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Interactions between heavy metals and clay matrix in fluid catalytic cracking catalysts

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Abstract

The interactions between heavy metals (vanadium and nickel) and kaolin had been investigated by X-ray diffraction and MAT test. In the process of phase transformation of kaolin containing 1–5% vanadium, vanadium-mullite phase emerged surprisingly at 660–700 °C. The unit cell size of the mullite was found to increase with increment of vanadium content. As compared with hydro-kaolin, acid-modified kaolin (AMK) and caustic-modified kaolin (CMK) reacted with vanadium to form much more mullite; CMK could even be reacted with nickel to form a rather stable $NiAl_{10}O_{16}$ compound, and this compound protected zeolite in fluid catalytic cracking catalyst effectively. The catalyst containing AMK had greater MAT activity retention than that of the contrastive catalyst with hydro-kaolin in the identical level of heavy metal contamination.

Keywords: Kaolin; Nickel; FCC catalyst; Vanadium; Mullite; Eutectic; Unit cell size

1. Introduction

Heavy metals such as vanadium and nickel existing in petroleum feedstock have the most significant impact on the fluid catalytic cracking (FCC) catalyst's performance [1]. During the cracking process, these metals are deposited on the catalyst and affect both catalytic activity and selectivity. The major effect of nickel is to produce additional hydrogen and coke, while vanadium, in addition to increasing gas and coke production, causes partial destruction of the zeolite under steam. In the case of nickel, the lower activity is primarily due to coke deposition and can therefore be regenerated. In the case of vanadium, the loss in activity is primarily due to zeolite destruction and is irreversible. Therefore, the study of the interactions between these metals and the components of FCC catalysts has remained an important research topic to refiners and catalyst manufacturers.

Commercial FCC catalysts contain faujasite (or zeolite Y) dispersed in a clay matrix (mainly kaolin). Although the zeolite provides most of the cracking activity of the FCC catalyst, the matrix fulfills both physical and catalytic functions. As to the interactions of Ni and V species with FCC catalyst, a great amount of research work had been focused on the active component (zeolite Y), and little concern had been given to kaolin matrix that amounts to 20–60% in FCC catalyst [2–4]. The interaction of vanadium–kaolin was conventionally considered as a physical process in which vanadium species were buried partially in kaolin through adsorption and were therefore passivated. In fact, vanadium species have mobility in the presence of steam at 700–800°C [1], and can migrate onto the surface of zeolite to destroy its framework. So such anti-metal contamination performance of FCC catalyst containing kaolin matrix could not be explained through the physical process [2,3]; it is therefore important to gain a deeper insight into the interaction of Ni and V–kaolin.

In this research, the interaction of Ni and V–kaolin has been intensively investigated by X-ray diffraction technique and MAT test. We aim to find out why FCC catalyst containing kaolin matrix performs well in anti-metal roles.

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2. Experimental

Acid-modified kaolin (AMK) was prepared from a metakaolin and HCl solution, as described elsewhere [3]. One hundred grams of kaolin calcined at 800 °C for 1 h was added to a 300 ml solution containing 21.9 g HCl and reacted at 92 °C for 12 h. The reaction mixture was dried at 120 °C for 12 h. Caustic-modified kaolin (CMK) was prepared from a pyrokaolin and NaOH solution, as described elsewhere [2]. One hundred grams of kaolin calcined at 1000 °C for 1 h was added to a 300 ml solution containing 50 g NaOH and reacted at 95 °C for 2 h. The reaction mixture was washed, filtrated and dried.

Catalysts were contaminated by the procedure of the Mitchell method [5]. A suitable amount of ammonium vanadate or nickel nitrate was added to the sample. The mixture was ground thoroughly and heated at 540 °C for 3.5 h, and then calcined at 600–900 °C for 1–6 h. The X-ray diffraction patterns were recorded on a Rigaku D/max-3C diffractometer using Cu kα radiation; pure silicon was used as internal standard for angle calibration. The unit cell parameters of mullite were determined by X-ray diffraction with a least square method, and its relative content was determined using the ratio of diffraction peak intensity in the area of Miller indices 1 2 1 (*h k l*). MAT conversion of catalyst was tested according to ASTM Method D-3907.

