



Studies of the synthesis of transition metal phosphides and their activity in the hydrodeoxygenation of a biofuel model compound

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ABSTRACT

A series of silica-supported metal phosphides was prepared by two methods involving the reduction of phosphite (I) or phosphate (A) precursors and was studied for the hydrodeoxygenation (HDO) of 2-methyltetrahydrofuran (2-MTHF). The I method required lower temperature than the A method and resulted in catalysts with higher surface area. The activity was evaluated in a packed-bed reactor on the basis of equal CO chemisorption sites (30 μmol) loaded in the reactor with comparison made to a commercial Pd/Al₂O₃ catalyst. At 300 °C and 1 atm, the order of activity was Ni₂P > WP > MoP > CoP > FeP > Pd/Al₂O₃. The principal HDO products for the iron group phosphides (Ni₂P and CoP) were pentane and butane, whereas for the group 6 metal phosphides (MoP and WP), the products were mostly pentenes and pentadienes. For the Pd/Al₂O₃ and the low-activity FeP/SiO₂ catalyst the products were mostly pentenes and C4 mixtures. There were no significant differences in the turnover frequency between materials prepared by the two methods, except possibly for the case of WP. There were likewise no great changes in selectivity toward HDO products at 5% total conversion, except for WP. The differences in the case of WP were attributed to the surface P/W ratio that X-ray photoelectron spectroscopy (XPS) showed to be twice as large for the I method than the A method. Contact-time studies were used to develop reaction networks for the most active catalysts, Ni₂P/SiO₂ and WP/SiO₂. For Ni₂P/SiO₂ by both methods, the selectivity profiles were similar and could be explained by a rake mechanism with pentenes as primary products, 2-pentanone as a secondary product, and pentane as a final product. In contrast, for WP/SiO₂, the selectivity depended greatly on the preparation method, but produced a preponderance of unsaturated compounds. The results could be explained from the surface composition.

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1. Introduction

The need to meet stringent environmental regulations and the depletion of fossil fuel reserves have led to interest in biomass as a renewable energy source. The utilization of biomass-derived fuels has several advantages over the use of conventional fuels, such as reduction in greenhouse gas emissions, localized production, and favorable economics of utilization [1–4]. One method of biomass conversion is pyrolysis – a thermal decomposition of biomass in the absence of oxygen that yields an energy-rich liquid mixture of oxygenated aromatic and aliphatic compounds called bio-oil [5,6]. Bio-oil, however, has a high oxygen content

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(35–50 wt.%) with 15–30 wt.% of water that results in low heating value, immiscibility with hydrocarbon fuels, high acidity, and chemical and thermal instability compared with hydrocarbon fuels [7,8]. To upgrade the bio-oil into a usable fuel, it is necessary to remove the oxygen [9]. A first objective of this work is to study the deoxygenation of a model compound, 2-methyltetrahydrofuran. This is a five-atom saturated ring compound and was chosen as a model substrate because previous work has shown that ring compounds are difficult to deoxygenate [10]. Furans are also common products in the thermal degradation of biomass, such as by pyrolysis [11]. The presence of the methyl group allows distinguishing between the ring-opening products and hence gives mechanistic information.

Standard catalysts for the elimination of S and N heteroatoms from petroleum feedstocks are sulfided CoMo and NiMo; these may also be used for the removal of O, for example, from phenols and furans in biomass-derived liquids [12–14], however, the

results have been modest, and it is clear that new catalysts are needed. Among new compositions that have been explored in hydrotreating processes, phosphides of transition metals are considered potential substitutes for the CoMo and NiMo sulfided materials [15–17]. In the past decade, a plethora of work has shown that MoP [18,19], WP [19,20], CoP [21,22], Fe₂P [21], and Ni₂P [21,23–25] are highly active for hydrodesulfurization and hydrodenitrogenation of petroleum feedstocks. Recently, their good hydrogen transfer properties have been applied to the hydrodeoxygenation (HDO) of biomass-derived feedstocks [26–28].

The most common method for the preparation of phosphides is temperature-programmed reduction (TPR), a simple process that can be carried out at relatively moderate temperatures with supported or unsupported precursors [15]. With regard to the use of supports, previous research has shown that less acidic supports such as silica or hexagonal mesoporous silica (SBA-15 [29] and MCM-41 [25]) favor the formation of metal phosphides due to the low interaction between the support and the precursor, usually a metal phosphate. Recently, precursors other than phosphates have also been investigated, for example, phosphosulfides [30], which were first studied in initial work on phosphides [31]. A substantial recent development is the use of metal phosphites/hypophosphites (e.g., H₂PO₃⁻ or H₂PO₂⁻) instead of phosphates (e.g., HPO₄²⁻) as precursors [25,32,33]. The former have phosphorous in a lower oxidation state, which makes them potentially reducible at a lower temperature; for example, using a batch reduction method, an active Ni₂P was formed at 300 °C compared to 450 °C using the traditional phosphate method [23,25,32,33].

A second objective of this work besides studying the HDO reaction is to compare the traditional phosphate method and the new phosphite method for the preparation of a variety of transition metals. This has not been done before, and so, no variations in synthesis method were attempted. For this purpose, five pairs of metal phosphides (Ni₂P, CoP, FeP, MoP, and WP) supported on silica were chosen. Their activity for HDO of the model compound 2-methyltetrahydrofuran was evaluated and compared. Furthermore, for the most active phosphide compounds, a study of reaction pathway was carried out.

