

## Effect of the Fluorine-Addition Order on the Hydrodesulfurization Activity of Fluorinated NiW/Al<sub>2</sub>O<sub>3</sub> Catalysts

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**Abstract**—Fluorinated NiW/Al<sub>2</sub>O<sub>3</sub> catalysts with different orders of fluorine addition have been prepared, tested for hydrodesulfurization (HDS) of thiophene, and characterized using nitric oxide chemisorption and temperature-programmed sulfidation. The catalyst surface area has been affected by fluorine addition but not by the order of fluorination. The fluorine addition-order does not affect the amount of fluorine retained in the catalysts after the calcination and the reaction steps, either. On the other hand, the order of fluorine addition changes the dispersion of the nickel and the tungsten species, incorporation of nickel with the tungsten edge sites, and consequently the HDS activity of the catalysts. The catalyst fluorinated in the last step, i.e., after addition of both tungsten and nickel, shows the highest activity in thiophene HDS, which is supported by other experimental results indicating the most nitric oxide chemisorption and the largest incorporation of nickel with the tungsten species. Accordingly, enhancement of the catalyst activity by fluorination is due to the repartition of the metal species rather than to partial solubilization of alumina in the fluorine-addition step.

Key words : Hydrodesulfurization, Fluorination, Nickel, Tungsten, Thiophene

### INTRODUCTION

Catalysts currently used in hydrotreating processes involve supported transition metal sulfides from Group VI (Mo, W) promoted by sulfides of Group VIII (Co, Ni) metals [Weisser and Landa, 1973]. Nickel-tungsten sulfide catalysts are used for hydroprocessing heavy hydrocarbons particularly to produce lube-oil blending stocks [Le Page, 1987]. An increase in the reaction temperature is not a suitable way to increase the catalytic activity because these catalysts are sensitive to fouling as a result of coke formation. This justifies the efforts to develop more active and durable catalysts. One of the methods to improve their performance is to modify them with fluorine [Muralidhar et al., 1984]. The promotional effect of fluorine depends on factors such as the fluorine content as well as the timing of fluorine addition in the catalyst preparation process.

Several authors investigated the effect of fluorine addition to the catalysts on the thiophene hydrodesulfurization (HDS) rate. Jiráťová and Kraus [1986] observed an increase in the HDS rate on NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts by addition of 3 wt% fluorine. Muralidhar et al. [1984] also observed an increase in the HDS activity on CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts by stepwise addition of fluorine of up to 0.5 wt%, but the activity decreased when the fluorine content was higher than 5.0 wt%. In other studies [Papadopolou et al., 1988; Matralis et al., 1988] with fluorine-added CoMo/Al<sub>2</sub>O<sub>3</sub> and NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts, the thiophene HDS activity increased with the fluorine content up to 0.8 wt%. At fluorine contents higher than 2 wt%, however, the activity of the

cobalt-promoted catalyst dropped substantially while that of the nickel-promoted catalyst continued to increase. In the case of NiW/Al<sub>2</sub>O<sub>3</sub> catalysts, Benítez et al. [1996] reported that the thiophene HDS activity was almost invariant with the fluorine addition. However, our recent study [Kwak et al., 1999] has reported enhanced HDS activity on NiW/Al<sub>2</sub>O<sub>3</sub> by fluorine addition up to 8 wt%. Although these results from different laboratories are not consistent in detail, fluorine definitely promotes HDS activity particularly when the catalysts are prepared by stepwise impregnation and the fluorine contents are proper. The inconsistencies are probably due to different impregnation conditions used in the catalyst preparation.

Studies on the effect of the fluorine-addition timing in the catalyst preparation procedure are limited. Lewis et al. [1989] reported that the order of fluorine deposition had a small effect on the HDS activity of NiMo/Al<sub>2</sub>O<sub>3</sub> catalysts. However, the deposition sequence influenced the hydrocracking activity of the catalysts because fluorination of the catalyst after the metal addition yielded a more acidic surface. Matralis et al. [1994] reported that fluorine deposition on CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts after the metal addition increased the density of the active sites, and thus the HDS rate. Sarbak [1997] reported relatively low activity of CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts when fluorine was added at the last stage.

