

Characterization and catalytic activities of supported NiW catalysts

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Introduction

Due to a number of structural trends in the refining industries, such as the shift towards an increased demand for middle-distillate products (i.e. kerosene and gas oil) relative to gasoline, the hydrocracking of crude oil fractions is gaining in importance and is applied in refineries all over the world [1]. Hydrocracking catalysts are bifunctional, combining a hydro-dehydrogenating function with an acidic one. The presence of sulfur- and nitrogen- containing molecules in the feeds to be treated imposes the use of mixed sulfide metals serving as the hydro-dehydrogenating function [2]. Supported NiW sulfide catalysts have excellent hydrogenation properties, this make them particularly interesting when a high hydrogenation potential is needed. Furthermore, in order to avoid cracking reactions which would yield gasoline instead of gas oil, the acidic function of the support should be moderated. Amorphous silica-alumina could have such an acid strength. Consequently, a sulfided NiW/silica-alumina catalyst was chosen in this study [2]. Improvement of this catalyst requires a better understanding of its structure. Thus, using the X-ray photoelectron spectroscopy (XPS) technique, we determine and quantify each chemical Ni and W surface species [3, 4]. Moreover, the support effect on the formation of the NiW mixed sites and on the catalytic activities was studied; for this purpose, silica and alumina supported NiW were synthesized. The distribution of surface species determined by XPS was correlated to the high-transmission resolution electron microscopy (HTREM) results and to the catalytic activities in the toluene hydrogenation (HYD) reaction in the presence of aniline.

Materials and Methods

Catalysts were prepared by co-impregnation of industrial supports (extrudates) with $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and $(\text{NH}_4)_6\text{W}_{12}\text{O}_{39} \cdot \text{H}_2\text{O}$ ($\text{Ni}/\text{W} = 0.4$). The impregnated extrudates were then dried, calcined and finally sulfided with H_2S . For XPS analyses, the samples were crushed and compacted on an indium foil in a glove box. The XPS spectra were recorded on a KRATOS AXIS ULTRA instrument with an Al monochromator source (1486.6 eV). Peak shifts were corrected by taking C1s contamination peak as a reference (284.6 eV) and the curves were integrated by applying a Shirley-type baseline. For HTREM analyses, performed on a JEOL 2010 microscope, the extrudates were crushed and dispersed in pure ethanol. Then a drop of homogenized suspension was deposited on a carbon-coated Cu grid and the solvent was evaporated (infrared light). Toluene HYD measurements were carried out in a fixed bed high-pressure (60 bar, 623K) flow microreactor in the presence of cyclohexane as a solvent, aniline as an inhibitor of the acidic function and dimethyldisulfide as an in situ sulfuration agent.

Results and Discussion

The XPS analyses carried out on the different promoted NiW catalysts revealed that the Ni atoms are not only incorporated in the NiWS mixed phase. More precisely, according to primary XPS studies realized on reference catalysts, three Ni surface species were detected: Ni oxide, Ni sulfide and mixed nickel tungsten phase (NiWS). The latter being considered as the

most active surface species and thus responsible for catalytic activities. The XPS spectra decomposition of the NiW-based HYD catalysts allowed the quantification of the various surface entities. Thus, higher promotion rates ($\text{NiWS}/\text{Ni}_{\text{tot}}$) were obtained on both NiW/silica-alumina and NiW/silica by comparison to NiW/alumina. This result is in good agreement with the HYD catalytic activities. HTREM analysis revealed that highly stacked slabs were obtained on silica (average stacking = 3.2) which is probably due to low "NiWS-silica" interactions. Additionally, similar slabs stacking were obtained on silica-alumina and alumina (average stacking = 2.5) according to HTREM analyses. Therefore, the slabs stacking cannot account for the better catalytic activities obtained when silica is present in the carrier. However, the catalytic activity enhancement can be attributed to weak "active phase-carrier" interactions, i.e. to less "W-O-Al anchoring points" due to the presence of silica sites. Indeed, in good agreement with this assumption, the XPS results revealed that higher amounts of sulfided WS_2 were obtained on both silica and silica-alumina. According to the literature, this result can be considered as a direct proof for the lower "W sites-carrier" interactions. Therefore, the higher sulfidation degree observed on both silica and silica-alumina generates more sites allocated to promotion leading to higher amounts of NiWS mixed phase and consequently inducing the better HYD activities obtained on NiW/silica-alumina and NiW/silica. The following figure shows us the direct correlation between the promotion rates ($\text{NiWS}/\text{Ni}_{\text{tot}}$) and the number of converted toluene molecules per atom of tungsten.

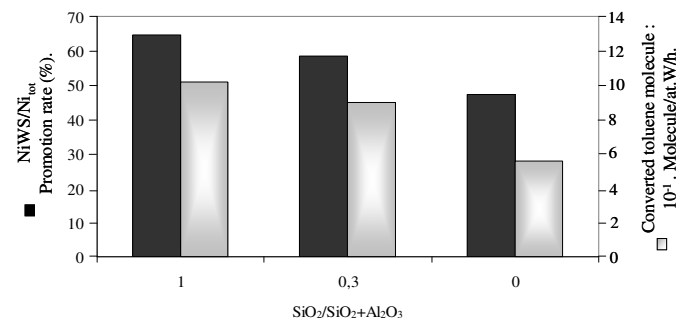


Figure 1. Promotion rates ($\text{NiWS}/\text{Ni}_{\text{tot}}$) and toluene HYD activity.

Significance

X-ray photoelectron spectroscopy showed that the toluene HYD activity is a direct probe of the promotion rates ($\text{NiWS}/\text{Ni}_{\text{tot}}$) of the NiW supported catalysts.

References

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