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Catalysis Today 74 (2002) 193–200

CATALYSIS TODAY

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Effect of fluorine addition on the formation of active species and hydrotreating activity of $NiWS/Al_2O_3$ catalysts

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Received 28 September 2001; received in revised form 9 November 2001; accepted 30 November 2001

Abstract

Fluorine-added Ni/Al_2O_3, W/Al_2O_3 and NiW/Al_2O_3 catalysts were prepared and their surface properties investigated using temperature-programmed reduction, diffuse reflectance spectroscopy and temperature-programmed sulfidation. The hydrodesulfurization (HDS) of thiophene was used as a model reaction to examine the activity of fluorinated NiW/Al_2O_3. Fluorination led to an increase in the formation of polymeric tungstates in W/Al_2O_3 and the surface nickel spinel species in the case of Ni/Al_2O_3. Fluorination promoted the sulfidation of the NiW/Al_2O_3 catalyst and the interaction of nickel with tungsten to produce the Ni–W–O species, a precursor of active catalytic sites. The activity of NiW/Al_2O_3 was increased by fluorination up to a fluorine content of 4 wt.%, and then decreased at higher fluorine contents. Two opposite effects of fluorination determine the characteristic changes in the activity of NiW/Al_2O_3: the enhanced sulfidation of the catalyst and incorporation of nickel with tungsten, both of which promote the activity, and a decrease in the dispersion of active species, which lowers the activity. The activity results obtained in this study are different from those reported previously [Appl. Catal. A 144 (1996) 343], suggesting that the extent of catalyst modification by fluorination is strongly dependent on the conditions of catalyst preparation. © 2002 Elsevier Science B.V. All rights reserved.

Keywords: Hydrodesulfurization; Fluorine; Nickel–tungsten

1. Introduction

Hydrotreating process in petroleum refinery has become increasingly important due to the recent stringent requirements for lower contents of environmentally hazardous species, such as sulfur- and nitrogen-containing compounds and aromatics, in oil products [1]. Molybdenum and tungsten sulfides supported on alumina and promoted with either cobalt or nickel are common catalysts used in the hydrotreating process. Nickel–tungsten sulfide, which exhibits higher hydrogenation activity than molybdenum-based catalysts, is particularly useful for the hydroprocessing of heavy hydrocarbons to produce lube-oil blending stocks [2].

Considerable efforts have been expended to improve the performance of hydrotreating catalysts [1], including the modification of the catalysts with fluorine [3–7]. Fluorine has been reported to enhance the activity of these catalysts. For example, Jirátová and Kraus [3] reported an increase in the hydrodesulfurization (HDS) rate on $NiMo/Al_2O_3$ by the addition of 3 wt.% fluorine. A similar trend was observed with $CoMo/Al_2O_3$ in the deep HDS of heavy hydrocarbons [4]. Muralidhar et al. [5] also observed an increase in the HDS activity of $CoMo/Al_2O_3$ by the stepwise

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PII: S0920-5861(02)00022-6

addition of fluorine up to 0.5 wt.%, but the activity decreased for fluorine contents higher than 5.0 wt.%. In other studies [6,7], the thiophene HDS activity on fluorine-added CoMo/Al_2O_3 and NiMo/Al_2O_3 increased with the fluorine contents up to 0.8 wt.%, but the activity of the cobalt-promoted catalyst dropped substantially while that of the nickel-promoted catalyst continued to increase when the fluorine content exceeded 2 wt.%.

The fact that the catalytic activity is variable and shows a maximum with the fluorine content suggests that two opposite effects are operating, with one promoting and the other retarding the activity, thus contributing to the overall catalyst performance. In fact, the effects of fluorination are not simple but are complicated and vary with the amount and the order of fluorine addition, the type of reaction and support materials used for the catalyst preparation [8–10].

Unlike the case of molybdenum catalysts, for which the effect of fluorination has been studied extensively, reports concerning the performance of fluorinated tungsten sulfide catalysts are few in number. Since molybdenum and tungsten sulfides show similar catalytic properties in many aspects [2], we may assume that the same effects of fluorination occur with tungsten catalysts as have been observed for molybdenum catalysts. However, previous studies do not report the same trend in activity between the two catalysts. For example, Benítez et al. [11] reported that the rate of thiophene HDS on NiW/Al_2O_3 was almost invariant with fluorine addition and the subsequent hydrogenation of intermediate products decreased linearly with the fluorine content. These results are in contrast with the observation by Benítez et al. [12] who reported that the activity of W/Al_2O_3 for gas oil HDS increased with fluorination due to the improved sulfidation of the tungsten species.

