Promoting effect of fluorine on titania-supported cobalt–molybdenum hydrodesulfurization catalysts

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Abstract

The species of a series of F–TiO$_2$ support containing various amounts of fluorine (0–4.30 wt.%) were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), and pyridine-adsorbed IR. The results show that the addition of fluorine has a large effect on titania support and two kinds of fluorides are found to be formed in titania support after titania support is treated by NH$_4$F. The state of the fluoride depends on the fluorine content. With lower fluorine content ($\leq$0.94 wt.%) only one kind of fluoride is formed. Further increase in the fluorine content ($\geq$2.07 wt.%) results in the formation of two kinds of fluorides. ESR analysis confirmed the formation of Ti^{3+} species after fluorine-modification, which actually exists as Ti^{4+} species containing an oxygen vacancy with an electron trapped in. Co–Mo catalysts supported on fluorine-modified titania presented higher HDS activities than Co–Mo catalyst supported on untreated titania. The hydrodesulfurization mechanism on sulfided fluorine-promoted cobalt–molybdenum/titania catalysts was discussed in this report.
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1. Introduction

Improved hydrodesulfurization catalysts are required to satisfy the increasingly strict environmental restrictions imposed on the sulfur content of transport fuels, prompting research into more active and selective catalyst formulations [1–3]. To this end, change of the catalyst support has been one of the most fruitful ways of investigation to improve catalyst activity and selectivity. Among these new supports, titania and alumina–titania mixed oxides [4–8] have shown promising results. Compared with conventional supports such as Al$_2$O$_3$ and SiO$_2$, TiO$_2$ support can be easily reduced to Ti^{3+} by H$_2$ even at low temperature [9]. It is well known that a strong metal–support interaction (SMSI) will occur on TiO$_2$-supported group VIII metals after high-temperature reduction [10], which plays important roles as follows: (1) metals dispersed on TiO$_2$ support as thin pillbox structures or composite clusters were significantly more stable than on other supports [11]; (2) a special interface between metal and partially reduced TiO$_2$ support was formed that includes a metal atom, a Ti^{3+} ion, and an anion vacancy [12,13]; (3) electron migration from the support to metal occurred and the extra electrons saturated the unfilled d orbital of the metal atoms [14]; (4) partially reduced TiO$_2$ migrated to the surface of metals [15,16].

Fluorine shows high electronegative and small atomic radius. Modification of solid acid supports (Al$_2$O$_3$, SiO$_2$, SiO$_2$–Al$_2$O$_3$, TiO$_2$, etc.) using fluoride has received much attention [17–19]. The modification of the supports can change the interaction with the active phase, the surface acidity and consequently the catalytic activity. Some studies suggested that fluoride modification of support could partly promote the catalytic activity such as hydrodesulfurizaiton (HDS), hydrodenitrogenation (HDN) and hydrocracking. The research work of Jorge's [17,19] shows that Co–Mo catalysts supported on fluorine-modified alumina and fluorine-modified titania performed higher HDS activity than those unmodified catalysts. They concluded that the addition of fluoride to the catalyst support results in higher dispersion of the molybdenum sulfide phase so that lead to more active HDS activity.

Sulfided Co–Mo catalysts have traditionally been used for hydrodesulfurization process. Generally these catalysts have been supported on γ-Al$_2$O$_3$. In the past, various models have been proposed to explain the nature of the catalytic sites [20–23]. However, little of the proposed model has been

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capable of explaining clearly the role of the support. Some studies suggested that the nature of the support played a role in determining the activity of the catalysts. The effect of the support on the catalytic activity has been explained in terms of differences in the dispersion of the active ingredients induced by the TiO_2 and Al_2O_3 supports. TiO_2 has attracted attention in view of reports that titania catalysts have higher intrinsic activity than alumina catalysts. Most research on Co–Mo HDS catalysts supported on titania has been focused on Co, Mo metal active phase. We previously investigated the reaction mechanism on sulfided TiO_2 support, Mo/TiO_2 catalysts and $CoMo/TiO_2$ catalysts. We proposed that TiO_2 in HDS catalysts acts not only as a conventional support but also as an electronic promoter of the molybdenum sulfide phase [24–27]. In the light of these previous findings we decided to examine further the nature of the support effect by comparing the activity of Co–Mo catalysts supported on unmodified titania and fluorine-modified titania in the thiophene HDS reaction. In present work, we studied the surface structure and species of fluorine-modified titania support to find the effect of fluorine incorporation on the titania support. Then hydrodesulfurization mechanism on sulfided fluorine-promoted cobalt–molybdenum/titania catalysts was discussed in this report.

2. Experimental

2.1. Catalyst preparation

All the catalysts were prepared by the incipient wetness method. The titania (anatase) support used in this study is supplied by Deqing Chemical Technology Company (PR China), which has a specific surface area of $100 \ m^2 \ g^{-1}$ and a pore volume of $0.4 \ ml \ g^{-1}$.

