

## Heteropolytungstate nickel salts : new starting materials for the preparation of hydrocracking catalysts

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### Introduction

The worldwide demand of fuels is expected to continue growing in the next decade. To satisfy these requirements and to respect more stringent regulations, the petroleum industry has to face the challenge of upgrading the heavier cuts into valuable products like diesel. Purposely, conversion processes, such as hydrocracking (HCK), will require a continuous improvement of the catalytic materials.

The active phase of the HCK industrial catalysts consists of well-dispersed WS<sub>2</sub> nanocrystallites decorated with Ni atoms. These active phases are obtained through the sulphidation of an oxide precursor prepared by incipient wetness impregnation of ASA with an aqueous solution containing the elements to be deposited. This work focuses on the interest of new starting materials for the preparation of the impregnating solutions, instead of ammonium metatungstate and nickel nitrate salts. Purposely, the use of nickel salts of heteropolytungstate, with Keggin or the derived lacunary based structures, as starting materials for the oxide precursors preparation, has been investigated. Various heteropolyanion (HPA) were prepared and impregnated on ASA support to provide a set of catalysts, whose Ni/W ratio were varying. Hydrogenation activity of HPA based catalysts was compared to conventional preparation. Catalytic performances are correlated to the nature and the morphology of the active phase as deduced from the study of the sulfidation by XPS (X-Ray photoelectron spectroscopy), TEM (Transmission Electron Microscopy) and EPR (Electron Paramagnetic Resonance) characterization techniques.

### Description of the new starting materials based catalysts

The preparation of the Keggin type HPA nickel salts has been described elsewhere<sup>1</sup>. The nickel salts of the Keggin HPA PW<sub>12</sub>O<sub>40</sub><sup>3-</sup> and SiW<sub>12</sub>O<sub>40</sub><sup>4-</sup> and of the derived lacunary (obtained by removing one WO<sub>6</sub> octahedron) HPA PW<sub>11</sub>O<sub>39</sub><sup>7-</sup> and SiW<sub>11</sub>O<sub>39</sub><sup>8-</sup>, were obtained in solution allowing to prepare directly impregnating solutions. The catalysts were then prepared with these solutions by incipient wetness impregnation of ASA support (SSA m<sup>2</sup>/g, V<sub>p</sub> = 0.7 cm<sup>3</sup>/g). Reference NiW solids having the same metal loadings were also prepared for comparison purposes by using the conventional impregnating solutions of ammonium metatungstate (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub> and nickel nitrate (Ni(NO<sub>3</sub>)<sub>2</sub>). The solids were dried overnight at 100°C and then calcined at 500°C under oxygen. Sulphidation (2°C.min<sup>-1</sup> followed by 2 h at 350°C), was performed in toluene hydrogenation test using dimethyldisulfide, as sulfiding agent. Table 1 lists the different nickel salts, the corresponding Ni/W ratio, nomenclature of new material based and reference catalysts. The quantity of WO<sub>3</sub> loading was chosen at 12 wt. % because it is the maximum of catalyst loading with the lowest soluble HPA nickel salt.

Table 1: Description of the catalysts

Catalysts nomenclature	Precursor	Ni/W	WO <sub>3</sub> loading (wt %)
A	Ni <sub>3/2</sub> PW <sub>12</sub> O <sub>40</sub>	0.13	12
B	Ni <sub>2</sub> SiW <sub>12</sub> O <sub>40</sub>	0.17	12
C	Ni <sub>3</sub> PW <sub>11</sub> NiO <sub>40</sub> H	0.36	12
D	Ni <sub>4</sub> SiW <sub>11</sub> O <sub>39</sub>	0.36	12
RefA	(NH <sub>4</sub> ) <sub>6</sub> H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> + Ni(NO <sub>3</sub> ) <sub>2</sub>	0.13	12
RefB	(NH <sub>4</sub> ) <sub>6</sub> H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> + Ni(NO <sub>3</sub> ) <sub>2</sub>	0.17	12
RefC/D	(NH <sub>4</sub> ) <sub>6</sub> H <sub>2</sub> W <sub>12</sub> O <sub>40</sub> + Ni(NO <sub>3</sub> ) <sub>2</sub>	0.36	12

### Results and discussion

Toluene hydrogenation test was performed on catalysts described in Table 1. Results are reported in Figure 1 and demonstrate that A, B and C catalysts were more or less equivalent to the reference catalysts. The use of new HPA (Ni<sub>3/2</sub>PW<sub>12</sub>O<sub>40</sub>, Ni<sub>2</sub>SiW<sub>12</sub>O<sub>40</sub>, Ni<sub>3</sub>PW<sub>11</sub>NiO<sub>40</sub>H) seemed not to impact the hydrogenation activity. Nevertheless, D catalyst prepared with Ni<sub>4</sub>SiW<sub>11</sub>O<sub>39</sub> appeared as more hydrogenating (HYD activity ~ 0,77 mmol/cm<sup>3</sup><sub>catal</sub>/h) than its reference catalyst (Ref C/D, HYD ~ 0,68 mmol/cm<sup>3</sup><sub>catal</sub>/h).

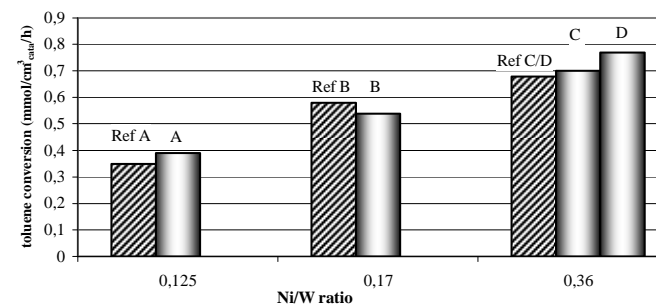


Figure 1. Hydrogenation activity of catalysts prepared with conventional impregnating solutions (hatched) and HPA nickel salts (bicolore).

The study of the sulphided phase of these various solids indicates an inhomogeneous distribution of the WS<sub>2</sub> phase already observed on ASA support<sup>2</sup>, however, the dispersion of the WS<sub>2</sub> crystallites (evaluated from TEM pictures) does not explain the catalytic results. Moreover, XPS analysis reveals that the better performances seems to be correlated with a better sulphidation rate and EPR confirms the formation of reduced W<sup>5+</sup> species during sulphidation.

### References

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