



A novel catalyst of Ni,W-surface-Ti-rich-ETS-10/Al₂O₃: Its role and potential of HDS performance for steric hindered sulfur compound 4,6-DMDBT



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ABSTRACT

There is growing interest in developing deep hydrodesulfurization (HDS) catalysts to obtain higher activity. This study provides an investigation of influence of surface-Ti-rich-ETS-10 (AT-ETS) on the performance of NiW-based catalyst (NiW-AT-ETS/Al₂O₃) using NiW-ETS-origin/Al₂O₃ as the reference. The HDS performance of dibenzothiophene (DBT) and 4,6-dimethyldibenzothiophene (4,6-DMDBT) as model sulfur compounds were tested in fixed reactor. NiW-AT-ETS/Al₂O₃ containing surface-Ti-rich-ETS-10 lowered H₂ reduction temperature compared to NiW-ETS-origin/Al₂O₃. NiW-AT-ETS/Al₂O₃ had higher WS₂ stacking numbers and shorter slab length though they showed similar sulfidation degree. Higher HDS performance was obtained over NiW-AT-ETS/Al₂O₃ due to higher WS₂ slab layers in contrast to NiW-ETS-origin/Al₂O₃. The advantage of NiW-AT-ETS/Al₂O₃ for 4,6-DMDBT removal may be also related to easy accessibility of active sites on the catalyst surface as a result of the higher dispersion compared to NiW-ETS-origin/Al₂O₃.

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1. Introduction

Large quantities of SO_x gas emission are generated from automobile exhaust. The discharge of SO_x gas emission could cause serious environmental pollution and human health problems. An efficient deep HDS process is needed to meet the increasingly stringent discharge standards in oil refining industry. Sulfur compounds removal, such as DBT and 4,6-DMDBT, are believed to be the hardest because the tremendous steric hindrance can restrain the accessibility of these compounds to the active sites of most HDS catalysts. Topsøe and co-workers have proposed the catalytic active site Co(Ni)Mo(W)S phase for industrial HDS catalysts Co(Ni)Mo(W)S/Al₂O₃, where Co(Ni) atoms as promoters are located on the edges of the Mo(W)S₂ particles [1–3]. There are two types of Co(Ni)Mo(W)S phases: type I and type II. The type I active phase is less stacked and strongly interacted with support. The type II active phase is highly stacked and weakly interacted with

support, exhibiting higher activity than type I active phase [4]. Novel supporting materials development is a promising approach for highly active HDS catalysts with highly dispersed Co(Ni)Mo(W)S type II phase [5–8]. Various support materials such as carbon nanotube [9], silica [10], V₂O₅/Al₂O₃ [11] and SiO₂/Al₂O₃ [12] have been studied for HDS catalysts. Of these supports, titania-containing supports, such as TiO₂ [13], nano-TiO₂ [14,15], Al₂O₃-TiO₂ [16,17], SiO₂-TiO₂ [18], showed remarkable HDS activity compared to the traditional alumina catalysts.

ETS-10, a microporous titanasilicate, has been attracting great attention and interest since it was synthesized and identified [19,20]. It is a molecular sieve with corner-sharing tetrahedral SiO₄ and octahedral (TiO₆)²⁻ link through bridging oxygen atoms, which composes three dimensional 12-membered ring porous system. The octahedral (TiO₆)²⁻ are connected as linear chains, which run into two perpendicular directions of the crystal and space with siliceous matrix from one another. Ti-O-Ti chains network in ETS-10 is similar to the structure of anatase. Generally Ti species can be octahedral (mainly in bulk titania) or tetrahedral (in framework of most molecular sieves) coordination in Ti-containing HDS catalysts. However, Ti-O-Ti chains in ETS-10 are spaced by siliceous

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matrix, which is not only octahedrally coordinated but also highly dispersed by the framework Si atoms. Ti-site exposure on the surface of ETS-10 is considered to be the extremely dispersed titania chains. Accordingly, ETS-10 has given rise to wide applications on adsorption, ion exchange and shape-selective catalysis due to its particular properties [21,22].

In our previous works, ETS-10 supported NiW catalyst exhibited high HDS and HDA activity for a FCC diesel feed hydrotreating (sulfur content 1052 $\mu\text{g/g}$) [23–26]. In our recent report, the surface-Ti-rich-ETS-10 was prepared by alkali-treatment process to remove Si atoms from the frameworks of ETS-10 [27]. To our knowledge, surface-Ti-rich-ETS-10 had not been used for HDS catalyst. The objective of this study was to develop a new support material to benefit the HDS reaction. The catalysts containing surface-Ti-rich-ETS-10 (AT-ETS) (NiW-AT-ETS/ Al_2O_3) and original ETS-10 (NiW-ETS-origin/ Al_2O_3) were characterized and evaluated for their role and potential in HDS of DBT and 4,6-DMDBT.

2. Experimental

2.1. Preparation of materials

ETS-10: The starting material ETS-10 (abbreviated as ETS-origin) was synthesized through hydrothermal method as reported by Ji and Sacco Jr. et al. [28]. Surface Ti rich ETS-10 (abbreviated as AT-ETS) was obtained by the method described in our previous work [27]. ETS-origin and AT-ETS were transformed to H-ETS-origin and H-AT-ETS respectively by NH_4^+ ion exchange using NH_4Cl at 60 °C for 12 h and calcination at 450 °C for 2 h.