Accordingly, additional studies on the properties of fluorinated NiW/Al_2O_3 are necessary, particularly with respect to the formation or suppression of the surface active species as the result of fluorination and also regarding the extent that the individual effects contribute to the overall activity of the catalyst.

In this work, we have prepared Ni, W and NiW catalysts supported on alumina treated with different amounts of fluorine and have monitored changes in their activity and surface properties as the result of these modifications. The activity was measured using thiophene HDS as a model reaction, and the surface properties were examined by temperature-programmed reduction (TPR), temperature-programmed sulfidation (TPS), and UV–Vis diffuse reflectance spectroscopy (DRS).

2. Experiment

2.1. Catalyst preparation

Fluorine-modified alumina was prepared by impregnating γ-alumina obtained from Japanese Catalysis Society (JRC-ALO-4; BET surface area 220 m^2/g, pore volume 0.9 cc/g) in an aqueous solution of NH_4F (Fluka). The modified alumina was then loaded with Ni, W and NiW, respectively, by stepwise impregnation using $Ni(NO_3)_2 \cdot 6H_2O$ (Aldrich) and $(NH_4)_6H_2W_{12}O_{40}$ (Fluka) as metal sources. The samples were dried in air at 383 K for 12 h and then calcined at 723 K for 4 h after each impregnation step. The catalysts contained 20 wt.% of WO_3 and 6 wt.% of NiO. The catalysts were designated as FNi*X*, FW*X* and FNiW*X*, *X* denoting the nominal amount of fluorine added to the catalysts in 0.1 wt.% units. The fluorine contents of the catalysts decreased significantly after the calcination step, as evidenced by ion chromatography (DIONEX4500I) analysis. The analysis data are listed in Table 1.

2.2. Catalytic activity

The activity of catalysts for thiophene HDS was measured in a fixed-bed micro-reactor operating under atmospheric pressure. Prior to each run, the

Table 1
Fluorine retention after calcination

Catalyst	Nominal content (wt.%)	Measured content (wt.%)
FNiW00	0.00	0.00
FNiW05	0.50	0.28
FNiW10	1.00	0.86
FNiW25	2.50	1.45
FNiW40	4.00	2.30
FNiW53	5.30	3.42
FNiW66	6.60	4.29
FNiW80	8.00	5.89

catalyst was pre-sulfided in a 15% H_2S/H_2 stream at 673 K for 2 h and the residual hydrogen sulfide was subsequently flushed from the catalyst surface with helium. For the reaction, a thiophene/hydrogen mixture, at a ratio of 1/40, was passed through a pre-heater and then into the reactor, which was maintained at 623 K. The outlet stream was analyzed for unreacted thiophene and product gases by gas chromatography (Tracor 565) using a column packed with Carbowax 20M on Chromosorb W. Because the catalyst underwent deactivation during the initial 1 h on stream, the activity was estimated from the average rates obtained between the first and the second hour after the beginning of 12 independent reaction runs. Butane was the only product obtained because the reaction proceeded in an excess of hydrogen.

2.3. Characterization

The TPR apparatus consisted of a flow-control system, a programmed-heating unit and a thermal conductivity cell detector. The catalyst sample was pre-heated in situ in argon (573 K, 1 h) to remove impurities and water, and then reduced in a stream of hydrogen/argon mixture (flow rate 40 cm^3/min, $H_2/Ar = 1$) while the temperature was raised from 293 to 1173 K at the rate of 10 K/min.

For the TPS experiment, the sulfiding gas mixture (hydrogen sulfide 3%, hydrogen 17%, helium 80%) was allowed to flow at 20 cm^3/min through the reactor, which was then heated from 293 to 1173 K at a rate of 5 K/min. A quadrupole mass spectrometer (VG) measured the hydrogen sulfide consumption. UV–Vis DRS spectra of the catalysts were obtained with Carry 2200 spectrometer between 750 and 350 nm using Halon (Varian) as a reference.