2. Experimental

2.1. Materials and catalysts

The transition metal phosphides Ni₂P, CoP, WP, MoP, and FeP supported on a high surface area fumed silica support (Cab-osil[®] EH5) provided by Cabot Corp. were synthesized. The sources of the chemicals were Aldrich and Alfa Aesar and details on purities are given in [Supplementary information file](#). The 5% Pd/Al₂O₃ commercial catalyst was provided by BASF Catalysts, Inc. The model compound used in the reactivity study was 2-methyltetrahydrofuran (Aldrich 99.95%). The gases employed were H₂ (Airgas, Grade 5), He (Airgas, Grade 5), CO (Linde Research Grade, 99.97%), 0.5% O₂/He (Airgas, UHP Grade), O₂ (Airgas, UHP Grade), and N₂ (Airgas, Grade 5).

The synthesis of the supported phosphide catalysts was carried out by a standard phosphate method and a more recently developed phosphite method. A silica support (Cab-osil[®] EH5) of surface area of 334 m² g⁻¹ and pore volume of 0.6 cm³ g⁻¹ was employed in both methods. The support was dried at 120 °C for 6 h and calcined at 500 °C for 4 h prior to use. Both synthetic routes required the preparation of a precursor in three steps. First, a mixed solution of metal and phosphorus compounds was made by adding an appropriate amount of a desired metal salt into a phosphorous solution; the phosphorous solution was made by mixing ammonium phosphate (phosphate method) or phosphorous acid (phosphite method) into distilled water. Second, the mixed solution was used to impregnate the silica support to the incipient wetness point (about 2 cm³ of solution per gram of support). Finally, the obtained phosphate precursor mixture was dried at 120 °C for 6 h and calcined at 500 °C for 6 h; whereas, the phosphite precursor mixture was only dried in air at 80 °C overnight without any calcination. Then, all samples were pelletized and sieved to 16/20 mesh size. In the same manner, the precursors from both methods were reduced to phosphides by a temperature-programmed reduction (TPR) at a heating rate of 2 °C min⁻¹ in flowing H₂ [1000 cm³ (NTP) min⁻¹ g⁻¹] and kept at the reduction temperature for 2 h. The reduction temperatures were determined in separate temperature reduction experiments as the temperature at which water production peaked (details are described in the characterization section). The resulting phosphides were cooled to room temperature in He [100 cm³ (NTP) min⁻¹], followed by passivation in a He stream containing 0.5% O₂ for 2 h.

[Table 1](#) summarizes the loadings of metal and phosphorous used in the preparation of the catalysts. For all metals Fe, Co, Ni, Mo, and W, equal moles of the element per gram of support (1.16 mmol/g support) were used.

The synthesis of the materials was carried out by temperature-programmed reduction (TPR) and monitored by mass spectrometry. The samples were characterized with carbon monoxide (CO) chemisorption, Brunauer Emmett Teller (BET) surface area measurements, X-ray diffraction (XRD), and X-ray photoelectron spectroscopy (XPS). Details of the TPR and BET measurements are given in [Supplementary information file](#).

Irreversible CO uptake measurements were used to titrate the surface metal atoms and to estimate the number of active sites on the catalysts. Uptakes were obtained after 0.3 g of passivated samples were re-reduced in H₂ at 450 °C for 2 h and cooled to room temperature in He. Pulses of known amounts of CO carried by He at 30 μmol s⁻¹ were injected into the sample. An on-line mass spectrometer monitored the signal of mass 28 (CO) throughout the experiment. CO uptake was calculated from the decrease in peak areas caused by adsorption of CO onto the catalysts surface. Measurements from CO chemisorption allowed estimation of the dispersion of metal sites using the following equation:

$$\text{Dispersion (\%)} = \frac{\text{CO uptake} \left(\frac{\mu\text{mol}}{\text{g}} \right)}{\text{Loading} \left(\frac{1.16 \mu\text{mol}}{\text{g}} \right)} 100\%$$

Table 1
Materials and amounts used in the preparation of phosphides supported on silica.

Sample	Conventional (phosphate) method (A)		New (phosphite) method (I)				
	Metal source (mmol/g support)	Phosphorous (NH ₄) ₂ HPO ₄ (mmol/g support)	Metal (mmol/g support)	Phosphorous H ₃ PO ₃ (mmol/g support)	Metal phosphide (wt.%)		
Ni ₂ P	Ni(NO ₃) ₂ ·6H ₂ O	1.16	2.312	Ni(OH) ₂	1.16	2.312	7.9
CoP	Co(NO ₃) ₂ ·6H ₂ O	1.16	2.312	Co(OH) ₂	1.16	2.312	9.4
WP	(NH ₄) ₆ W ₁₂ O ₃₉ ·H ₂ O	1.16	1.156	(NH ₄) ₆ W ₁₂ O ₃₉ ·H ₂ O	1.16	2.312	19.9
MoP	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	1.16	1.156	(NH ₄) ₆ Mo ₇ O ₂₄ ·4H ₂ O	1.16	2.312	12.8
FeP	Fe(NO ₃) ₃ ·9H ₂ O	1.16	2.312	Fe(NO ₃) ₃ ·9H ₂ O	1.16	2.312	9.1

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