



Support effects of NiW catalysts for highly selective sulfur removal from light hydrocarbons



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ABSTRACT

The intrinsic support effect was explored in the preparation of NiW hydrodesulfurization catalysts through building correlations of catalytic performance to extensive surface characterization results. We found that the catalytic activity on the hydrodesulfurization of 3-methyl-thiophene correlates well with the normalized intensities data of NO adsorbed on Ni active sites. Also, a correlation between the catalytic activity and the number of tungsten edge atoms in the WS₂ slabs was observed. The characterization of the NiW catalysts revealed that is possible to modulate the metal-support interaction by substituting the carrier. This specific interaction with each support derived into particular morphological parameters for the sulfide active phase. Optimal values for the slab length and the stacking of the WS₂ slabs were proposed.

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1. Introduction

More stringent environmental regulations have been implemented to reduce the sulfur content of gasoline and diesel fuels to ever lower levels. In Europe and the USA, sulfur content limits of about 10–50 ppm in gasoline and diesel are thus required. Furthermore, these sulfur levels are expected to be lowered to 10 ppm or less, and the “zero sulfur” emissions are targeted shortly [1]. Moreover, the sulfur must be removed selectively from aromatic thiophene and its derivatives from gasoline, keeping at a minimum the olefins hydrogenation (HYD) [2]. It has to be considered that the fluid catalytic cracking (FCC) naphtha stream at the refinery is usually used for the production of clean gasoline. This stream contains undesired organic sulfur compounds and is rich in olefins. Therefore, a careful removal of the sulfur-containing compounds without olefin saturation is highly needed. In that sense, we recently reported enhanced catalytic activity and excellent selectivity with the use of supported NiW catalysts. These catalysts supported on Al₂O₃-Ga₂O₃ binary mixed oxides showed that the 3-methyl thiophene (3MT) hydrodesulfurization (HDS) reaction

preferentially occurred by the direct desulfurization pathway [3]. Likewise, a linear increment of the hydrogenation pathway was observed with the increase of Ga₂O₃ wt.% in the support composition. Therefore, we confirmed that the catalytic activity of HDS catalysts might increase by changing the nature of the support [4]. Additionally, clear differences in the formation of the sulfide active phases, morphology, dispersion and sulfiding capacity have been discussed in a wide number of reports as a function of the chosen support [5–9]. Some carriers may impart four to five folds higher activities in typical CoMo and NiMo HDS catalysts as compared with Al₂O₃. However, the vast majority of research on HDS materials have been done concerning the CoMo and NiMo systems, and that acquired knowledge has been extended to the NiW system by similarity. Furthermore, direct information for the NiW system is scarcely found despite the fact that NiW catalysts have shown different sulfidation and catalytic activity [10]. Also, some early studies indicate that the NiW base catalysts could perform high HDS while promoting olefin skeletal isomerization [11,12]. This property of the NiW case catalysts helps to increase the octane number again and compensate the olefin saturation.

In the light of previous findings, we have focused the present work on elucidating the support effects for the NiW based catalysts. Hence, NiW catalysts supported on Al₂O₃, TiO₂, ZrO₂, and SiO₂ as well as on Al₂O₃-TiO₂ and ZrO₂-TiO₂ mixed oxides were

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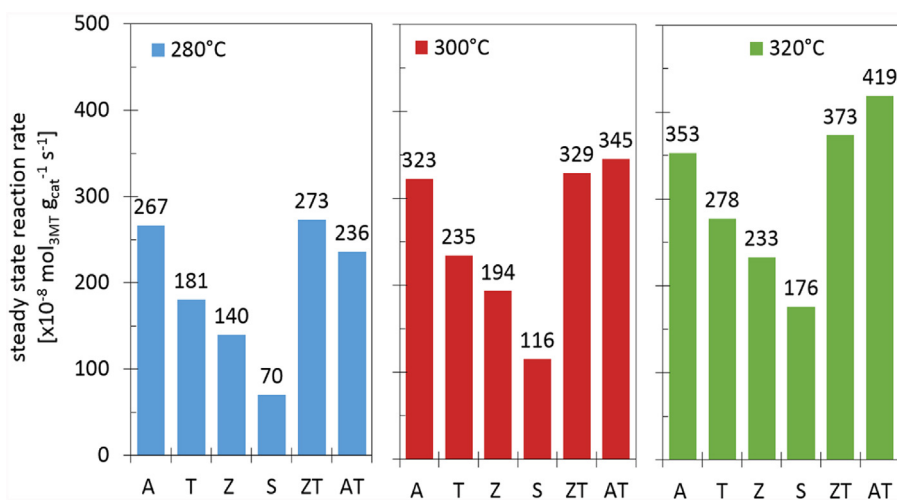


Fig. 1. Steady state catalytic activities for NiW-x catalysts in the HDS of 3MT.

prepared and widely characterized. The physicochemical properties of the supports and catalysts were explored by a variety of techniques (N_2 physisorption, XRD, TPD- NH_3 , FT-IR of NO adsorbed and HRTEM). All materials were tested on atmospheric 3-methylthiophene (3MT) HDS as olefin model molecule.