3. Results

3.1. Catalyst texture and fluorine content

When alumina is treated with fluorine, its pore structure may change because fluorine reacts with alumina to produce AlF_3 [13], which dissolves in the aqueous solution. To examine the possible pore modification by fluorination, we have measured the BET surface area and the pore size distribution of alumina before and after the fluorine treatment. However the results which are not shown here, indicated that the pore structure was neither affected by the fluorination as far as the fluorine content was below about 5 wt.% nor was AlF_3 detected on the calcined, fluorinated alumina as evidenced by X-ray photoelectron spectroscopy. Consequently, we conclude that alumina was not fluorinated to an extent of producing AlF_3 and therefore the pore structure remained almost intact in the fluorination range of this study.

Fluorine initially added to the catalyst was substantially lost after the calcinations step, but the data in Table 1 indicate that the amount of fluorine retained in the catalysts are almost proportional to the initially added amounts. According to a separate study [8], fluorine is lost mostly during the initial calcination step after the addition of fluorine. Fluorine loss during the subsequent sulfidation and the HDS reaction in this study is expected to be small because the reactions were carried out at temperatures lower than those used in the calcination step.

3.2. Reaction results

Since the reproducibility of HDS rates on fluorinated NiW/Al_2O_3 was relatively poor, the reaction data were collected from three independent reaction runs starting from the sulfidation of catalysts containing specific amounts of fluorine. Fig. 1 shows conversions obtained from the reaction runs, with the error range given by vertical bars, versus the fluorine contents of the catalysts. Although the data are somewhat scattered, it is apparent that the HDS activity of NiW/Al_2O_3 is enhanced by fluorination up to a fluorine content of FNiW66 and then lowered slightly at higher fluorine contents. This trend is different from that reported by Benítez et al. [11], which showed no variation in the activity with fluorination, but is similar to the observations reported by Muralidhar et al. [5] on fluorinated $CoMo/Al_2O_3$.

3.3. Characterization

3.3.1. TPR

Fig. 2 indicates that Ni/Al_2O_3 containing no fluorine shows a major peak at 630–930 K while the fluorinated catalysts show several peaks appearing over a broad temperature range. Catalysts containing

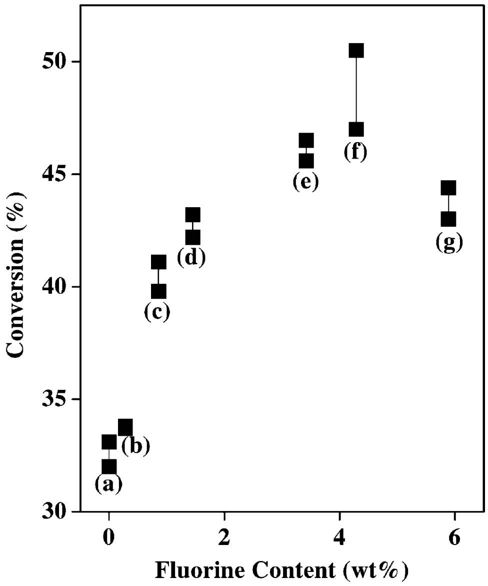

Fig. 1. HDS of thiophene on: (a) FNiW00; (b) FNiW05; (c) FNiW10; (d) FNiW25; (e) FNiW53; (f) FNiW66; (g) FNiW80.

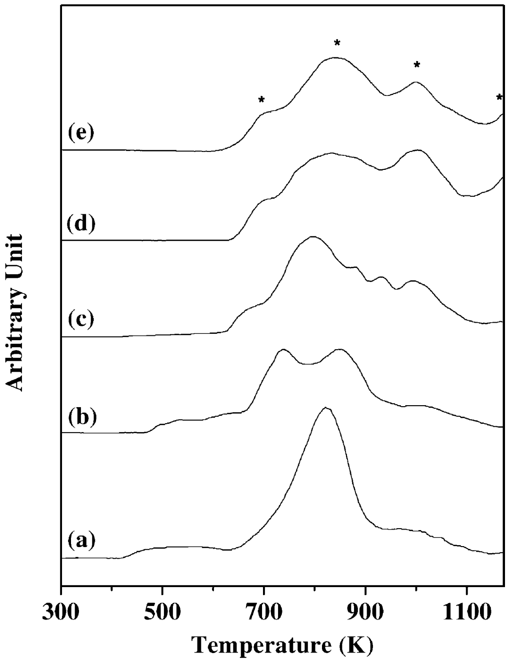

Fig. 2. TPR patterns of: (a) FNi00; (b) FNi10; (c) FNi25; (d) FNi40; (e) FNi80.