As described above, the effect of the fluorine-deposition order on the activity of hydrotreating catalysts is controversial among researchers. In this study, we have examined the activity of fluorine-added NiW/Al<sub>2</sub>O<sub>3</sub> catalysts varying the order of the fluorine deposition. We have characterized the catalysts by temperature-programmed sulfidation (TPS) and nitric oxide chemisorption to understand the species produced on the catalyst surface by the fluorine deposition.

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## EXPERIMENTAL

### 1. Catalyst Preparation

Fluorinated nickel-tungsten catalysts supported on  $\gamma$ -alumina (JRC-ALO-4) were prepared by the incipient wetness method using aqueous solutions of NH<sub>4</sub>F (Fluka), (NH<sub>4</sub>)<sub>6</sub>H<sub>2</sub>W<sub>12</sub>O<sub>40</sub> (Fluka), and (Ni(NO<sub>3</sub>)<sub>2</sub>)<sub>6</sub>H<sub>2</sub>O (Aldrich). After each impregnation step, the catalysts were dried at 383 K for 12 h and calcined at 723 K for 4 h. The catalysts were designated as W-Ni, F-W-Ni, W-F-Ni, and W-Ni-F according to the order of fluorine deposition and analyzed for fluorine content by ion chromatography (DIONEX4500I).

### 2. Catalytic Activity

The rates of thiophene HDS on the catalysts were measured in a fixed-bed microreactor at atmospheric pressure. Prior to each reaction test, the catalysts were presulfided with a 15.1% hydrogen sulfide/hydrogen mixture at 673 K for 2 h. Residual hydrogen sulfide was flushed from the catalyst surface with helium before start-up of the reaction. A thiophene/hydrogen mixture (hydrogen/thiophene=40) was passed through a preheater, then into a reactor maintained at 623 K. The outlet steam was analyzed for unreacted thiophene and product gases by gas chromatography (Tracor 565) using a column packed with Carbowax 20 M on Chromosorb W. Deactivation of the catalysts was observed during the first hour on stream. Therefore, all the catalyst activities reported here were measured 12 times between the first and second hour after the catalysts were exposed to the reaction stream.

### 3. Catalyst Characterization

Before nitric oxide chemisorption, the catalysts were presulfided in a 15.1% hydrogen sulfide/hydrogen stream at 673 K for 2 h. The amounts of chemisorbed nitric oxide were measured volumetrically at room temperature using a constant-volume adsorption system equipped with precision pressure gauges.

At the beginning of the TPS experiment, a sulfiding mixture (flow rate 30 cc/min, hydrogen sulfide 0.3%, hydrogen 2.7%, helium 97%) was allowed to flow through the reactor at 300 K. When no further sulfiding or adsorption took place at 300 K, the reactor was continuously heated up to 1,200 K at the rate of 5 K/min. A quadruple mass spectrometer (VG Sensorlab 200) measured the hydrogen-sulfide consumption.

## RESULTS

### 1. Surface Area

Table 1 lists the composition and the surface area of the sample catalysts prepared in this study. While tungsten deposition decreases the surface area of  $\gamma$ -alumina by about 25%, fluorine addition reduces the surface area only slightly, and furthermore the area is unaffected by the order of fluorine addition.

To explain the reason for the surface-area reduction, Matralis et al. [1988] showed that narrow pores with radii smaller than 15 Å were modified by fluorine addition. That is, dissolution of alumina in the fluorine-addition step resulted in the removal of thin walls between the micropores and eventually the formation of larger pores [Scokart, 1979].

Matralis et al. [1994] claimed that the largest change in the

**Table 1. Composition and surface area ( $S_{BET}$ ) of catalyst samples**

| Catalyst                                 | Composition (wt%) |     |             | $S_{BET}$ (m <sup>2</sup> /g) |
|------------------------------------------|-------------------|-----|-------------|-------------------------------|
|                                          | WO <sub>3</sub>   | NiO | F (nominal) |                               |
| $\gamma$ -Al <sub>2</sub> O <sub>3</sub> | 0.0               | 0.0 | 0.0         | 223.0                         |
| W-Ni                                     | 20.0              | 6.0 | 0.0         | 167.3                         |
| F-W-Ni                                   | 20.0              | 6.0 | 2.5         | 156.1                         |
| W-F-Ni                                   | 20.0              | 6.0 | 2.5         | 154.2                         |
| W-Ni-F                                   | 20.0              | 6.0 | 2.5         | 157.0                         |

