

Effect of citric acid on the synthesis of tungsten phosphide hydrotreating catalysts

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Introduction

Hydrotreating is an important process in crude oil refining that ensures the production of clean fuels by the removal of various contaminants (sulfur, nitrogen and oxygen-containing compounds as well as reduction of aromatics) commonly found in various oil fractions. Recent studies have shown that transition metal phosphides can effectively function as hydrotreating catalysts [1-5]. High temperatures that are needed in the reduction stage of the synthesis of this class of catalysts result in the catalysts having low dispersions. Two suggested approaches used to address this problem are: the use of phosphine (PH_3) in the synthesis at moderate temperatures and the synthesis of unsupported catalysts with high surface area [6, 7]. This study examines the use of citric acid as a chelating agent in the synthesis of bulk tungsten phosphide (WP) catalysts.

Materials and Methods

Four samples of WP were prepared via the reduction method with varying amounts of citric acid. The samples were calcined in air at 500°C and subsequently reduced in flowing hydrogen at 650°C . The surface area and pore volume were determined by nitrogen physisorption (Tristar, Micromeritics), while the carbon monoxide (CO) uptake was determined by pulse titration (CHEMBET-3000, Quantachrome). Temperature programmed reduction (TPR) profiles were obtained by reducing a calcined sample (< 0.2 g) in a flow of 5% hydrogen in helium and heating at $2^\circ\text{C}/\text{min}$ to 1000°C . The prepared samples were also analyzed with X-ray diffraction (XRD, Rigaku Multiflex) to determine the phases present, and scanning electron microscope (SEM, Philips XL30) to determine the sample morphology. Reactivity measurements were performed on a high pressure kinetics apparatus at 1.72 MPa, 320°C , and a WHSV of 1 h^{-1} with pyridine (20 vol%) in n-heptane and hydrogen. The exit stream from the reactor was analyzed with a gas chromatograph/mass spectrometer (6890N, Agilent).

Results and Discussion

The characterization of the catalysts (Table 1) indicates that the pore volume, surface area and CO uptake all increased with the addition of citric acid during the preparation of WP. The SEM images (Figure 1) show that the addition of citric acid resulted in the formation of micro-sized WP particles. The TPR profiles of the catalysts have only one peak which corresponds to WP (Figure 2) while the XRD patterns of the catalysts (not shown) are all identical, regardless of the amount of citric acid present during preparation. The pyridine conversions obtained over WP_1 and WP-4 are shown in Figure 3. Consistent with the characterization results, the catalyst prepared with citric acid was more active.

Only physical changes resulted from the use of citric acid and no new chemical phases were formed. Citric acid is acting as a template to reduce the aggregation of WP particles during formation. The presence of citric acid resulted in a change in the viscosity of the solution during drying but more investigation is needed to determine if the viscosity change, surface tension change, electrostatic forces or a combination of these effects is responsible for the decrease in particle size.

Table 1. Characterization results for WP catalysts.

Catalyst	WP: Citric Acid Molar Ratio	Surface Area (BET) m^2/g	CO Uptake ($\mu\text{mole}/\text{g}$)	Pore Volume (cm^3/g)
WP_1	1:0	2.5	3.25	0.01
WP_2	1:1.5	7.8	10.6	0.03
WP_3	1:2	8.4	12.4	0.03
WP_4	1:4	19	13.1	0.1

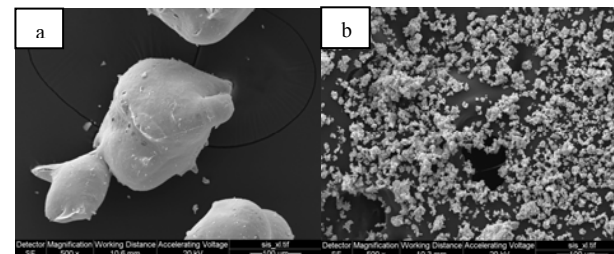


Figure 1. SEM images for catalysts: a. WP_1, and b. WP_4.

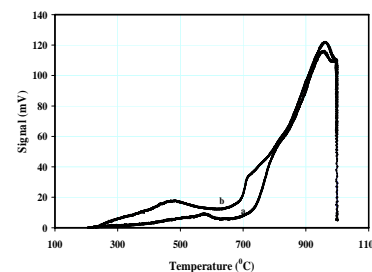


Figure 2. TPR of WP_1 (a) and WP_4 (b).

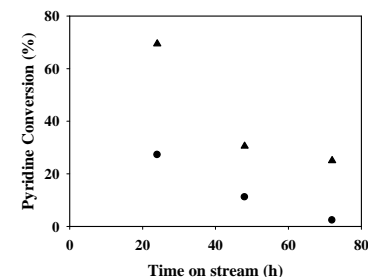


Figure 3. Reactivity of WP catalysts prepared without citric acid (●, WP_1) and with citric acid (▲, WP_4).

Significance

This work demonstrates that citric acid acts as a chelating agent in the synthesis of bulk WP and results in smaller particles with higher surface area, pore volume and activity.

References

- Oyama, S.T., *J.Catal.* **216** 343 (2003)
- Shu, Y., Oyama, S.T., *Carbon* **43** 1515 (2005)
- Wang, X., Clark, P., Oyama, S.T. *J.Catal.* **208** 321 (2002)
- Stinner, C., R. Prins, Weber T., *J.Catal.*, **191** (2) 438 (2000)
- Stinner, C., Prins, R.; Weber, T. *J.Catal.* **202**(1)187 (2001)
- Yang, S., Liang, C., Prins, R. *J.Catal.* **241** 465 (2006)
- Genuit, D., Afanasiev, P., Vrinat, M.; *J.Catal.* **235** 302 (2005)