large amounts of fluorine, e.g. FNi80, show distinct peaks in four temperature regions: 630–750, 750–930, 930–1100 and above 1100 K. Since the Ni^{2+} species are reduced to Ni^0 without the formation of intermediate oxides, the TPR peaks in different temperature regions represent the reduction of different nickel species [14]. Based on previous studies [14–16], peaks at 630–750 and 750–930 K are assigned to the reduction of highly dispersed nickel surface species (NiO-like species), that at 930–1100 K to the reduction of surface nickel spinel species (surface $NiAl_2O_4$-like species), and that above 1100 K to the reduction of sub-surface nickel spinel species (sub-surface $NiAl_2O_4$-like species).

When fluorine is added to the catalyst, the single peak at 630–930 K is split into two peaks because the anion vacancy of alumina, which affects the reduction of dispersed nickel species, is modified by the fluorination.

Even in the case of an unfluorinated catalyst, small amounts of surface nickel spinel species are formed via the isomorphic substitution of nickel ions for aluminum ions in octahedral positions [17]. Sub-surface nickel species are formed by the diffusion of nickel ions into alumina when calcination is performed above 800 K [18]. In our case, fluorine promotes the bonding of nickel with alumina even at low calcination temperatures [19] and therefore peaks due to the reduction of the surface and the sub-surface spinel species are stronger for the case of FNi80 than for FNi00.

When W/Al_2O_3 is devoid of fluorine, it is difficult to reduce tungsten completely even at high temperatures as shown for FW00 in Fig. 3. Unlike nickel, tungsten is reduced in a stepwise fashion from the oxide states of +6 via +5 and +4 to the metallic state [20] and therefore the TPR peaks in Fig. 3 represent the reduction of tungsten species in different oxide states. According to Vermaire and van Berge [21], peaks above 1000 K are due to the reduction of monomeric tungstates, which are highly dispersed on alumina, and those below 1000 K represent the reduction of polymeric tungstates or polytungstates [12], which are stacked in large crystallites on the support.

Fig. 3 indicates that the reduction of polymeric tungstates increases while that of the monomeric species decreases as fluorine is added to the catalyst. Fig. 3 also shows that the peak maximum below 1000 K shifts to lower temperatures suggesting that

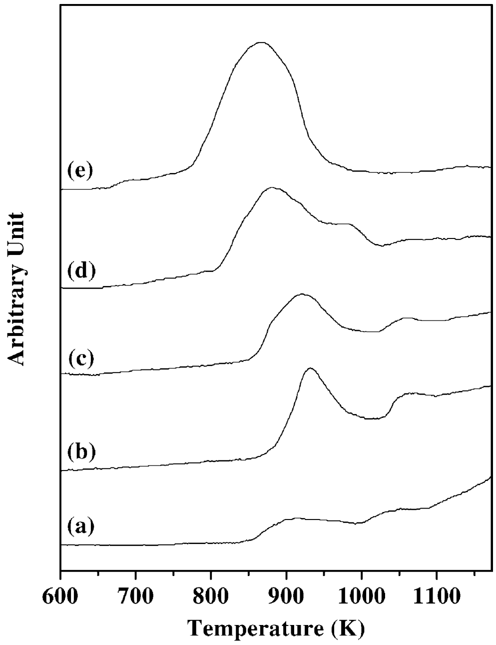

Fig. 3. TPR patterns of: (a) FW00; (b) FW05; (c) FW10; (d) FW25; (e) FW80.

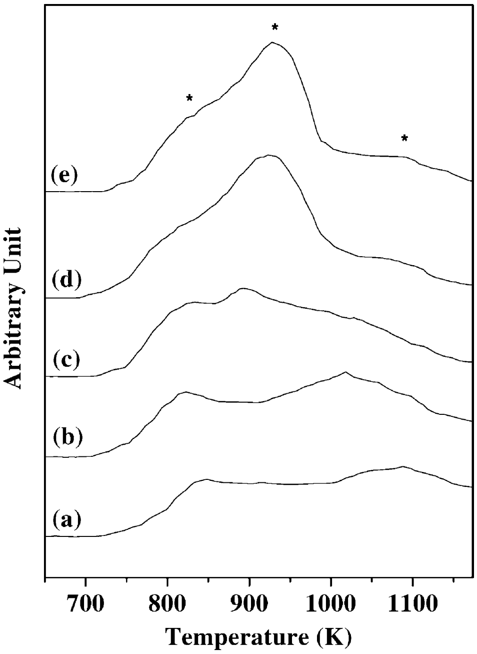

Fig. 4. TPR patterns of: (a) FNiW00; (b) FNiW05; (c) FNiW25; (d) FNiW66; (e) FNiW80.