3. Results and Discussion

3.1. Chemical interaction of kaolin–vanadium

Kaolin samples containing different amounts of vanadium were heated at 750 °C for 2 h in air. There was no obvious new phase formation detected by X-ray diffraction when vanadium was less than 0.5%; a little amount of new phase emerged if vanadium was about 1.5%. When the vanadium content increased to 3.0–5.0%, a great amount of the new phase formed in a short time. A typical X-ray diffraction pattern of the new phase is shown in Fig. 1. It was identified as mullite phase by comparison with PDF 15-776(Powder Diffraction File, Inorganic Phase, Published by the International Centre for Diffraction Data, JCPDS, USA, 1988. PDF cards that follow are quoted like this).

It was surprising that the mullite phase appeared at such a low temperature in the above-mentioned reaction system. Mullite phase emerged at not less than 1200 °C through silica and alumina reaction while it arose at more than about 1000 °C in the phase transformation of kaolin [6,7]. The temperature of mullite formation dropped to 750 °C in the transformation of kaolin loaded with a suitable amount of vanadium, which showed that vanadium reacted significantly with kaolin.

3.2. Change of mullite's unit cell parameter

Mullite is an aluminosilicate consisting of chains of octahedral aluminum atoms parallel to the c axis cross-linked by silicon or aluminum atoms in tetrahedral coordination. A variety of synthetic mullite types can be prepared from solid solutions of silica and alumina. The silica-rich ($3Al_2O_3{\cdot}2SiO_2$) and alumina-rich ($2Al_2O_3{\cdot}SiO_2$) phases are called α- and β-mullite respectively. Substitution of aluminum in mullite can cause a change of the unit cell parameter and unit cell size [8]. Typically, mullite displays an orthorhombic structure. In order to understand the structure change of mullite formed at lower temperature, the calculated unit cell param-

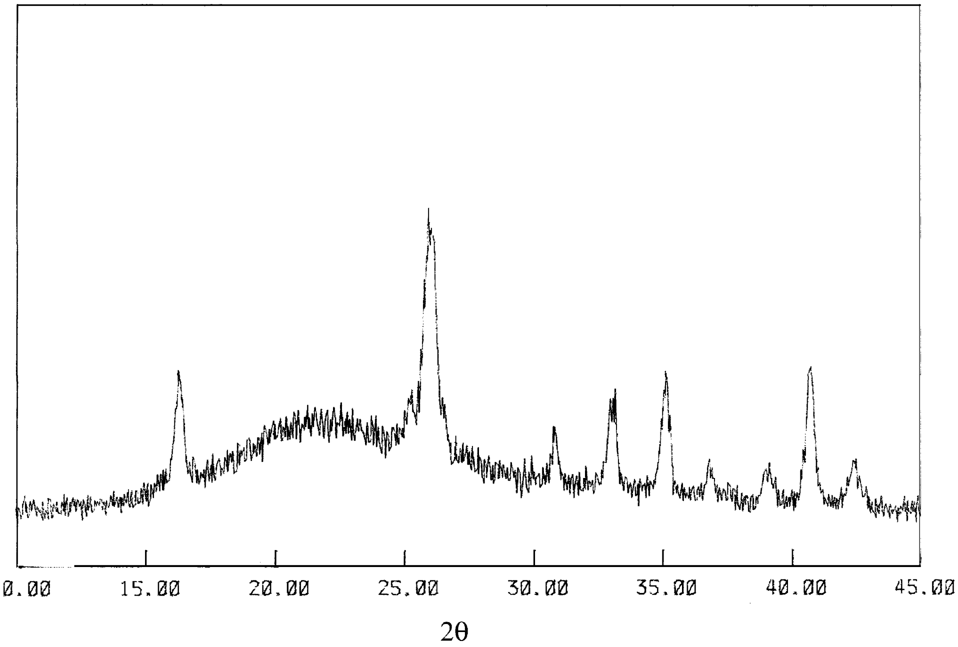

Fig. 1. XRD pattern of kaolin heated in air at 750 °C/2 h in the presence of 5.0% vanadium.

