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A new concept for catalysts of asphaltene conversion

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Abstract

One must understand the mechanism of bottoms cracking in asphaltene conversion in order to design a catalyst to affect this change. Asphaltene molecules are big, multiple stacked, porphyrin structures containing high concentrations of heteroatoms. They readily deactivate catalysts. Until now, the first stage of asphaltene conversion has not been given much attention. This first stage, that of demetallization, has been regarded as a simple metal take-up zone which guards the subsequent hydrotreating portion of the catalyst from undue fouling by metal sulfides. Large pore size and good strength are more important for a demetallization catalyst than are hydrotreating activity. Supported sepiolite catalysts and modifications thereof are good candidates to meet these targets.

Keywords: Cracking; Conversion; Demetallization; CCR reduction; Hydrotreatment; Hydrodesulfurization; Asphaltene; Catalyst; Sepiolite; Alumina; pH swing

1. Introduction

Crude oil being supplied today throughout the world has a comparatively high API gravity and low sulfur content. However, in the future, it is expected that the quality of the available crude will decline, that the API gravity will decrease and the sulfur content rise. At the same time, demand for distillate products such as kerosine and gas oil will increase with no change in the demand for heavy oil.

The imbalance between increasingly lower quality crude oil and higher demand for distillate products cannot be resolved without upgrading residual oil. Hydrotreatment is a preferable approach to upgrading residual oil, since it pretreats, cracks and hydrodesulfurizes the oil. However, asphaltenes contained in residual oil are hard to crack because of their size, stacking, and porphyrin content. Sepiolite-supported catalysts are good candidates for a bottoms conversion catalyst.

2. The hydrotreating process

The purposes of hydrotreating residual oil are:

1. production of a low sulfur fuel oil;
2. cracking to produce mid-distillate;
3. pretreatment of RFCC or Coker feedstocks.

In the hydrotreating process, a large pore size cracking and demetallization catalyst is used in the front end and a high activity hydrodesulfurization catalyst is employed subsequently. The lead reactor can be considered to be simply a guard reactor for removing metals. However, it also cracks asphaltenes, thus, facilitating their hydrodesulfurization later.

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Large pores facilitate the hydrotreatment of the macromolecular asphaltenes, allowing them to diffuse into the catalyst pores, after which the stacked sheets of asphaltenes disintegrate when metals or heteroatoms such as sulfur in the asphaltenes are removed to produce the basic structure of a condensed polycyclic aromatic compound. At this point, the remaining structures reacting on the catalyst are almost the same as the so-called 'maltene' structures in the residual oil.

If the catalyst has pore size so large as to facilitate the diffusion of all the asphaltene molecules within the catalyst, it may become too physically weak to be useful and the surface area may decline to the point that the activity of a catalyst falls. Therefore, catalysts in use today cannot transport all asphaltene molecules to the catalyst surface through the smaller pores necessary to maintain strength and surface area. This situation leads to thermal reactions in which asphaltenes undergo an increased degree of polycondensation. As a result, the product oil consists of hydrogenated maltenes and high polycondensed asphaltenes. These materials become increasingly incompatible, and ultimately this can result in a portion of the product being deposited as dry sludge.

3. Characteristics of sepiolite catalyst

A catalyst for hydroprocessing heavy residual oil must have a pore size distribution designed so that it is not easily plugged and the rate of reaction is not controlled by the pore diffusion of the reacting substance. However, Fig. 1 shows that when a catalyst is manufactured with larger pore size [1], the catalyst crush strength declines significantly. An effective commercial catalyst must have a specific pore structure for processing heavy residual oil and the mechanical strength for practical use at the same.

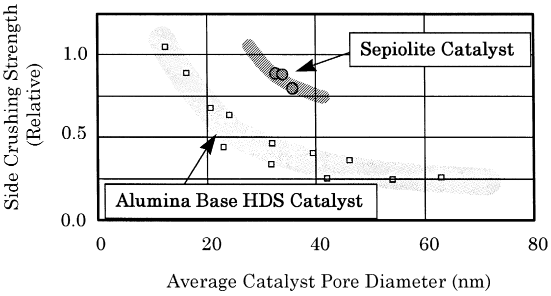

Fig. 1. Mechanical strength of the sepiolite catalyst.