Titania support was impregnated with the desired amount of fluoride using an aqueous solution of ammonium fluoride (the weight of ammonium fluoride is 10%, 20%, 30% and 40% of that of titania), dried at 393 K for 12 h and calcined at 723 K for 4 h. The actual weight percent of fluorine in the supports were determined by ion-selective electrode analysis to be 0.14%, 0.94%, 2.07% and 4.30%. Then the corresponding fluorine-modified titania supports were named 0.14%F–TiO_2, 0.94%F–TiO_2, 2.07%F–TiO_2 and 4.30%F–TiO_2.

The fluorine-modified supports were impregnated with an aqueous solution of the required amount of cobalt nitrate hexahydrate (corresponding to 2 wt.% CoO) and ammonium heptamolybdate tetrahydrate (corresponding to 10 wt.% MoO_3) solution for 24 h. The catalysts were then dried at 393 K for 12 h and calcined at 723 K for 4 h. The fluorine-modified $CoMo/TiO_2$ catalysts with various fluorine contents were named 0.14%F-Cat., 0.94%F-Cat., 2.07%F-Cat. and 4.30% F-Cat.

The support surface area diminished slightly from 100 to $90 \ m^2 \ g^{-1}$ with the incorporation of 4.30 wt.% fluorine. A commercial $CoMo/TiO_2$ catalyst (T205) containing 2 wt.% CoO and 10 wt.% MoO_3 was used to compare the HDS activity of the fluorine-modified catalysts, which was supplied by Deqing Chemical Technology Company (PR China).

2.2. Catalytic activities

The thiophene HDS activities of the catalysts were measured in a pulse fix-bed microreactor apparatus using 0.4 g catalyst. The apparatus with temperature regulation was connected with a gas chromatography using a six-way valve. Hydrogen was passed through the apparatus and the chromatography as a carrier gas. Thiophene was injected in the reactor with a pulse feeder. Product analysis was performed on-line by the gas chromatography with a 2-m squalane-Porasil column, which was held at 348 K, with thermal conductivity detector. Sulfidation of the catalysts took place at 1.8 atm and 623 K by injecting CS_2 in the reactor with a pulse feeder, until the peak of H_2O disappeared according to the product analysis result. Before the sulfidation procedure, activation of the catalyst was performed as following: the catalysts were reduced with H_2 carrier gas for 8 h at 1.8 atm and 623 K. Catalytic activities were measured in the temperature range 523–623 K at the same pressure 1.8 atm. The HDS activities were measured in the pulse reactor until the activity reached a steady state.

2.3. Catalyst characterization

In order to find the effect of fluorine incorporation in the titania support, the fluorine-modified and unmodified titania supports were characterized by X-ray diffraction (XRD), transmission electron microscopy (TEM), X-ray photoelectron spectroscopy (XPS), and electron spin resonance (ESR). XRD spectra were obtained using a D/MAX-γA diffractometer employing Cu Kα radiation (1.54 Å). The X-ray tube was operated at 37.5 kV and 35 mA, and was scanned at 0.3°/min. TEM studies were conducted using a JEM-100CXII equipment. The electron accelerating voltage was 100 kV. The samples were prepared by ultrasonic dispersion in acetone and deposition of a drop of the suspension on a carbon film supported on a standard copper grid. XPS measurements were performed in a PHI-5300ESCA spectrometer using monochromatic Mg Kα (1253.6 eV) radiation at 13 kV and 250 W. The C 1s binding energy (BE = 284.5 eV) was taken as an internal standard. ESR spectra were recorded with a JES-FE1XG spectrometer, operating in X-band mode and connected to a personal computer for data handling. Spectra were recorded at 298 K and atmospheric pressure. Mn sample ($g_1 = 2.034$, $g_2 = 1.981$) was used as a standard for g-value determination. Pyridine-adsorbed IR spectra were obtained in a PEKIN ELMER 683 spectrometer at room temperature. Beforehand, samples to be analyzed by IR were extracted by a vacuum pump at 723 K for 2 h, following pyridine-adsorption for 30 min at room temperature, and then were extracted at 473 K for 1 h.

3. Results

3.1. HDS catalytic activities on sulfided fluorine-promoted cobalt–molybdenum/titania catalysts

The thiophene HDS activities were measured on Co–Mo/ TiO_2 (T205) and Co–Mo/F–TiO_2 catalysts with different
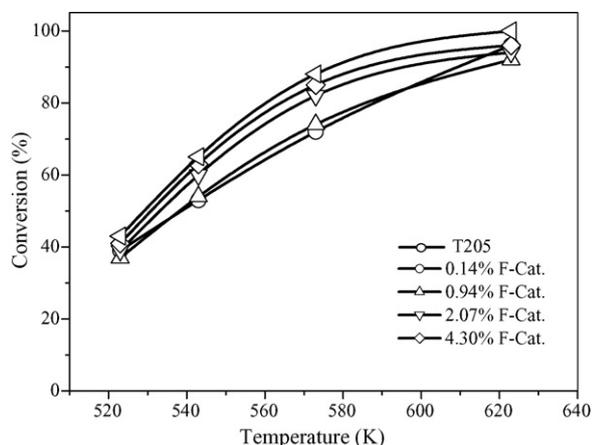
Fig. 1. Fluorine-promoted effect of fluorine content on HDS activities. (T205 is Co–Mo/TiO$_2$ catalyst.)