**Table 2. Changes in fluorine content of catalysts prepared with different impregnation order**

| Catalyst | Nominal (wt%) | After calcination (wt%) | After reaction (wt%) |
|----------|---------------|-------------------------|----------------------|
| W-Ni     | 0             | 0                       | 0                    |
| F-W-Ni   | 2.5           | 1.65                    | 1.60                 |
| W-F-Ni   | 2.5           | 1.68                    | 1.59                 |
| W-Ni-F   | 2.5           | 1.51                    | 1.51                 |

catalyst surface area was obtained when fluorine was incorporated in the last step. They suggested that partial dissolution of the cobalt and the molybdenum phases and the subsequent adsorption of polymolybdate species on the inner walls near the very thin necks of narrow pores resulted in the closing of the bottom part of these pores. In our study, however, the order of fluorine addition does not affect the catalyst surface area.

### 2. Fluorine Retention

The amounts of fluorine retained on the catalyst after the calcination or the reaction step are given in Table 2. It is clear that the calcination step induces a significant loss of fluorine, but the amount of fluorine loss is independent of the impregnation order. That is, W-Ni-F has been calcined once, W-F-Ni twice and F-W-Ni for three times after the fluorination step, but the final fluorine contents are almost equal among the three catalysts. Therefore, we may conclude that the fluorine loss occurs in the first calcination step. The fluorine loss after the HDS reaction is insignificant probably due to lower temperatures of the sulfidation and the reaction steps.

### 3. Catalytic Activity

A typical reaction course according to the time is shown in Fig. 1 for HDS of thiophene on F-W-Ni. Because the reproducibility of the thiophene HDS rates is usually low as reported by Jiráťová and Kraus [1986], we have repeated the reaction experiments starting from the sulfiding step. Conversions shown within error bars in Fig. 2 have been obtained from 12 repeated experiments after the catalysts were used in the reaction for 1 h. It is obvious from Fig. 2 that fluorine deposition enhances the catalytic activity. Fig. 2 also indicates that the activity is enhanced the most when fluorine is added after molybdenum and cobalt have been deposited.

Among the controversial results obtained about the effect of the order of the fluorination step, our result is similar to one by Matralis et al. [1994], who claimed that CoMo/Al<sub>2</sub>O<sub>3</sub> catalysts fluorinated in the last step of the catalyst preparation were more active than those fluorinated in the first step.

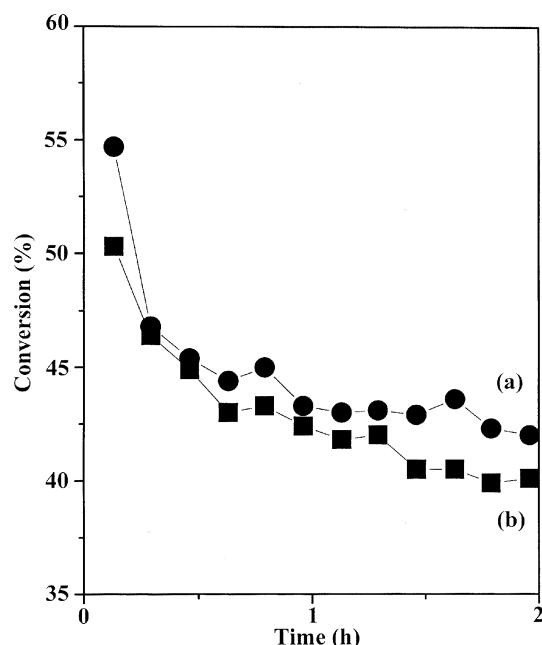


Fig. 1. HDS conversions on F-W-Ni as a function of time: (a) first and (b) second. Reaction was carried out at 623 K under atmospheric pressure.

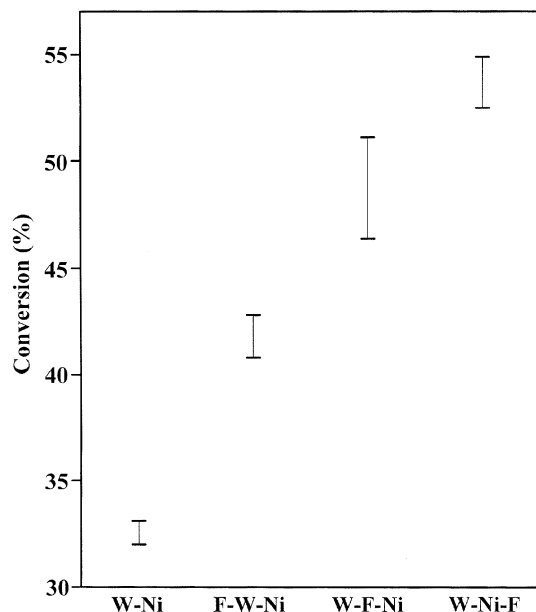


Fig. 2. HDS conversions on NiW/Al<sub>2</sub>O<sub>3</sub> catalysts with different orders of fluorine addition. Reaction was carried out at 623 K under atmospheric pressure.