Table 1
The determination of mullite's unit cell parameters

Sample	Vanadium content (%)	a_o (nm)	b_o (nm)	c_o (nm)	Unit cell size ($nm^3 \times 10^3$)
m-5	5.0	0.7605	0.7693	0.2896	169.43
m-23	3.0	0.7592	0.7685	0.2887	168.44
m-24	1.5	0.7587	0.7672	0.2888	168.10
m-10	0	0.7546	0.7688	0.2884	167.31
PDF card[a]	0	0.7546	0.7690	0.2884	167.35

[a] 15–776.

eters for several mullites are shown in Table 1. The unit cell size of pure mullite sample (m-10) was nearly equal to the value in PDF card 15-776,which indicated that the method of determination was reliable [8]. With the vanadium content increasing from 1.5 to 5.0%, the unit cell size of mullite expanded continuously. The cell dimensions shown in Table 1 indicate that vanadium caused an expansion of the unit cell volume, resulting mainly from an increase in a dimension. Thus, V incorporation into these mullites probably occurs mainly by substitution of Si or Al atoms in the cross-linking tetrahedra. Vanadium substituting into mullite crystal structure in place of Si (+4) or Al (+3) would normally be in either the V (+3) or V (+4) oxidation state. Both of these ions should be larger than the Si or Al ions, so the unit cell size will increase with vanadium substitution. Vanadium was passivated through incorporation into the framework of mullite, which was probably the reason that kaolin exhibited certain anti-vanadium contamination performance in the FCC catalysts.

3.3. Process of mullite formation

Mullite formation through kaolin phase transformation had been investigated early [7], while the process of low temperature phase transformation by addition of vanadium has not yet been found in the literature. The effect of vanadium load on mullite content formed through kaolin transformation is shown in Fig. 2. The amount of mullite formation increased quickly with vanadium increment in kaolin. Other experiments had shown that when vanadium content amounted to 5%, a large amount of mullite formed even if the calcination time was only 10–15 min. Mullite formation did not increase with increasing calcination time, but much cristobalite (SiO_2) emerged. The mullite phase could be found even if the temperature dropped to 660°C which was almost equal to the melting point of V_2O_5 (670 °C). One could deduce that the reaction of mullite formation during kaolin phase transformation was a process of low eutectic transition. When calcination temperature increased to the melting point of V_2O_5, it began to smelt and combined with meta-kaolin to form a eutectic. The bond of Si–O and Al–O could happen to cleave, migrate and rearrange in the eutectic, resulting in components suitable to mullite formation. When the control rate step of kaolin phase transformation finished, the mullite phase formed rapidly.

3.4. Interaction of modified kaolin–Ni and V

Heavy metals existing in petroleum feedstocks are mainly Ni and V. The chemical interaction of modified kaolin–Ni is shown in Fig. 3. The NiO phase was rather distinctive in the products of interaction of kaolin and acid-modified kaolin (AMK) with nickel oxide ($2\theta = 43.5°, 37.2°$ as shown in PDF 4-0835), pointing to the fact that they could not react with nickel. In the product of caustic-modified kaolin (CMK) and nickel reaction, NiO phase could not be examined, in-

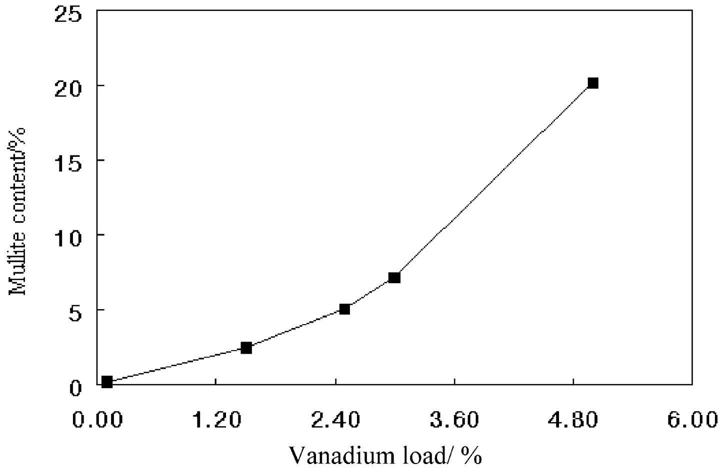

Fig. 2. Effect of vanadium loading on mullite content formed through kaolin phase transformation (750 °C/2 h).