A proprietary asphaltene conversion catalyst was proposed in 1979 containing sepiolite [2]. It has specific characteristics of chemical composition, pore structure and catalyst crushing strength that alumina catalysts do not have [3]. The resistance of sepiolite catalysts to coke deposition is better than that of alumina catalysts, and it has excellent capability for asphaltene cracking and metal removal. Fig. 2 plots the catalyst activity of the original sepiolite catalyst

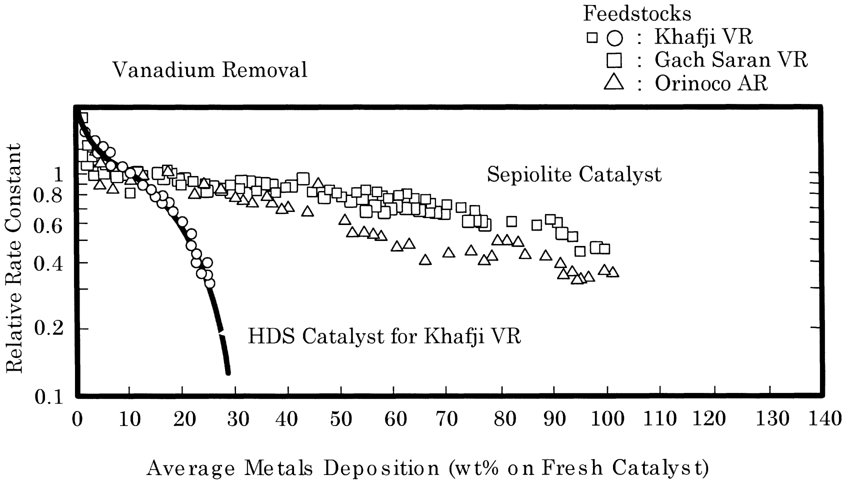

Fig. 2. Sepiolite catalyst activity and stability.

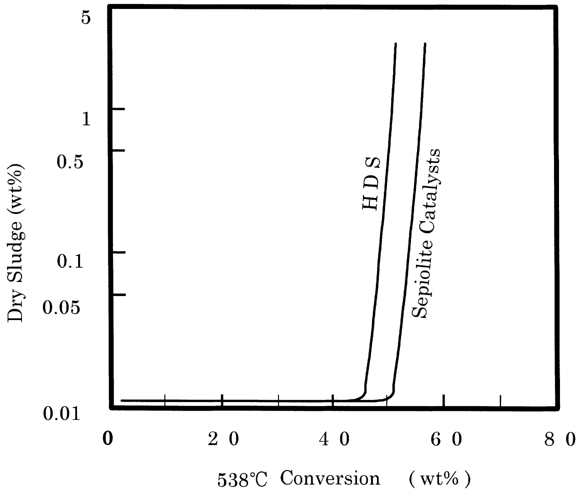

Fig. 3. Effect of conversion on dry sludge formation.

for vanadium removal against average metals deposition in the catalyst bed. The activity of the original sepiolite catalyst decreases very slowly until the metals deposition reaches about 70 wt%. It shows that the original sepiolite catalyst has a superior stability in catalytic hydroprocessing of heavy oils containing a high level of asphaltenes and metals.

Recently, it has become very common to operate residue HDS units at elevated temperatures to hydroconvert heavier atmospheric residual bottoms to more valuable products in a trade-off with hydrogen consumption [4]. In the mode of such a residual conversion in the HDS process, the maximum conversion is controlled by the compatibility of bottoms, not by the cracking activity of the catalyst [5]. When conversion is increased over a certain limit, the product oil becomes unstable and easily forms dry sludge. Fig. 3 shows the predicted amount of dry sludge sedimentation. The maximum conversion obtained with the sepiolite catalyst is clearly higher than that of the conventional HDS process. The original sepiolite catalyst allows higher conversion without dry sludge formation.

The characteristics of high asphaltene cracking activity and moderate hydrogenation activity of the sepiolite catalyst are well suited in the hydroconversion of residual oil, and maximum conversion is expected to be more than that of alumina catalysts.

4. Improvement of sepiolite catalyst

Although the original sepiolite catalyst, as mentioned above, performs well in asphaltene cracking and metal removal with a large metal capacity, its hydrodesulfurization activity was not satisfactory and it was hard to increase its HDS activity. The dispersion of active metals over the catalyst support was inferior compared to the alumina catalyst. The activity of desulfurization could not be improved by simply increasing the amount of supported metal on catalyst. Figs. 4 and 5 show that activities for hydrodesulfurization and metal removal were not improved beyond that of 5–8 wt% supported molybdenum.