fluorine contents (0.14–4.30 wt.%). All catalysts have the same amount of CoO and MoO$_3$ contents as calculated. We reduced the oxide precursors before sulfidation because the activity of the catalyst reduced was higher than that of catalyst unreduced. This may be explained by previous study [25] that TiO$_2$ can be easily reduced under hydrogen atmosphere and temperature, the forming Ti^{3+} ions is considered to be related to HDS activity, which is discussed in Section 4.2. Fig. 1 summarizes the thiophene HDS activities on the fluorine-promoted CoMo/TiO$_2$ catalysts with various fluorine contents at different temperatures. The catalytic activity of unmodified TiO$_2$ supported CoMo catalyst was also shown in Fig. 1 to compare with those of fluorine-modified catalysts. As shown in Fig. 1, it appears clearly that the addition of fluoride on the titania support increases the reaction rate of hydrodesulfurization. With lower fluorine content (0.14 wt.%), the conversion of thiophene increased a little, with increasing fluorine content the catalytic activity increased. The maximum increase in the
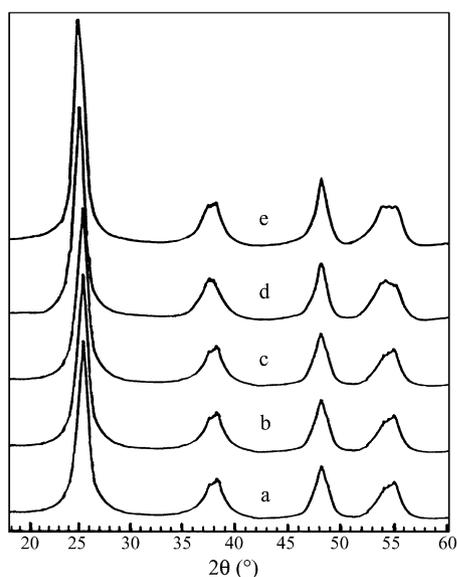

Fig. 2. X-ray diffraction spectra of titania and fluorine-modified titania supports with various fluorine contents. ((a) TiO$_2$, (b) 0.14%F–TiO$_2$, (c) 0.94%F–TiO$_2$, (d) 2.07%F–TiO$_2$ and (e) 4.30%F–TiO$_2$).

catalytic activity was obtained for the 4.30 wt.% fluorine-modified catalyst. The results indicate that fluoride incorporation on the titania support gives a large effect on HDS activity. It is clear that the catalytic activity of the fluorine-modified catalyst is superior to that of the unmodified catalysts.

3.2. XRD study of the fluorine-modified and unmodified titania supports

X-ray diffraction measurement was used to investigate the fluorine-modified titania supports. The X-ray diffraction spectra of TiO$_2$ and F–TiO$_2$ supports containing various amounts of F (0.14–4.30 wt.%) are shown in Fig. 2. Compared with unmodified titania support, although no new diffraction peak is observed for fluorine-modified titania supports, the diffraction profiles of fluorine-modified titania supports are changed. The width and the intensity of the peaks increased with increasing fluorine content. The diffracted intensity of the peaks was shown in Table 1.

3.3. Transmission electron microscopy results

Since fluorine addition has an effect on the titania support as obtained by XRD results, transmission electron microscopy (TEM) was used to study morphological changes in fluorine-treated titania support. Fig. 3 shows transmission electron micrographs of untreated titania support, 0.94 wt.% fluorine-treated and 4.30 wt.% fluorine-treated titania support. In appearance untreated titania particles have regular particle shape of a rectangle and clear particle edges. After fluorine-modification, with increasing fluorine content the particle size decreased. The shape of the titania particles becomes irregular and the particles seem to be corroded by fluorine. The surface of titania particles presents flocculated structure, and in the clearance of the particles small pieces of floccule are formed. These results imply that new species are formed on the surface of titania particles or in the clearance of the titania particles. In order to further confirm the formed new species, electron diffraction (SAED) was examined by TEM. The electron diffraction patterns of the floccule are very different from the pattern of titania, which implied the formation of new species.