Catalyst: The composite support was prepared by mixing 12.0 g H-ETS-origin (or H-AT-ETS) with 43.1 g pseudo-boehmite (Al_2O_3 , 68 wt%) and extruding to form cloverleaf appearance support. The obtained extrudate was dried overnight at 120 °C and calcined in the air at 500 °C for 2 h. The corresponding NiW based catalysts (NiW-ETS-origin/ Al_2O_3 and NiW-AT-ETS/ Al_2O_3) were prepared by wetness impregnation of the composite supports using ammonium metal tungstate and nickel nitrate solution. The impregnated catalysts were dried at 120 °C for 12 h and calcined at 500 °C for 4 h. The amount of NiO and WO_3 loading was 3.6 wt% and 18 wt%, respectively. The obtained catalysts (40–60 mesh particles) were evaluated in a 1 ml fixed bed micro-reactor for HDS reaction of DBT and 4,6-DMDBT, respectively.

2.2. Characterization

The porosity of each sample was determined by measuring the N_2 isotherm at -196°C on a Micromeritics ASAP 2020 automated system. The pore size distribution (PSD) was determined by the desorption branch of the data of N_2 adsorption-desorption using BJH method. The total surface area was calculated according to the BET equation. The microporous volume, mesoporous volume, and external surface area were evaluated by the t -plot method.

The bulk phase Si/Ti and Al/Ti molar ratios of the materials were determined on a Rigaku ZSX-100e X-ray fluorescence (XRF) spectrometer. The sampling depth was over than 2 μm . The relative analysis error in quantification was $\pm 5\%$.

X-ray photoelectron spectroscopy (XPS) results were obtained on a VG ESCA Lab 250 photoelectron spectrometer using Al $K\alpha$ radiation ($h\nu = 1486.6\text{ eV}$). For these experiments, Ti 2p, Ni 2p and W 4f bands were recorded. Apparent atomic ratios in the XPS sampling region were evaluated from peak area integration ratios using sensitivity factors. The sampling depth was 2–5 nm. The relative analysis error in quantification was $\pm 1\%$.

Temperature-programmed reduction (TPR) experiments were carried out, prior to the reduction about 0.1 g sample in a quartz

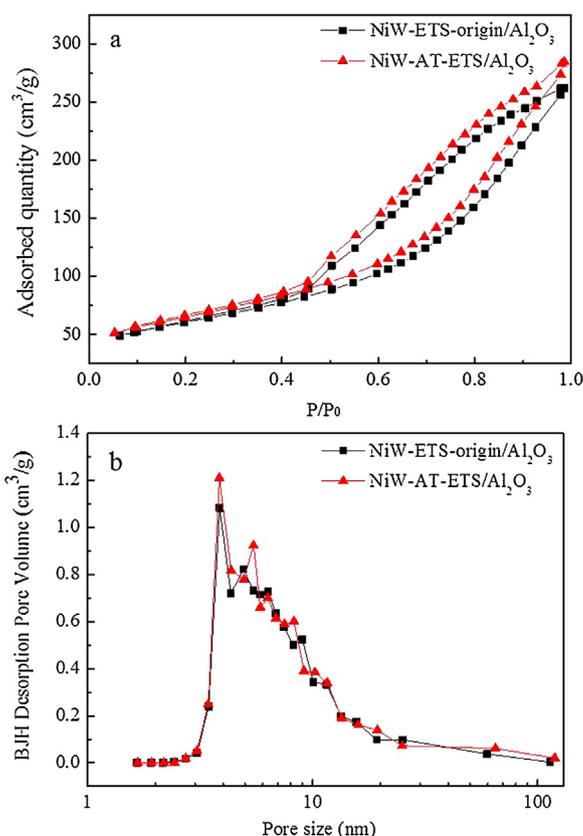


Fig. 1. Adsorption-desorption curves (a) and pore size distribution (b) of catalysts.

Table 1

Pore structure data of composite supports and catalysts.

Sample	S_{ext} (m^2/g)	V_{meso} (cm^3/g)	D_{Avg} (nm)
ETS-origin/ Al_2O_3	300.6	0.549	7.31
AT-ETS/ Al_2O_3	313.5	0.570	7.27
NiW-ETS-origin/ Al_2O_3	214.5	0.405	7.56
NiW-AT-ETS/ Al_2O_3	230.2	0.440	7.65

tube reactor was pretreated in a nitrogen stream at 400 °C for 30 min and then cooled down to room temperature. The temperature was then increased linearly at a rate of 10 °C/min under a flow of H_2 - N_2 mixture (20% H_2 by volume, 30 mL/min). The consumption of H_2 was detected on an online thermal conductivity detector.

The morphology of the Ni, W sulfide was observed by high resolution transmission electron microscopy (HRTEM) on a JEOL-2100FX instrument operated at 200 kV (Samples were prepared by the drop method).

2.3. HDS catalytic activity of the catalysts

The catalysts were first pre-sulfurized in situ with a sulfurizing feed of 10 vol% CS_2 in decane at 4.0 MPa and 320 °C for 3 h. The HDS of DBT (or 4,6-DMDBT) was evaluated in a continuous flow fixed bed microreactor under the following conditions: a model feed of 1000 ppm DBT (or 500 ppm 4,6-DMDBT) in decane, a catalyst load of 0.6 g, a reaction pressure of 4.0 MPa, a reaction temperature of 260 °C, a feed flow rate of 6.6 mL/h, and an H_2 /oil ratio of 370 (v/v). The liquid effluents were periodically collected and measured through microcoulometry instrument to give total S content when the steady-state conditions were reached. The products were analyzed on an Agilent 7890-5975C GC-MS.

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