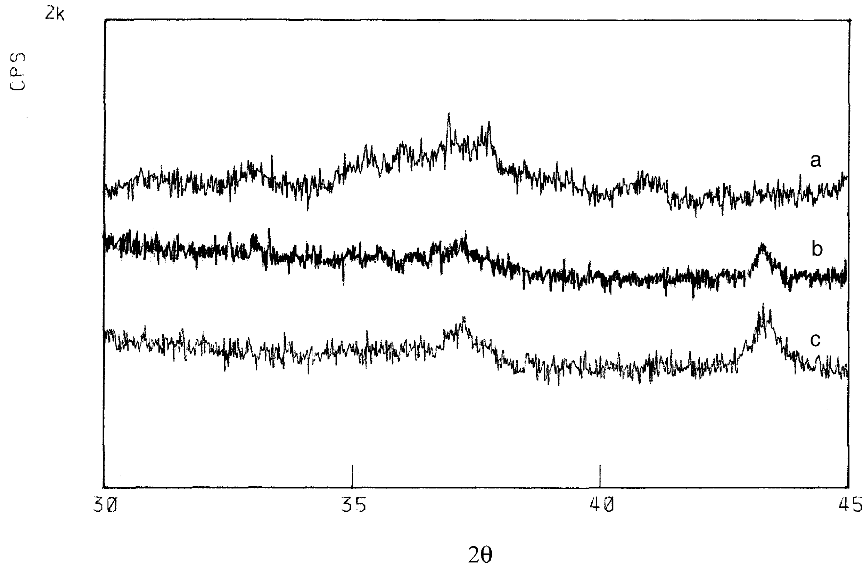

Fig. 3. XRD patterns of product of nickel–kaolin interaction(Ni = 50%, 750 °C/2 h): (a) CMK, (b) AMK, (c) hydro-kaolin.

dicating that CMK reacted with nickel and formed a new crystal phase—$NiAl_{10}O_{16}$ ($2\theta = 37.6°$ and 37.0° as shown in PDF 37-1292) that was more stable than $NiAl_2O_4$ [4]. This was why CMK displayed excellent anti-nickel contamination performance in FCC catalyst. Furthermore, in comparison with hydro-kaolin, modified kaolin (AMK, CMK) could react with vanadium to form more mullite in the same reaction conditions (as shown in Fig. 4 in which the two extra diffraction lines near 25° that did not appear in Fig. 1 may be assigned to the phase of titanium oxide that existed in hydro-kaolin examined by PDF 4-0477 and PDF 4-0551), which leads to excellent anti-vanadium contamination performance [2,3].

3.5. Role of catalyst's matrix in anti-vanadium contamination

There were two matrices—hydro-kaolin and acid-modified kaolin (AMK) to be considered. Interactions of the two matrices in cracking catalysts (calcined REY served as active component) with vanadium are shown in Figs. 5 and 6. In Fig. 5, when the vanadium content amounted to 0.75%, the XRD patterns of REY almost disappeared after treatment of 750 °C/2 h in 100% steam. In RE-containing Y crystals it is believed that Ce^{4+}, present as an oxycerium complex, is preferentially loaded near the supercages where it can more readily react with vanadium species and form