3.4. X-ray photoelectron spectroscopy results

In the search for an electronic fluorine–titania interaction, the surface atom contents for titania and fluorine-modified titania supports were examined by XPS. The results were summarized in Table 2. An excessive proportion of oxygen

Table 1
X-ray diffracted intensity of the peaks

2θ (°)	TiO$_2$	0.14%F–TiO$_2$	0.94%F–TiO$_2$	2.07%F–TiO$_2$	4.30%F–TiO$_2$
25.4	813	861	953	1019	1078
48.1	274	308	310	312	313

TiO₂ Sample

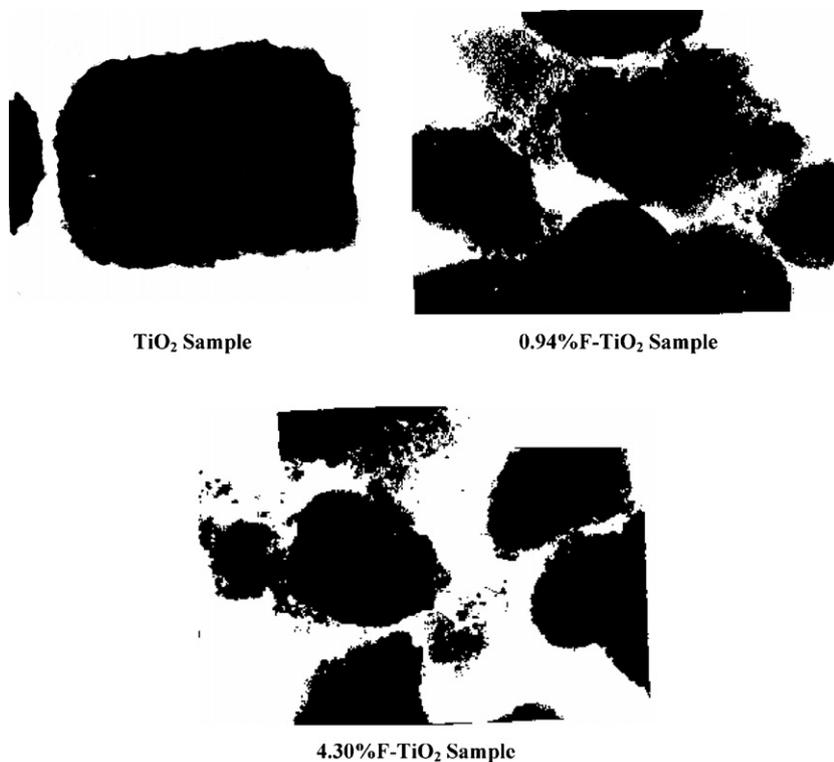**0.94%F-TiO₂ Sample**

4.30%F-TiO₂ Sample

Fig. 3. Transmission electron micrographs of the samples.

atom content was observed for each sample, indicating that the surface of the samples should be completely hydroxylated. With increasing fluorine weight content in titania support, the surface atom content of fluorine increased and reached 26.7% for 4.30 wt.%F–TiO₂ sample. The surface atom content of fluorine for each sample is much higher than the weight content of fluorine for each sample, which was obtained by ion-selective electrode analysis, indicating that the formed fluoride would be mainly concentrated on the surface of titania support. With increasing surface atom content of fluorine, the surface atom content of oxygen decreased almost with the same proportion. This result implied that fluorine–titania interaction could be attributed to the replacement of oxygen atom with fluorine atom. Moreover, the ratio of fluorine atom to titanium atom increased with increasing fluorine content, which means that much more fluoride was formed on the surface of titania. Further, the value of the F/Ti ratio shows a tendency to 2, from this results it could be inferred that the fluorides with F/Ti ratio = 2 would be formed on the surface of titania.

To examine further the possibility of a significant interaction between the fluorine and the TiO₂ support, XPS spectra of the Ti 2p, F 1s and O 1s bands were recorded for titania and fluorine-modified titania samples. The results of F 1s spectra are shown in Fig. 4 and the results of O 1s spectra are shown in Fig. 5. The results of the binding energies, which were determined from the spectra, were shown in Table 3. Examination of Ti 2p spectra did not show any significant shift in the binding energy of the titanium bands when comparing the various fluorine–titania supports with the titania support. The value for the Ti 2p band is BE = 458.4–458.8 eV. In contrast with Ti 2p band, significant changes in the binding energy for F 1s band were detected for the fluorine-modified titania supports. As shown in Fig. 4 and Table 3, with lower

Table 2
Surface atom content for titania and fluorine-modified titania supports

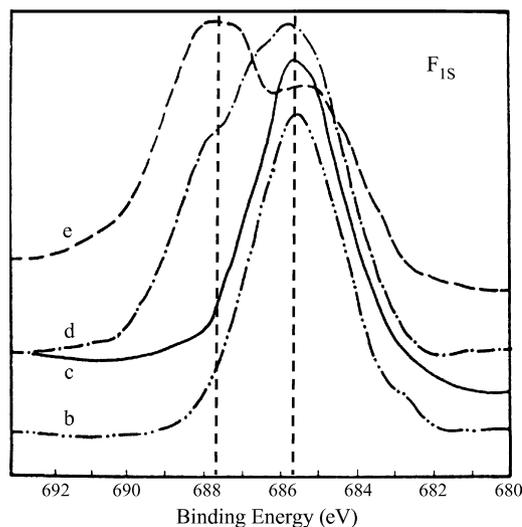| Atom content (%)	Ti	O	F	F/Ti
TiO₂	6.50	93.50	–	–
0.14%F–TiO₂	9.12	83.86	7.02	0.77
0.94%F–TiO₂	12.61	76.63	10.76	0.85
2.07%F–TiO₂	15.74	67.81	16.45	1.05
4.30%F–TiO₂	15.45	57.85	26.70	1.73

