

Synthesis of noble metal phosphides for aqueous phase hydrodechlorination

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Abstract: We report the synthesis of noble metal phosphides by a temperature-programmed reduction method for aqueous hydrodechlorination (HDC) of 4-chlorophenol (4-CP). Pd₃P_{0.95}/SiO₂, Rh₂P/SiO₂ and PtP₂/SiO₂ catalysts were successfully prepared and showed higher 4-CP HDC rates than their corresponding noble metal catalysts. Pd₃P_{0.95}/SiO₂ sample exhibited a higher HDC rate than the other phosphide catalysts and Pd/SiO₂ catalysts. Pd₃P_{0.95}/SiO₂ possesses better sulfide resistance than Pd/SiO₂ because P can prevent the conversion of Pd metallic sites into inactive Pd₄S compounds with a sulfide treatment. As a result, Pd₃P_{0.95}/SiO₂ shows a better HDC stability than the Pd/SiO₂ catalysts.

Keywords: Hydrodechlorination; metal phosphide; 4-chlorophenol.

1. Introduction

The removal of organochlorinated pollutants is a priority in water treatment because of their toxicity and restrictive environmental legislation [1, 2]. Catalytic hydrodechlorination (HDC) reaction has been investigated during the last several decades and is very effective in the elimination of chlorinated pollutants, such as chlorophenols, in aqueous phases with H₂ over a wide range of concentrations at ambient or near-ambient temperatures. The main problem with the use of this aqueous-process is catalyst deactivation caused by active phase leaching and the poisoning effect of Cl⁻ ions, which are released during the reaction, and of S²⁻ ions, which are present in ground water. Here, platinum, rhodium and palladium phosphides have been successfully prepared and used in the aqueous-phase HDC reaction of 4-chlorophenol (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 HDC reaction, reaction kinetic models based on the Langmuir-Hinshelwood (L-H) model have been extensively applied to investigate the catalytic process.

2. Experimental (or Theoretical)

The SiO₂-supported noble metal phosphides (PtP₂, Pd₃P_{0.95}, and Rh₂P) were successfully prepared by a temperature-programmed reduction (TPR) method. A typical TPR method procedure is described as follows. First, PdCl₂, RhCl₃·xH₂O and H₂PtCl₆ 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 NH₄H₂PO₄ solution with an atomic ratio of P to noble metal of 2 (for Pd), 5 (for Pt) and 4/3 (for Rh). SiO₂ 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 cm³ 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 cm³ g⁻¹ s⁻¹) at 773 K (0.033 K S⁻¹) for 5 h. The samples were passivated under 0.5% O₂/Ar (0.5 cm³ g⁻¹ s⁻¹) for 1 h at 300 K before air exposure. The 4-chlorophenol HDC experiments were performed in a 500 mL batch mode three-necked flask under continuous stirring at room temperature and atmospheric pressure.

3. Results and discussion

Figure 1 shows the effect of the particle size of the metal and phosphide nanoparticles on the initial TOR value. Both Pd/SiO₂ and Pd₃P_{0.95}/SiO₂ possess similar trends. The initial TOR value increases with the particle size for particles smaller than ~8 nm and decreases slightly with further growth of the particle size. These data show that the structure sensitivity appears to be a determining factor in the HDC reactivity. The rate-limiting step of the HDC reaction is C–Cl hydrogenolysis in an adsorbed molecule, which is initiated by an ensemble of a large number of surface palladium atoms. The formation probability of such an ensemble increases as the nanoparticle size increases, and the initial TOR value enhances accordingly. Clearly, the nanoparticle size affects the nature and strength of the interaction of 4-CP with the Pd surface since the size determines the number of particles surrounding each surface metal atom. Moreover, the coordination of the surface atoms depends on the particle size. Smaller particles contain more surface atoms on the edges of the crystallographic planes or on the edge junctions, increasing the number of active sites that are accessible to the 4-CP molecules. These factors together show that an optimal particle size is required for the HDC reaction and the particles must possess a sufficient ensemble to adsorb and activate 4-CP. Metal particles with a large particle size and high coordination number will have a low reactivity. For particles larger than 10 nm, Pd₃P_{0.95}/SiO₂ exhibits a slightly lower activity than the Pd/SiO₂ catalyst. Here, geometric or ensemble effects arise due to the dilution of the surface of the active metal (Pd) by an inactive one (P).

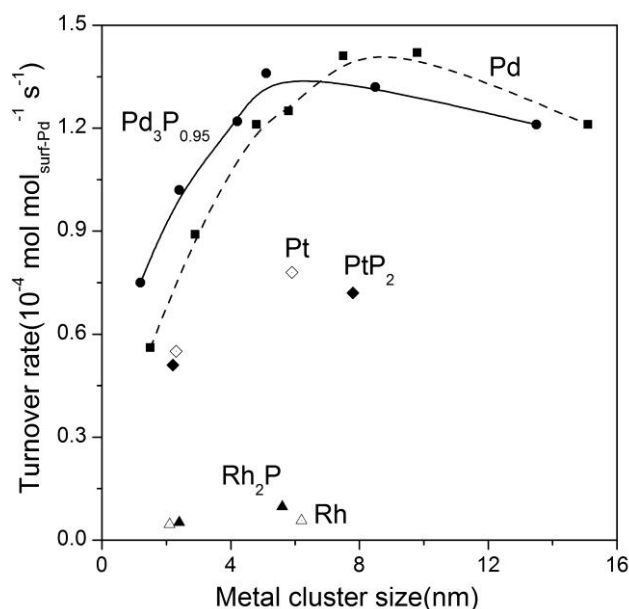


Figure 1. Effect of the metal and phosphide catalyst cluster size on the initial TOR value for the 4-CP HDC reaction (298 K, 3.1 mmol L⁻¹ 4-CP).

4. Conclusions

Pd₃P_{0.95}/SiO₂, Rh₂P/SiO₂ and PtP₂/SiO₂ catalysts were prepared via a temperature-programmed reduction and were utilized for aqueous-phase HDC of 4-CP under mild reaction conditions (298 K). Pd₃P_{0.95}/SiO₂ was shown to be the most active phosphide catalyst. The introduction of P into the metallic lattice of the Pd/SiO₂ catalysts changes the valence of the Pd atoms. The surface interactions between Pd and P species promote the adsorption of 4-CP but inhibit the sorption of Cl ions after the HDC reaction. The HDC of 4-CP over Pd₃P_{0.95}/SiO₂ catalysts is a structure-sensitive reaction and the electronic and ensemble effects of the palladium phosphide particles determine the initial TOR. Pd₃P_{0.95}/SiO₂ catalysts can be the basis for highly active and highly stable catalysts for groundwater treatment applications.

Acknowledgements

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References

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