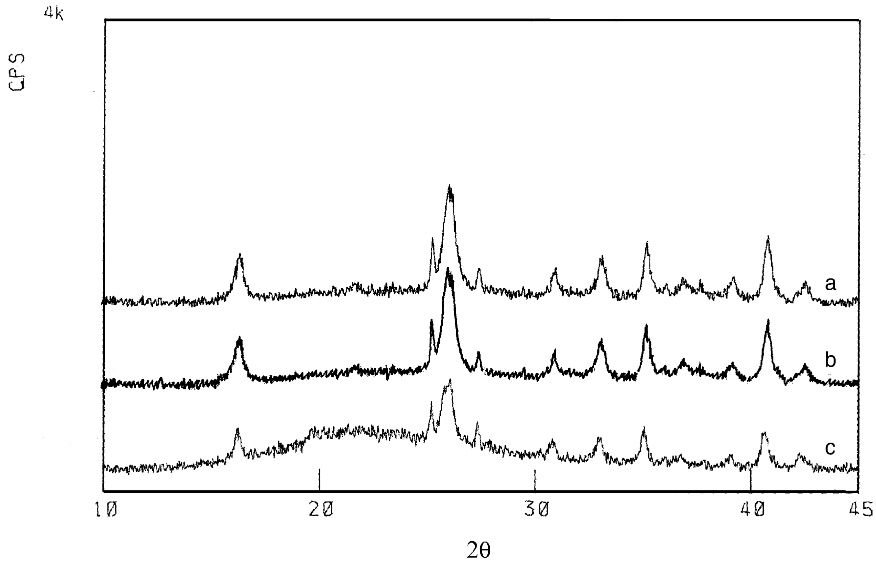

Fig. 4. XRD patterns of product of vanadiun–kaolin interaction (V = 50%, 750 °C/2 h): (a) CMK , (b) AMK , (c) hydro-kaolin.

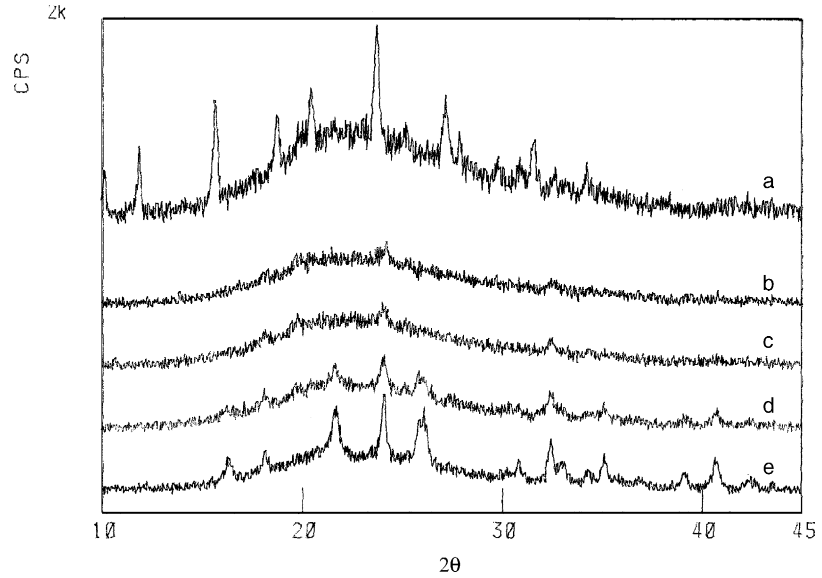

Fig. 5. XRD patterns of product of hydro-kaolin cracking catalyst reacting with different vanadium (V) content (750 °C/2 h): (a) 0, (b) 0.75%, (c) 1.5%, (d) 2.5%, (e) 5.0%.

cerium vanadate [8]. The diffraction peak in $2\theta = 24.0^{\circ}$ actually indicated that the rare earth in REY had already reacted with V_2O_5 to form rare earth vanadate, such an interaction resulted in destruction of the zeolite's framework. The amount of rare earth vanadate increased with increasing vanadium. When vanadium content amounted to 2.5%(pattern d in Fig. 5), a little mullite phase came out, accompanying with some cristobalite phase ($2\theta = 21.9^{\circ}$). These results showed that hydro-kaolin could react with vanadium to form mullite only after REY zeolite reacted with vanadium to form rare earth vanadate, and then the zeolite was destroyed seriously, indicating that zeolite was not protected effectively by hydro-kaolin matrix. As to the AMK matrix—acid-modified kaolin, its interaction with vanadium is shown in Fig. 6. When vanadium content was about 0.75% (pattern a in Fig. 6), the diffraction intensity of REY zeolite dropped to some extent, and some mullite phase emerged simultaneously. With the vanadium content increased to 2.5% (pattern d in Fig. 6), there were still weak diffraction peaks of zeolite, which indicated that the framework of REY zeolite hadn't yet been destroyed completely. The amount of mullite phase increased gradually, but rare earth vanadate couldn't be observed yet when vanadium content was not more than 2.5%. It could