Fig. 4. Fluorine photoelectron spectra for various titania supports ((b) 0.14%F–TiO₂, (c) 0.94%F–TiO₂, (d) 2.07%F–TiO₂ and (e) 4.30%F–TiO₂).
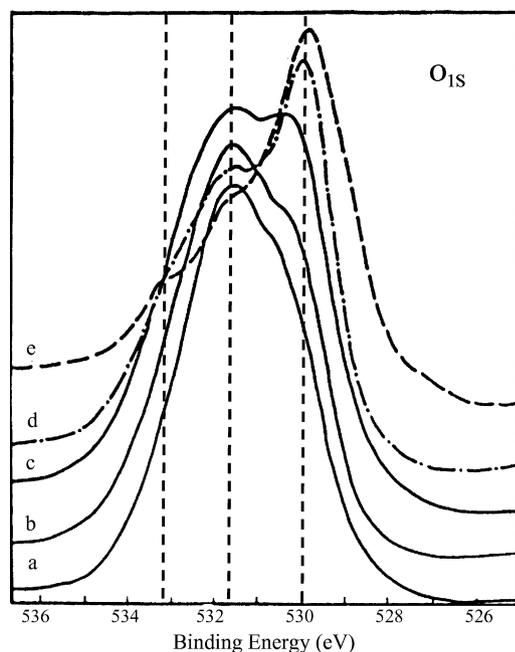
Fig. 5. Oxygen photoelectron spectra for various titania supports ((a) TiO$_2$, (b) 0.14%F–TiO$_2$, (c) 0.94%F–TiO$_2$, (d) 2.07%F–TiO$_2$ and (e) 4.30%F–TiO$_2$).
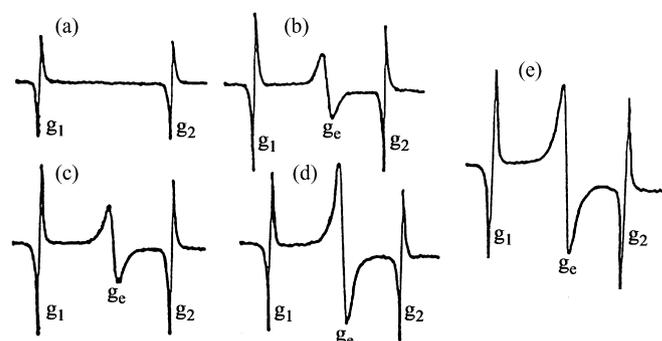

Fig. 6. Electron spin resonance spectra for various titania supports ((a) TiO$_2$, (b) 0.14%F–TiO$_2$, (c) 0.94%F–TiO$_2$, (d) 2.07%F–TiO$_2$ and (e) 4.30%F–TiO$_2$).

band. A new peak located at higher binding energy (BE = 533.21 eV) appeared in O 1s band with higher fluorine content ($\geq$2.07 wt.%), indicating the formation of the fluoride corresponding to the higher binding energy in F 1s band.

3.5. Electron spin resonance results

Since it is proposed that two kinds of fluorides were formed on the surface of titania after fluorine incorporation, electron spin resonance analysis was further used to confirm the presence of the fluorides. Fig. 6 shows the ESR spectra recorded at atmospheric pressure and room temperature for various titania samples. No peak was observed for non-modified titania sample, in contrast, a significant ESR signal (g_e = 2.002) was detected in fluorine-modified titania samples. From the position of the ESR peak this signal is assigned to be the free electrons trapped in oxygen vacancies, indicating the formation of the stoichiometric Ti^{3+} state. With lower fluorine content (=<0.94 wt.%), the peak intensity is weaker. With increasing fluorine content, the peak intensity of the free electrons increased, indicating the amount of Ti^{3+} formed in titania increased.

4. Discussion

4.1. The formation mechanism of fluorine incorporation with titania

The results show clearly that fluorine modifying of titania lead to significant changes in the thiophene HDS activities of Co–Mo catalysts. However, it is not a straightforward conclusion that the observed results are due either to an electronic effect of the support or to a geometric or dispersion effect. In the following we attempt to throw some light on this question.