the reduction of polymeric tungstates becomes easier at high fluorine contents. The same trend has been reported in previous studies using high-resolution transmission electron microscopy [12], X-ray photoelectron spectroscopy [11], TPR and Raman spectroscopy [22]. The transition from monomeric to polymeric tungstates occurs because the adsorption of tungsten on alumina is retarded due to the lowered isoelectric point [13,23] and in some cases due to the reduced surface area [6] of fluorinated alumina.

In Fig. 4, the TPR pattern of FNiW80 shows three peaks in different temperature regions: 800–860, 860–980 and 980–1200 K. Based on the results of FNi*X* and FW*X*, the peak at 800–860 K can be assigned to the reduction of highly dispersed nickel species, the peak at 860–980 K to the reduction of polymeric tungstates and that at 980–1200 K to monomeric tungstates. Fig. 4 also shows that the intensity of the peak for polymeric tungstates increases while that for monomeric tungstates decreases with increasing fluorine content, which is similar to the case of FW*X*.

Peaks due to the surface nickel spinel species observed with FNi*X* at 930–1100 K are not observed with FNiW*X*, indicating that the interaction between nickel and alumina is not strong when the catalyst contains both nickel and tungsten. In fact, a thermodynamic analysis of the system containing Ni, W, Al and O elements indicated that nickel interacts preferentially with tungsten to produce Ni–W–O species rather than with aluminum to produce Ni–Al–O compounds [14,24].

3.3.2. UV–Vis DRS

In Fig. 5, the DRS spectra of FNiW*X* processed for the SKM (absorption) scale show a broad band at 370–500 nm indicating that the nickel species are in octahedral symmetry. It is noteworthy that the spectra do not show a significant band around 600 nm representing the nickel species in tetrahedral symmetry [25]. According to Scheffer et al. [14], nickel is octahedrally coordinated in highly dispersed nickel species, surface and sub-surface nickel spinel, and nickel incorporated with tungsten, whereas it is tetrahedrally coordinated in bulk nickel spinel formed through the diffusion of nickel ions into alumina. Since nickel spinel species are produced at insignificant levels in FNiW*X*, as confirmed by TPR results, the DRS band at 370–500 nm must represent

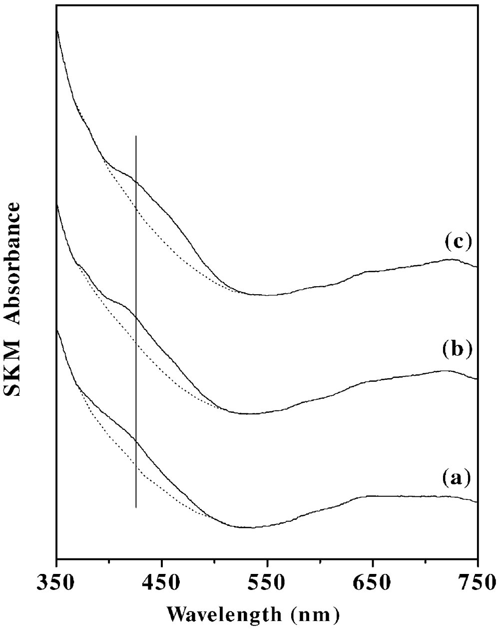

Fig. 5. UV–Vis DRS spectra of: (a) FNiW00; (b) FNiW25; (c) FNiW66.

either highly dispersed nickel species or nickel incorporated with tungsten. Fig. 5 also shows that the octahedral nickel band shifts to higher wavenumbers with increasing fluorine content. Since the band for nickel incorporated with tungsten appears at higher wavenumbers than the band corresponding to the highly dispersed nickel species [25], the band shift indicates an enhanced incorporation of nickel with tungsten producing Ni–W–O species.