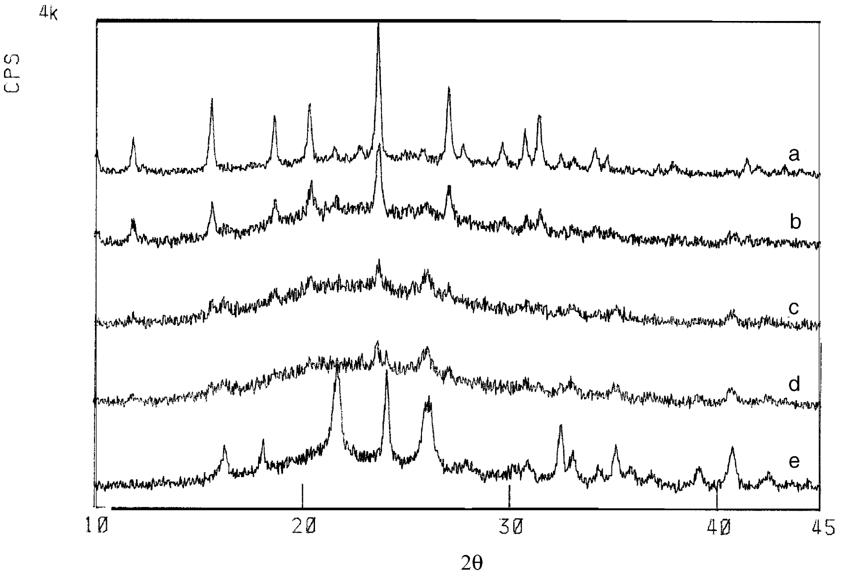

Fig. 6. XRD patterns of product of AMK cracking catalyst reacting with different vanadium (V) contents (750 °C/2 h): (a) 0, (b) 0.75%, (c) 1.5%, (d) 2.5%, (e) 5.0%.

Table 2
Performance of Nickel (3000 ppm) and Vanadium (5000 ppm) loaded catalysts

Catalyst[a,b]	MAT (%)		MAT retention (%)
	Fresh	Contaminated	
A	72	58	81
B	69	45	65

[a] Catalyst A: 25% calcined REY + 60% AMK + 15% Al_2O_3 (used as adhesion agent).

[b] Catalyst B: 25% calcined REY + 60% hydro-kaolin + 15% Al_2O_3 (used as adhesion agent).

be inferred that the rare earth oxide coming from partially destroyed REY zeolite did not react with vanadium immediately, while it reacted predominantly with AMK matrix to form vanadium-mullite phase. These results mean that AMK matrix could protect REY zeolite effectively. When vanadium amounted to 5.0% (pattern e in Fig. 6), the REY zeolite was thoroughly destroyed, accompanied with large amount of rare earth vanadate and cristobalite forming. As shown in Table 2, the catalyst containing AMK (catalyst A) had greater MAT retention than that of the catalyst B in the identical level of heavy metal contamination. The preferential reaction of vanadium species with AMK and vanadium incorporation of mullite were probably the main causes that can be used to rationalize the structural stability of REY crystals when steam-aged in the presence of vanadium.

4. Conclusions

An obvious chemical reaction between Ni and V and kaolin matrix took place at about 700 °C. In the presence of suitable vanadium, the temperature of mullite formation during kaolin phase transformation was at least 400 °C lower than the conventional mullite formation temperature. Vandium partially replaced Si and Al in the framework of mullite and was therefore passivated, which led to expansion of mullite's unit cell size. Vanadium-mullite forming through kaolin phase transformation in the presence of vanadium at 660–700 °C resulted in good anti-metal performance of the FCC catalyst containing modified kaolin matrix (AMK,CMK).

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