Our observation of the formation of Ti^{3+} is the first time to be reported. It can be inferred that it make significant contribution to the catalytic activity. In the research work of Jorge Ramirez [19], explanations of the role of fluorine-modification have been given in terms of a geometrical effect, i.e. modification of the dispersion or the orientation of the molybdenum sulfide crystallites. They ruled out the existence of an electronic effect. In contrast, our studies support the electronic effect as the main

fluorine content (=<0.94 wt.%), only one peak (BE = 685.6 eV) was observed for the fluorine-modified titania, suggesting that only one kind of fluoride was formed on the titania support with fluorine-incorporation. When the fluorine content increased to 2.07 wt.%, new peak located at higher binding energy (BE = 687.62–687.68 eV) appeared in F 1s band. This result clearly indicated that there were two kinds of fluorides formed on the titania support with higher fluorine content. A further increase in the fluorine content to 4.30 wt.% led to a decrease in the intensity of peak located at lower binding energy and an increase in the intensity of peak located in higher binding energy, suggesting that part of the fluoride formed with lower binding energy converted to the fluoride formed with higher binding energy.

As shown in Fig. 5 and Table 3, only two kinds of peaks were observed in O 1s band with lower fluorine content (=<0.94 wt.%), which were assigned to be surface oxygen (BE = 529.75–530.00 eV) and surface hydroxyl oxygen (BE = 531.39–531.81 eV) according to the binding energies. With increasing fluorine content, the peak intensity of surface hydroxyl oxygen decreased and the peak intensity of surface oxygen increased, which can be attributed to the formation of the fluoride corresponding to the lower binding energy in F 1s

Table 3
Ti 2p, F 1s and O 1s binding energies for various titania supports

Binding energy (eV)	Ti 2p	F 1s		O 1s	
TiO$_2$	458.5	–		531.39	529.75
0.14%F–TiO$_2$	458.6	685.60		531.54	529.79
0.94%F–TiO$_2$	458.8	685.60		531.73	529.87
2.07%F–TiO$_2$	458.6	687.68	685.40	533.21	531.81	529.90
4.30%F–TiO$_2$	458.4	687.62	684.81	533.21	531.71	530.00

explanation for the differences in catalyst activity for titania and F–TiO_2 supported catalysts in terms of the formation of Ti^{3+}. In subsequent discussion, the formation mechanism of Ti^{3+} was inferred and this electronic effect can be well explained.

In terms of the identification of the XRD, TEM, XPS and ESR spectra, the floccule appeared in titania particles after fluorine-modification is due to the formation of two kinds of fluorides. The results indicated that with lower fluorine content only one kind of fluoride was formed, while with higher fluorine content two kinds of fluorides were formed. Stoichiometric Ti^{3+} was formed on titania after fluorine-modification, which presents an oxygen anion vacancy with an electron trapped in.

In our previous studies [24,25], we have reported that, unlike Al_2O_3 support, TiO_2 support can be sulfided and the sulfided Ti species can be reduced to Ti^{3+} under H_2 atmosphere involving formation of sulfur anion vacancies with electron trapped in. Some studies also reported that compared with conventional Al_2O_3 support, TiO_2 can be easily reduced under hydrogen atmosphere and temperature [28,29], although partial reduction of TiO_2 only results in the formation of electrons that can be trapped in forming Ti^{3+} ions detectable by ESR at liquid-nitrogen temperature (77 K) [30]. On the other hand, according to previous studies, an exchange reaction between sulfur and the oxygen of TiO_2 can easily take place [31]. That is, sulfidation of TiO_2 with H_2S will lead to the formation of TiS_2 [32,33]. Compared with TiO_2, TiS_2 can be reduced more easily under hydrogen atmosphere and the Ti^{3+} ions formed in TiS_2 are more stable. Ramirez et al. [34] also reported that in the case of TiO_2-supported hydrotreating catalysts, after sulfidation and under reaction conditions, where the catalyst is under a high hydrogen partial pressure, TiO_2 can be reduced and sulfided in part. It is also suggested that the sulfur on sulfided TiO_2 could be hydrogenated to H_2S and that this ability for sulfur hydrogenation is equivalent to the ability of creating sulfur vacancies and must be related to HDS activity. Therefore, it can be inferred in this study that due to the formation of fluorides and Ti^{3+}, the fluorine-modified titania should be more easy to be sulfided to TiS_2 and $TiS_{1.5}$, which created sulfur vacancies and must be related to HDS activity. The relationship between the sulfur vacancies created in sulfided titania-supported catalyst and the HDS activities will be consequently discussed in Section 4.2.