Consequently, DRS results indicate that nickel in fluorinated catalysts is present mostly as the surface species in octahedral symmetry rather than the tetrahedrally coordinated, bulk spinel species. In addition, the incorporation of nickel with tungsten is promoted by fluorination.

3.3.3. TPS

When FNiW*X* is sulfided, broad peaks of hydrogen sulfide consumption appear over a wide range of temperatures, as shown in Fig. 6. The sulfidation of nickel and tungsten species takes place even at room temperature because the catalyst changes in color after exposure to the sulfiding gas. When the temperature is raised slightly above the room temperature, hydrogen sulfide which is physically adsorbed on the catalyst is liberated and consequently a peak of negative intensity is observed.

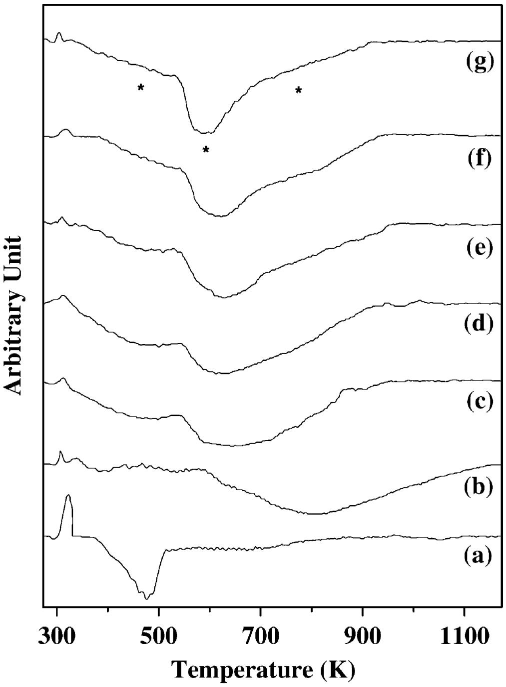

Fig. 6. TPS patterns of: (a) FNi00; (b) FW00; (c) FNiW00; (d) FNiW05; (e) FNiW10; (f) FNiW25; (g) FNiW80.

As the temperature is raised further, the TPS pattern shows three major peaks although they are overlapped with each other due to their broad peak width. The peaks can be assigned as follows based on a previous study [26] as well as on our independent TPS results obtained with FNi00 and FW00. The peak at 300–550 K is due to the sulfidation of highly dispersed nickel species, the peak at 550–700 K is due to polymeric tungstates and that at 700–900 K to monomeric tungstates. With an increase in the fluorine content, the peak at 700–900 K becomes weak in intensity and shifts to lower temperatures so that the peak at 550–700 K, which represents polymeric tungstates, becomes relatively intense and appears as a single major peak centered at about 600 K. Consequently, the TPS results also indicate that the tungsten species are converted from the monomeric to the polymeric type, the latter being sulfided at relatively low temperatures, due to the fluorination of the catalyst.

4. Discussion

4.1. Sulfidability and active species

The experimental results obtained in this study can be summarized as follows. The addition of fluorine to W/Al_2O_3 promotes the formation of polymeric tungstates instead of monomeric species on the catalyst, the former being reduced and sulfided at lower temperatures than the latter. Accordingly, the sulfidability of W/Al_2O_3 is enhanced by fluorination. On the other hand, fluorinated Ni/Al_2O_3 contains increased amounts of surface nickel spinel species, which are difficult to reduce as well as to sulfide [26], and therefore the sulfidability of Ni/Al_2O_3 is lowered by fluorination.

When fluorine is added to NiW/Al_2O_3, the formation of polymeric tungstates is promoted as in the case of W/Al_2O_3 and consequently the catalyst sulfidability is improved. It is noteworthy however that the nickel spinel species observed for the case of FNi*X* are not observed for FNiW*X* because nickel interacts with tungsten to form Ni–W–O species in preference to alumina to form nickel spinel species. The incorporation of nickel with tungsten is enhanced for fluorinated catalysts, as evidenced by DRS data.

Accordingly, surface properties of NiW/Al_2O_3 are modified by fluorination in two aspects: enhanced sulfidability and incorporation of nickel with tungsten. Ni–W–O species, produced by nickel–tungsten interaction, were claimed by many researchers [14,26,27] to be the precursor of active sites for HDS, so-called Ni–W–S species, whose analogous species in CoMo/Al_2O_3 catalysts have been studied extensively [28].

