1} in wastewater that contains phenols) require effective remediation due to their high toxicity, persistency, low biodegradability [3–5] and their present in both surface and ground water. Catalytic hydrodechlorination (HDC) reaction has been investigated in the past decade and is found to be very effective in eliminating aqueous chlorinated pollutants, such as chlorophenols, using hydrogen over a wide range of concentrations at ambient or near-ambient temperatures [6,7]. Because of the low solubility of CPs in water,

kinetic analysis of HDC in aqueous solution has been mainly limited to 4-CP (4-chlorophenol) since it is relatively soluble (ca. 27 g L^{-1} (0.21 mol L^{-1}) in water at 293 K) compared with its isomers [5,7–10]. In order to develop a more effective catalyst and to build a kinetic database for industrial process, it is important to advance the fundamental understanding of catalytic HDC of chlorophenols.

Beside Raney Ni [11] catalysts, noble metal catalysts, especially Pd [12–25], Pt [6,26] and Rh [27–29] metal catalysts and Pd-based bimetallic catalysts [30–33], have been reported to be good catalysts for the aqueous phase CP HDC reaction under mild conditions. For example, Yuan et al. [14] and Roy et al. [16] achieved the HDC of CPs over Pd-based catalysts at ambient temperatures (273–303 K) under atmospheric pressure. The main products from the HDC reaction of monochlorophenol over Pd-based catalysts are typically phenol (e.g., >90% selectivity), cyclohexanone, and trace amount of cyclohexanol (<0.05% selectivity) [14,34]. The most commonly

used support materials are alumina and activated carbon (AC) [14,16]. While the turnover frequency (TOF) of HDC of 4-CP over Pd/C catalyst ranging from 0.12 to 0.17 $mol_{4\text{-}CP}\,mol_{active\text{-}Pd}^{-1}\,s^{-1}$ [19,34–36], it can be further increased to between 0.43 and 0.7 $mol_{4\text{-}CP}\,mol_{active\text{-}Pd}^{-1}\,s^{-1}$ by modifying the carbon support itself or introducing polymers to the catalyst matrix.

Factors that influence activity and selectivity, such as the relationships between the size of the metallic phase clusters and the HDC performance, have been studied [20,37]. The HDC of 4-CP is a structural sensitive reaction [38] that the activity-and-size correlation revealed a volcano plot with Rh metal clusters being the optimum. Among all tested metals, Pd is the least susceptible to catalytic poisoning due to chloride ions. It is also considered as the most suitable active phase catalyst for the liquid phase HDC reactions [7,12–25,39], especially for the system in which carbon materials are used as the support. The carbon supported catalysts exhibit high HDC activities due to promotion of reactive spillover hydrogen [9] or enhancement of the sorption of CPs [40]. A critical issue associated with the liquid phase HDC is that substantial catalyst deactivation can easily happen due to metal leaching caused by the HCl by-product. Nevertheless, due to the weak acidity of CPs, the addition of base can help increase the solubility and limit the HCl poisoning [8]. In the study, a kinetic analysis based on the Langmuir–Hinshelwood mechanisms is performed. The effect of the size of the active phase on the HDC and the applicability of the kinetic model are carefully assessed.

The rise of sulfur utilization in various chemical industries in the last decade not only means that the sulfur present in water and wastewater is becoming more significant, but the form of sulfur also varies from HS^-, S^{2-}, SO_4^{2-}, SO_3^{2-} and to other sulfur-containing anions. On the other hand, the widespread water contamination with chlorinated solvents, pesticides and sulfur has spurred intense effort to develop efficient and cost-effective treatment methods for chlorinated compounds, especially with co-contamination of sulfur. The HDC reactions over metal catalysts are regarded as a potential route to remove chlorinated compounds. However, the metal catalysts are often suffered from deactivation due to chloride (Cl^-) and hydrosulfide (SH^- or "sulfide" in short) ions [30,41,42]. Therefore, the strong poisoning effects associated with traces of sulfur compounds need to be addressed in order to develop noble metal catalysts with long-term durability. For example, Wong et al. developed Pd/Au nanoparticles for HDC reaction of trichloroethene in aqueous phase by promoting the effect of gold on the catalyst resistance to sulfur poisoning at room temperature [30].