4.2. Hydrodesulfurization mechanism on sulfided fluorine-promoted cobalt–molybdenum/titania catalysts

Sulfided fluorine-promoted cobalt–molybdenum/titania catalysts have shown remarkable capabilities for hydrodesulfurization compared with unmodified cobalt–molybdenum/titania

catalyst and cobalt–molybdenum/alumina catalyst under the reaction conditions. This capability seems to be related to the electronic properties of the sulfided and reduced TiO_2 and, in particular, to the presence of sulfur anion vacancies in Ti^{3+} ions as discussed in Section 4.1. As reported in a previous study using a ^{35}S tracer method [35], in the HDS reaction on Mo-based catalysts, the portion of sulfur in the Mo–S phase was labile and present as SH groups under the H_2 atmosphere. When H_2S formed and subsequently desorbed from the catalyst, an anion vacancy was generated. The sulfur in the sulfur compound occupied the S^{2-} anion vacancy and the carbon–sulfur bonds were cleaved; the sulfur remained on the catalyst as a Mo–S species and the old anion vacancy disappeared. Therefore, exchange between the sulfur in the sulfur compound and the sulfur on the catalyst occurred, and as an intermediate, a sulfur anion vacancy was generated. In a recent study [25], Mo/Al_2O_3 and Mo/TiO_2 were compared catalyst using the ^{35}S tracer method. The latter shows three times higher activity per Mo atom. It has almost the same amount of labile sulfur, and about two times higher rate constant of H_2S release. Such results indicate that the presence of TiO_2 makes the sulfur on the sulfided Mo/TiO_2 catalyst more mobile rather than increasing the number of the active sites.

A structure of sulfided Mo/TiO_2 catalyst is proposed in Fig. 7 [25]. In this model, it is considered that the structure of MoS_2 is a deformed tetrahedral structure, which is similar to that on Al_2O_3 support. As shown in Fig. 7a, TiO_2 support can be sulfided to TiS_2 simultaneously during the presulfidation procedure. In Fig. 7b, under the reaction conditions (H_2 atmosphere), the sulfided TiO_2 support can be reduced to Ti(III) involving formation of sulfur anion vacancies with electrons trapped in them. In Fig. 7c, due to the formation of sulfur anion vacancy and the capability of electron transfer from Ti(III) to Mo, the sulfur S^* neighboring to the formed sulfur anion vacancy can be weakly bonded with the two neighboring Ti atoms, leading to the formation of new TiMoS active phase. Then, the Mo–S^* bond strength was considered to be weaker and the sulfur S^* became more labile. This is consistent with the result when the promotion effect of Ti was postulated to be due to increased mobility of the sulfur in MoS_2 phase [25]. Therefore, it can be concluded that TiO_2 electronic promotion on the Mo phases is similar in nature to that of Co [34], which is supposed to bring about the decrease in the strength of Mo–S bond by the formation of TiMoS active phase.

In a proposed CoMoS model for Co–Mo/Al_2O_3 catalysts, one cobalt atom will bond four sulfur atoms in the two neighboring MoS_2 phases. In this case, the promotion effect of cobalt on the Mo/Al_2O_3 catalyst should occur at a molar ratio of
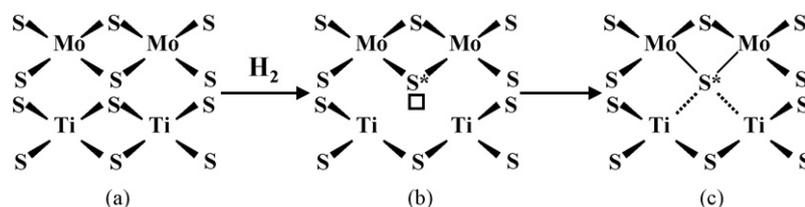

Fig. 7. Schematic view of the structure of TiMoS phase on sulfided Mo/(F)–TiO_2 catalyst. (□ represents an sulfur anion vacancy with an electron trapped in).

Co/Mo of 0.5. This is in good agreement with the results obtained in our previous work [35]. The rate of HDS was promoted with increasing Co/Mo molar ratio up to 0.5, suggesting that cobalt could be dispersed on Mo/Al$_2$O$_3$ and could form a CoMoS phase with the two neighboring MoS$_2$ phases at Co/Mo < 0.5. Although similar variation of HDS rate constant over TiO$_2$-supported catalyst was observed in our previous study [27], the synergetic effect produced by the Co promoter on Al$_2$O$_3$-supported catalyst is greater than that found on TiO$_2$-supported catalyst. These results indicate that a limited activity enhancement by Co promotion was obtained over TiO$_2$-supported catalysts.

The fact that Mo/TiO$_2$ catalysts are more active than Mo/Al$_2$O$_3$ ones, together with the observation that the synergistic effect produced by the Co promoter on Al$_2$O$_3$-supported catalyst is greater than the effect on TiO$_2$-supported catalyst, indicate that TiO$_2$ electronic promotion of the Mo phases is similar in nature to that of Co [27]. Furthermore, quite possibly there is a limit to this type of promotion, since the observed Co promotion effect on the mobility of sulfur is greater on Al$_2$O$_3$-supported catalyst than on TiO$_2$-supported catalyst, where the interaction between Mo and Ti occurred under H$_2$ atmosphere, leading to the formation of TiMoS phase.