4.2. Correlation with catalytic activity

Our reaction results, shown in Fig. 1, indicate that the HDS activity of FNiW*X* is enhanced by fluorination until the fluorine content increases to the level of FNiW66, which is in contrast with the activity invariance reported by Benítez et al. [11]. The activity increase can be attributed to two characteristics of the fluorinated catalysts: an enhanced sulfidation of the catalyst and the incorporation of nickel with tungsten to produce Ni–W–O species. In fact, the same characteristics were observed in previous studies of tungsten-based catalysts [11,12,22], but apparently their contribution to the overall activity was smaller than in this study.

The reason for why the activity is affected to different extents by fluorination, as observed herein vis-a-vis the study by Benítez et al. [11], may be explained by considering conditions used in the catalyst preparation in the two studies. Catalysts prepared in this study contained larger amounts of fluorine, up to 6 wt.%, than those in the other study [11] which contained fluorine levels of up to 2.5 wt.%. Consequently, the effect of fluorination would be expected to be larger in this study than in the other. In addition, the catalyst prepared in this study contained more nickel, the NiO/WO_3 ratio being 6/20 than those used by Benítez et al. [11] where the NiO/WO_3 ratio was 3.17/20.9. Consequently, the amounts of Ni–W–O species produced by fluorination are expected to be larger in this study than in the other one.

Benítez et al. [11] indicated that the activity invariance of their catalysts was due to a decrease in the dispersion of the nickel and tungsten phase by fluorination. In other words, the positive effect of enhanced sulfidation was cancelled out by the negative effect of poor dispersion and consequently the overall activity of the fluorinated catalysts remained invariant. The activity loss due to a decrease in dispersion would also be expected in this study, but the reaction results in Fig. 4 show that the overall activity decreases only when the fluorine content is greater than 4 wt.%. This indicates that the positive effect of enhanced sulfidation and the formation of Ni–W–O species observed in this study is significant enough to compensate for the negative effect of poor dispersion when the fluorine content is less than 4 wt.%.

A decrease in the dispersion by fluorination, as observed with the tungsten catalysts, is not always observed with molybdenum catalysts. For example, Ramirez et al. [10] reported an increase in the dispersion of MoS_2 crystallites on titania and consequently the HDS activity of CoMo/TiO_2 as a result of fluorination. On the other hand, Matralis et al. [7] observed that the dispersion of molybdenum active species on CoMo/Al_2O_3 increased up to a fluorine content of 0.8 wt.% but decreased when the content was 2 wt.%. Other studies [29,30] reported that the dispersion of molybdenum was suppressed by pre-existing fluorine ions, resulting in a decrease in the HDS activity.

Accordingly, the effect of fluorination on the dispersion of the active species is different between tungsten and molybdenum catalysts, which eventually modifies the HDS activity of the catalysts in different manners. The extent to which the activity of tungsten-based catalyst is modified by fluorination is also strongly dependent on conditions used in catalyst preparation, as demonstrated by the different results obtained in this study compared to the report of Benítez et al. [11].

5. Conclusions

Based on the above experimental observations and discussions, the following conclusions can be made concerning the effect of fluorine addition to NiW/Al_2O_3 on its surface properties and HDS activity:

1. Fluorine promotes the formation of polymeric tungstates, which exhibit superior sulfidability compared to the monomeric type, and the incorporation of nickel with tungsten to produce Ni–W–O species. Both effects contribute to the enhanced HDS activity of the catalyst. Fluorine also decreases the dispersion of active species on the catalyst, which contributes negatively to catalyst activity. Consequently, the overall activity of fluorinated NiW/Al_2O_3 is determined by the above two opposite trends, whose contributions to catalytic activity vary with conditions of catalyst preparation.
2. Based on the data obtained in this study, the overall HDS activity of NiW/Al_2O_3 was enhanced by fluorination when the fluorine content was small but was lowered when the fluorine content was large, i.e. beyond 4 wt.%. This result is different from that obtained in a previous study [11] which reported that the activity was invariant with the fluorine content. Difference in the activity results between the two studies may be explained based on differences in the conditions used for preparing the catalysts.

Acknowledgements

This work was supported by Brain Korea 21 project and S-Oil Refinery Co. Ltd.

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