2. Experimental section

2.1. Supports preparation

Pure γ - Al_2O_3 (A), SiO_2 (S), TiO_2 (T), ZrO_2 (Z) and mixed Al_2O_3 - TiO_2 (AT) and ZrO_2 - TiO_2 (ZT) supports were synthesized by sol-gel method. The sol-gel method was as follows: 10 mL of metal oxide precursor (full list of precursors are given as Supplementary information A1) were dissolved in 166 mL of 2-propanol (Aldrich 98%) under continuous stirring for 2 h at 0 °C. Subsequently, the hydrolysis solution (a mixture of 11.5 mL H_2O and 0.57 mL HNO_3 70%) was added dropwise to the previous solution. The sol was left at 0 °C for 24 h to form the gel and then it was put into a crystallizer at 70 °C for 48 h to eliminate the solvent. The obtained solids were calcined at 500 °C for 4 h with a heating rate of 1 °C min^{-1} . The AT mixed oxide was prepared with an atomic ratio (Al/Ti) = 2 [13], for the ZT material the atomic ratio (Zr/Ti) was fixed at 1 [14]. In the case of the SiO_2 (S) material, 1 g of P123 (MW 5800, Aldrich) was dispersed in an HCl solution (0.1 g, 2 M) and H_2O (0.9 g) in EtOH (10 g). After 2 h of stirring, TEOS (2.08 g, 10 mMol) was added. The solution was aged for 24 h and then dried at 120 °C. Finally, the white solid was calcined at 500 °C for 4 h with a heating rate of 1 °C min^{-1} .

2.2. Catalysts preparation

In a typical preparation of NiW/(x) catalyst (where x is any of the supports), a solution of $(NH_4)_6W_{12}O_{39} \cdot xH_2O$ (AMT, Aldrich Chemical, 99.99%) was first impregnated on the support. Later, it was left for maceration for 12 h and then dried under an air stream at 125 °C for 12 h, with a heating rate of 3 °C min^{-1} . Finally, Ni was impregnated under the same conditions, and the green final solid was dried in the same terms. The concentration of AMT solution was selected to obtain 2.8 W atoms nm^{-2} (pH \approx 3.7) while nickel was adjusted to define a nominal atomic ratio $r = (Ni/(Ni+W))$ equal to 0.41 (pH \approx 4). After calcination at 450 °C, all materials were sieved between 80 and 100 mesh (0.15–0.18 mm). Similar impregnation procedures were used to compare materials with very different surface areas [15,16].

2.3. Characterization methods

2.3.1. N_2 adsorption-desorption isotherms

The textural properties of the materials were determined by N_2 adsorption-desorption isotherms at -196 °C on a TriStar II 2020 Micromeritics equipment. Before the experiments, the materials were degassed at 125 °C in vacuum for 5 h. The volume of the adsorbed N_2 was normalized to the standard temperature and pressure. Specific surface areas (S_{BET}) were calculated by the Brunauer-Emmet-Teller (BET) equation, considering the range of relative pressures $0.1 < P/P_0 < 0.3$. The average pore diameter (P_d) was calculated by applying the Barret-Joyner-Halenda method (BJH) to the adsorption branches of the N_2 isotherms. The total pore volume (P_v) was obtained from the saturation point ($P/P_0 \sim 0.99$).

2.3.2. X-ray diffraction

X-ray diffraction (XRD) measurements of the samples were performed in a Philips spectrometer model X'pert using the CuK_{α} 1 radiation (40 kV, 30 mA) with a wavelength of 0.154 nm.

2.3.3. Temperature programmed desorption of ammonia (TPD- NH_3)

The acidities for the oxide precursors were determined by TPD- NH_3 measurements carried out with an AMI 90 TPR/TPD instrument with a thermal conductivity detector (TCD) and interfaced to a data station. The catalysts (50 mg) were placed inside a 4 mm ID U-shaped quartz tube. Before ammonia adsorption, the catalysts were heated at a rate of 10 °C min^{-1} to a final temperature of 200 °C and kept for 0.5 h at this temperature under a He flow to remove water and other contaminants. Then the samples were cooled down to 100 °C, and the surface was ammonia-saturated on a stream of 50 mL min^{-1} of 5 mol% ammonia in He during 1 h. After catalysts equilibration in He flow at 100 °C for 15 min, ammonia was desorbed using a linear heating rate of 10 °C min^{-1} to 900 °C.

2.3.4. Fourier transform infrared spectroscopy (FT-IR) of adsorbed NO on the sulfided catalysts

Fourier transform infrared spectroscopy (FT-IR) of adsorbed NO on the sulfided catalysts was recorded on an Agilent 660 FTIR spectrophotometer at a resolution of 4 cm^{-1} with a specially designed Praying Mantis diffuse reflection attachment and low-temperature cell (Harrick) for in situ measurements. The samples were out-gassed at 350 °C for 2 h and cooled down to 25 °C before contact with ca. 20 mbar of nitrogen monoxide for 5 min, after which the spectrum was recorded. Then the samples were degassed under

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