#### 4. Nitric Oxide Chemisorption

Nitric oxide adsorbs mostly on the edge sites of MoS<sub>2</sub> and WS<sub>2</sub> structures, and also on cobalt and nickel atoms located at the edges of MoS<sub>2</sub> and WS<sub>2</sub>, which are regarded as the active sites for HDS [Topsøe and Topsøe, 1983]. A relationship was established between the nitric oxide uptake and the dispersion assessed by X-ray photoelectron spectroscopy [Portela et al., 1995]. Another reason for using nitric oxide as a probe molecule of the HDS active sites is that the HDS rate is inhibited

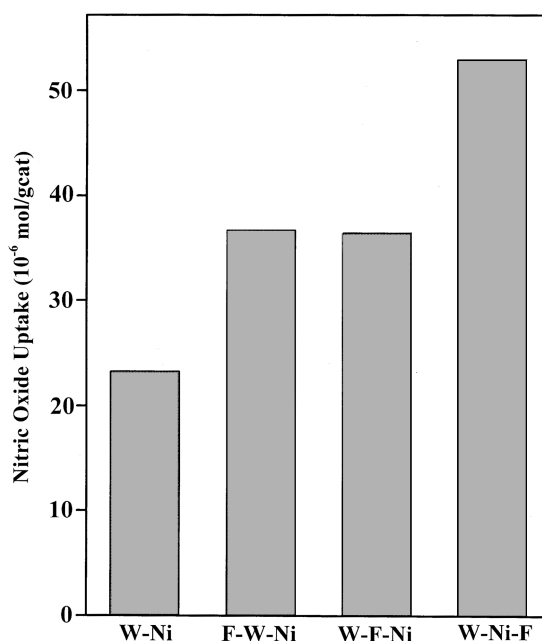


Fig. 3. Nitric oxide uptake by catalysts with different order of fluorine addition.

when hydrogen sulfide adsorbs on the catalysts and the same adsorption sites may be titrated with nitric oxide [Okamoto et al., 1981].

Fig. 3 shows that the amount of nitric oxide adsorbed on sulfided catalysts is the largest on W-Ni-F, agreeing with the reaction results. Accordingly, fluorine addition after the metal impregnation increases the active sites to the greatest extent, possibly due to enhanced dispersion of the nickel and the tungsten species. The amounts of nitric oxide adsorbed on W-F-Ni and F-W-Ni are similar although the catalytic activity of W-F-Ni is larger than that of F-W-Ni. The inconsistency is due to the difficulty of establishing a direct relationship between the nitric oxide uptake and the catalytic activity. Portela et al. [1995] reported that establishing such a direct relationship for specific reactions was difficult because conditions of nitric oxide adsorption were different from reaction conditions. Furthermore, the activity is influenced by other factors such as reducibility as well as dispersion [Fierro et al., 1991].

#### 5. Temperature-programmed Sulfidation

Fig. 4 shows changes in the TPS pattern of the catalysts with different impregnation orders. Hydrogen sulfide is consumed even at room temperature, which indicates that the catalyst sulfidation proceeds at relatively low temperatures. When the catalyst is heated above the room temperature, hydrogen sulfide is liberated from the catalyst and then is consumed again at higher temperatures.

In the case of Ni/Al<sub>2</sub>O<sub>3</sub>, the TPS pattern shows two consumption bands: a sharp peak centered at 590 K and a broad one appearing over a wide range of temperatures up to 1,200 K. The peak below 650 K is usually assigned to sulfidation of the NiO-like phase and the peak above 650 K to sulfidation of the surface and the bulk spinel species [Scheffer et al., 1990]. We believe that the broad sulfidation band originates from the nic-

kel species which are stabilized by interaction with the alumina support through Ni-O-Al bonds.