Therefore, it can be inferred in this study that due to the formation of the fluorides and Ti^{3+}, the fluorine-modified titania should be more easy to be sulfided to TiS$_2$ and TiS$_{1.5}$, which created sulfur vacancies. Subsequently, the sulfur vacancies created in sulfided titania-supported catalyst under H$_2$ atmosphere led to the formation of TiMoS phase. The higher HDS activities then can be well explained by the formation of TiMoS phase.

4.3. The effect of fluorination on catalysis of the titania and alumina supported catalyst

In recent years, much attention has been focused on fluorine-modified alumina support [36]. Fluorine enhances the acidity of alumina and, therefore, improves its activity for acid-catalyzed reactions such as hydrocracking [37], which is used in removing sulfur [38–40], nitrogen [41–45] and metal atoms from heavy feedstocks. Many explanations have been proposed for the effect of fluorine on hydrotreating reactions. For instance, the effect of fluorine in alumina has been attributed to an increase in acidity, to changes in the dispersion and distribution of the active MoS$_2$ or WS$_2$ phases, to their improved sulfidation and to a change in their morphology. The effects of fluorine on the reaction mechanism and the catalyst structure indicate that fluorine affects the catalytic performance by changing the metal sulfide phase rather than being directly involved in the hydrotreating reactions. It was found that fluorine did not significantly change the activation energy and heat of adsorption of 2-methylcyclohexylamine and *o*-toluidine on the active sites [46–48]. These kinetic results indicate that fluorine does not change the nature of the active sites but changes the dispersion and distribution of the active phase. Fluoride ions interact with the alumina support by replacing the hydroxyl groups on the support surface. Finally, isolated
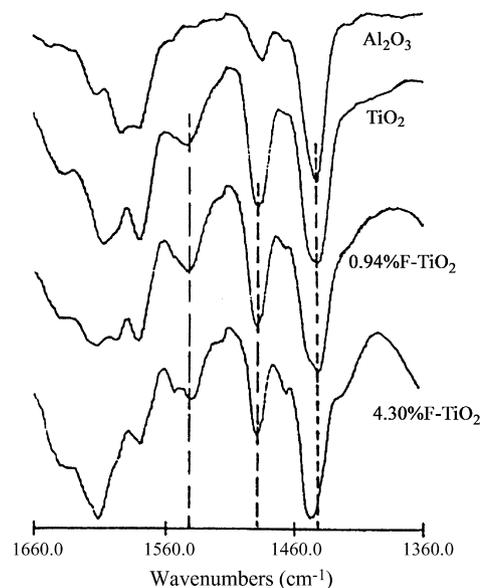
Fig. 8. Pyridine-adsorbed IR spectra for the samples.

AlF$_3$·xH$_2$O is formed at high fluorine loadings [49,50]. As a consequence, the metallate anions can only react with the small number of non-basic hydroxyl groups. In this way, fluorination of the alumina support weakens the metal–support interaction and leads to the formation of polymolybdate or polytungstate on the catalyst surface [51]. These polymetallates can be more easily sulfided.

The effects of fluorine on the catalyst structure and the reaction mechanism of the titania-supported catalyst were discussed in Section 4.1 and Section 4.2. Further, the effect of fluorine on the acidity of the titania support was investigated to compared with that of alumina support as discussed above. Fig. 8 shows pyridine-adsorbed IR spectra for the samples. The absorbed peak located at 1450 cm^{-1} was assigned to be Lewis acid site, the absorbed peak located at 1540 cm^{-1} was assigned to be Brönsted acid site, and the absorbed peak located at 1490 cm^{-1} was assigned to be Lewis plus Brönsted acid site. Alumina shows almost no Brönsted acid site, while titania presents large amount of Brönsted acid site. After fluorine-modification, for 4.30 wt.%F–TiO$_2$ sample, a significant shift to higher wavenumber for Lewis acid site was observed, and at higher wavenumber a new absorbed peak for Brönsted acid site was formed. These results suggest that fluorine enhances the acidity of titania, which can be explained by the formation of two kinds of fluorides. This result is consistent with that obtained by alumina, that is, fluorine enhances the acidity of alumina.

5. Conclusions

Fluorine incorporation on the titania support lead to the formation of two kinds of fluorides. With lower fluorine content (≤0.94 wt.%) only one kinds of fluoride is formed. Further increase in the fluorine content (≥2.07 wt.%) results in the formation of two kinds of fluorides. ESR analysis confirmed the presence of Ti^{3+} species.

Co–Mo catalysts supported on F–TiO$_2$ show higher HDS activity than those supported on unmodified titania. This increase is attributed to the formation of fluorides and Ti^{3+}. The fluorine-modified titania would be more easy to be sulfided to TiS$_2$ and TiS$_{1.5}$, which lead to the formation of TiMoS phase for Mo-based catalyst under H$_2$ atmosphere.

Acknowledgements

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