In light of the excellent performance of metal phosphides in hydrotreating reactions, such as hydrodesulfurization (HDS) [43–49], metal phosphides should be suitable catalysts for the HDC reaction and have a sulfur resistance. In the past 10 years, transition-metal phosphides have been used in the gas phase HDC reaction at high temperatures because their activities are lower than those of noble metal catalysts at low reaction temperature [50–52]. Little work has been devoted to the catalytic performance of noble metal phosphide catalysts in the aqueous phase HDC reaction. Here, we firstly screened noble metal phosphides (platinum, rhodium and palladium phosphides) for the aqueous phase HDC reaction of 4-CP. We studied the effects of sulfide and chloride ions on the 4-CP HDC reaction rates of the palladium phosphide catalyst and observed that chloride and sulfide had slight effects that were markedly less than those observed with the Pd catalyst. To clarify the chloride and sulfide resistances of the noble metal phosphide in the aqueous phase HDC reaction, reaction kinetic models based on the Langmuir-Hinshelwood (L-H) model have been extensively applied to investigate the catalytic process.

2. Experimental section

2.1. Chemicals

$NH_4H_2PO_4$ (≥99%), $NH_3·H_2O$ (25–28%), NaCl (≥99.5%), NaOH (≥96%) and Na_2S (≥98.0%) were purchased from Guanfu Chemical, Ltd. (Tianjin, China). $PdCl_2$ (60% Pd basis), H_2PtCl_6 (≥99.8%), $RhCl_3·xH_2O$ (39% Rh), 4-chlorophenol (≥99%), $AgNO_3$ (99.8%), phenol (≥99%), cyclohexanone (≥99.5%) and cyclohexanol (≥98%) were obtained from Sinopharm Chemical Reagent Co., Ltd. (Beijing). All the reagents were used as purchased without any further purification.

Silica gel (SiO_2, 99%) was obtained from the China National Offshore Oil Corp. (CNOOC) Tianjin Chemical Research and Design Institute (Tianjin, China). For the catalyst preparation, SiO_2 was dried at 393 K in an oven for 6 h and then calcined in air at 823 K for 4 h.

2.2. Catalyst synthesis

The SiO_2-supported noble metal phosphides (PtP_2, $Pd_3P_{0.95}$, and Rh_2P) were successfully prepared by a temperature-programmed reduction (TPR) method [44]. Ammonium dihydrogen phosphate ($NH_4H_2PO_4$) was used as the phosphorus source. $PdCl_2$ and $RhCl_3·xH_2O$ were dissolved in an ammonia solution to create a homogenous clear solution. A typical TPR method procedure is described as follows. First, $PdCl_2$, $RhCl_3·xH_2O$ and H_2PtCl_6 solutions with various concentrations were prepared to obtain supported catalysts with 1, 2, 3, 5 and 10 wt% noble metal loadings. Then, the noble metal salt solution was mixed with the $NH_4H_2PO_4$ solution. To obtain pure phase of phosphide, various ratios of P to noble metal in raw materials were screened and an atomic ratio of P to noble metal of 2 (for Pd), 5 (for Pt) and 4/3 (for Rh) has been achieved. SiO_2 was then added to the solutions with at a solid to solution weight ratio of 1/20, and the mixture was stirred (400 rpm) for 4 h and subsequently treated at 318 K overnight under rotation in a rotary evaporator to remove the water. The solid samples were treated in ambient air at 373 K for 6 h and then heated in air at 673 K (0.067 K s^{-1}) for 3 h. To obtain the phosphides, the calcined samples were treated in pure hydrogen gas (1 $cm^3\,g^{-1}\,s^{-1}$) from room temperature to 523 K (0.067 K s^{-1}), and then, they were treated in pure hydrogen gas (1 $cm^3\,g^{-1}\,s^{-1}$) at 773 K (0.033 K s^{-1}) for 5 h. The samples were passivated under 0.5 vol% O_2/Ar (0.5 $cm^3\,g^{-1}\,s^{-1}$) for 1 h at 300 K before air exposure.

The SiO_2-supported noble metal catalysts were prepared with procedures similar to those of the metal phosphides without the introduction of $NH_4H_2PO_4$. To obtain the metallic active sites, the samples were directly reduced in pure hydrogen gas (1 $cm^3\,g^{-1}\,s^{-1}$) at 673 K (0.033 K s^{-1}) for 4 h. The samples were passivated under 0.5 vol% O_2/Ar (0.5 $cm^3\,g^{-1}\,s^{-1}$) for 1 h at 300 K before air exposure.

To obtain supported noble metal catalyst samples with different metal particle sizes, the precursors of the metal catalysts were treated in flowing dry air (1.0 $cm^3\,g^{-1}\,s^{-1}$) by increasing the temperature to 673–873 K at 0.05 K s^{-1} and holding the samples there 5 h to prepare samples with a broad range of metal fraction dispersion (0.07–0.97, Table 1 for Pd/SiO_2 samples with 5 wt% theory metal loading) measured by H_2 chemisorptions as described below.

2.3. Catalyst characterization

The powder X-ray diffraction (XRD) patterns of the obtained samples were collected on a Bruke AXS D8 Advance X-ray