W/Al<sub>2</sub>O<sub>3</sub> also shows a broad sulfidation band which is strong even at 1,200 K. The peak is a result of sulfidation of the monomeric and the polymeric tungsten species [Scheffer et al., 1990] that are highly dispersed on alumina. The low sulfidability of tungsten is due to strong W-O-Al bonds that link the dispersed tungsten species with the alumina support and consequently make the tungsten species less reactive [Salvati et al., 1985].

The TPS pattern of NiW/Al<sub>2</sub>O<sub>3</sub> clearly shows that sulfidation of W/Al<sub>2</sub>O<sub>3</sub> is improved by nickel addition. The improved sulfidability of NiW/Al<sub>2</sub>O<sub>3</sub> suggests that the number of the W-O-Al bonds, which explains the low sulfidability of the tungsten species, has been reduced in the catalyst. This is possible when the W-O-Al bonds are partially replaced by the W-O-Ni bonds.

Two aspects are notable with the TPS pattern for NiW/Al<sub>2</sub>O<sub>3</sub> in Fig. 4. One is that the peak below 640 K representing the sulfidation of nickel alone decreases in the order of W-Ni>F-W-Ni>W-F-Ni>W-Ni-F. The other is that the amount of the sulfided species estimated from the area of the broad band between 400 K and 1,200 K increases in the order of W-Ni-F>W-F-Ni>F-W-Ni>W-Ni. These two results suggest that incorporation of nickel with the tungsten species increases in the above order. Consequently, the Ni-W-O phase, a precursor of the active phase for the HDS reaction, is enhanced in the same order.

## DISCUSSION

Activity results show clearly that fluorine addition to the nickel-tungsten catalyst leads to an increase in the HDS activity. Moreover, fluorination of the catalyst in the final step, i.e., after

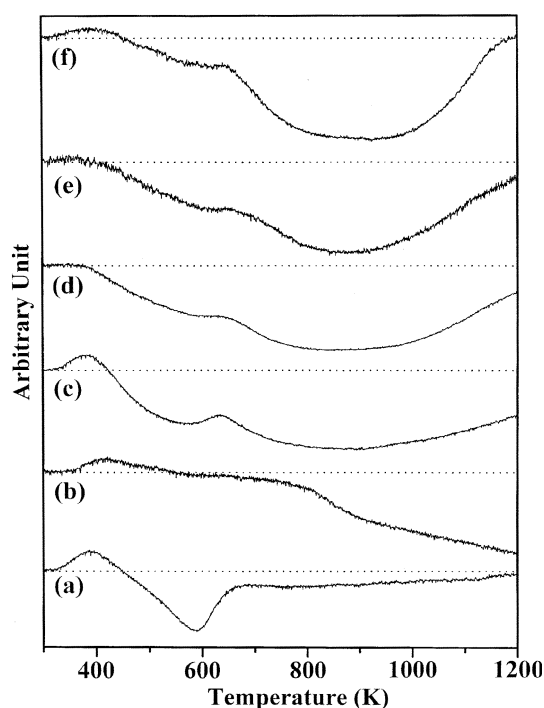


Fig. 4. TPS patterns of: (a) NiO/Al<sub>2</sub>O<sub>3</sub>, (b) WO<sub>3</sub>/Al<sub>2</sub>O<sub>3</sub>, (c) W-Ni, (d) F-W-Ni, (e) W-F-Ni, and (f) W-Ni-F.

loading of tungsten and nickel, has yielded the highest HDS activity. Our results are different from those obtained by Sarbak [1997] who reported that the HDS activity of CoMo/Al<sub>2</sub>O<sub>3</sub> was lowered when fluorine was added at the last stage. He explained the result to be due to the reduced surface area of the catalyst by fluorination. In the case of our catalysts, however, the catalyst area has remained almost constant after fluorination. We have also confirmed that the amount of fluorine retained on the catalyst is the same regardless of the impregnation order.

To explain the reason for the highest activity of W-Ni-F, we need to understand the mechanism of metal deposition on alumina. Tungsten is deposited on  $\gamma$ -alumina in three modes: by adsorption of tungsten ions on the protonated surface hydroxyls of  $\gamma$ -alumina [Spanos et al., 1990], by reaction of tungsten ions with the neutral surface hydroxyls of  $\gamma$ -alumina [van Veen et al., 1987], and finally by uncontrolled precipitation of the tungsten species during the catalyst drying after the impregnation step. On the other hand, nickel is deposited following two mechanisms: by adsorption of nickel ions on the deprotonated surface hydroxyls of  $\gamma$ -alumina as well as of tungsten [Vordonis et al., 1992] and by precipitation of the nickel species during the catalyst drying. The metal dispersion usually increases linearly with the amount ratio of the adsorbed species to the precipitated ones and also with the number of the surface hydroxyls. Fluorination of alumina affects the metal dispersion in two ways. One is partial solubilization of alumina particularly when fluorine is added prior to metal deposition, and the other is the repartition of the surface metal species when fluorine is added after metal deposition.

Ramirez et al. [1990] observed partial solubilization of alumina by fluorine addition on Ni(Co)Mo/Al<sub>2</sub>O<sub>3</sub> catalysts. The solubilization occurs as follows during the initial period of fluorine addition. A small fraction of the surface aluminum cations dissolves in water during the impregnation step, which remains in the solution until water is removed by evaporation. In the drying step, the aluminum cations precipitate as Al(OH)<sub>3</sub>, thus forming a surface layer on alumina. After calcination at 723 K, the surface layer is partially decomposed and provides new sites for adsorption of the tungsten and the nickel species in the subsequent impregnation steps.

Matralis et al. [1994] observed the repartition of the metal species in CoMo/Al<sub>2</sub>O<sub>3</sub> by fluorine addition. During the final addition step of ammonium fluoride, a portion of the tungsten and the nickel species which are loosely bound on the support are dissolved. The dissolved metal species are then distributed in the liquid phase inside the catalyst pores and eventually deposited again on the catalyst when the catalyst is dried after the impregnation step. The metal species are expected to be redeposited mostly near the bottom of the pores where the metal ions are enriched as the solution in the pores gradually vaporizes in the drying step. Therefore, the dispersion of the metal species is enhanced as observed in our study. Fluorination after the metal deposition brings about partial solubilization of alumina to a lesser extent than in the case of fluorination before the metal deposition because a large part of the alumina surface is covered by metal species. In this case, partial solubilization of alumina does not affect the dispersion of

the metal species.

As described in the previous section, the amount of the active sites has increased by fluorine addition in the order of W-Ni-F>W-F-Ni>F-W-Ni. In F-W-Ni, the dispersion of both tungsten and nickel should be improved by partial solubilization of alumina. In W-F-Ni, the dispersion of tungsten is improved by the repartition mechanism and the nickel dispersion by partial solubilization of alumina. Finally, in the case of W-Ni-F, the dispersion of both tungsten and nickel is improved by the repartition. Consequently, we may conclude that the dispersion of the metal species is further enhanced by the repartition mechanism than by partial solubilization of alumina. Apparently, the enhanced dispersion produces more tungsten edge sites that are responsible for the HDS activity.

Incorporation of nickel with the tungsten edge sites is also enhanced in the same order of fluorine addition because of enhanced dispersion. In W-Ni-F, the repartition of nickel as well as tungsten also enhances the incorporation of nickel with the tungsten species. Nickel aluminate may not be formed because our calcination temperature is not sufficiently high. Matralis et al. [1994] reported that fluorination in the last step decreased the tetrahedral cobalt species which include the cobalt aluminate species.

When nickel is loaded before the tungsten deposition, the catalyst fluorinated in the last step of the catalyst preparation shows the highest activity [Kwak, 1995]. The above explanation that the repartition mechanism affects the dispersion of the catalysts more greatly than partial solubilization of alumina may be applied to this case.

## CONCLUSIONS

Based on the above experimental observations and discussions, we may conclude the following about the effect of the order of fluorine addition to NiW/Al<sub>2</sub>O<sub>3</sub> catalysts.

1. The order of fluorine addition does not affect the catalyst surface area; neither does it affect the amount of fluorine retained in the catalyst after calcination.
2. Fluorine addition enhances the thiophene HDS activity in the order of W-Ni-F>W-F-Ni>F-W-Ni.
3. The dispersion of the metal species and incorporation of nickel with the tungsten edge sites also increase in the order of W-Ni-F>W-F-Ni>F-W-Ni. The HDS activity of NiW/Al<sub>2</sub>O<sub>3</sub> is enhanced more by the repartition of the metal species than by partial solubilization of alumina in the fluorine-addition step.

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