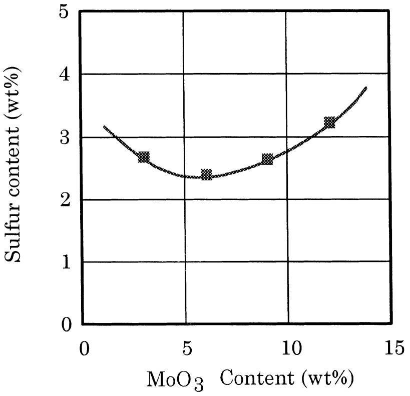

Fig. 4. Correlation between supported metal and content and desulfurization activity on the original sepiolite catalyst.

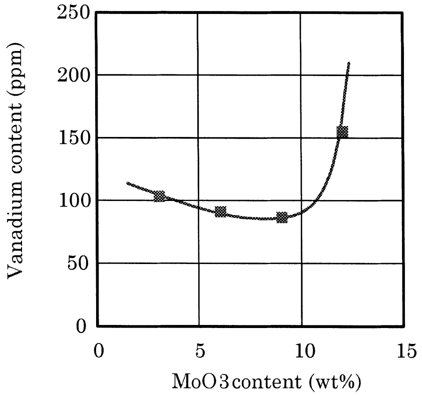

Fig. 5. Correlation between supported metal and content and vanadium removal activity on the original sepiolite catalyst.

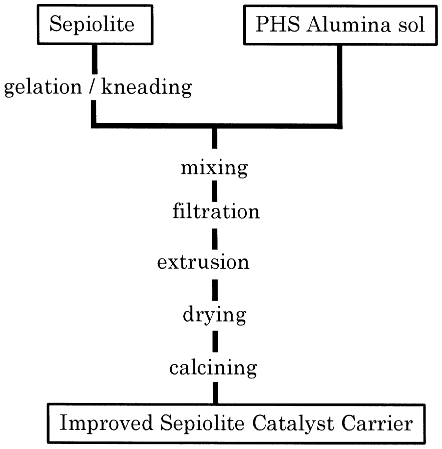

Fig. 6. Improved sepiolite catalyst, manufacturing method.

Several efforts were carried out to improve hydrodesulfurization activity without sacrificing the specific characteristics of the sepiolite catalyst such as catalyst crushing strength and resistance to metal and coke deposition.

4.1. Alumina blending

Alumina blending with the sepiolite carrier was one solution to improve hydrodesulfurization activity. Fig. 6 shows the procedure for manufacturing the improved sepiolite catalyst. The proprietary manufacturing procedure using the pH swing (PHS) method [6] had been developed to make alumina catalyst carriers with uniformly sized and shaped pore structures [7]. Fig. 7 shows the sharp pore size distribution of typical PHS alumina. The numbers correspond to the number of PHS. Repeated PHS increase the pore diameter and the pore volume of the alumina carrier.

The blending ratio of alumina was changed using two kinds of alumina with different crystal sizes in the catalyst preparation. The effects of alumina blending on the activity of the sepiolite catalyst for sulfur, asphaltene and vanadium removal are shown in Figs. 8–10, respectively.

They show that the catalytic activity was improved by increasing the alumina ratio. The figure also shows the optimum ratio of alumina blending varied depending on the respective reaction and the kind of alumina.

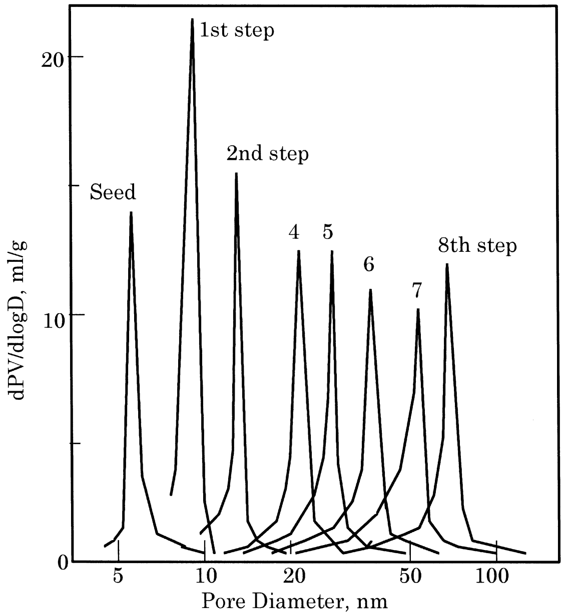

Fig. 7. Sharp pore size distributions of typical PHS aluminas.

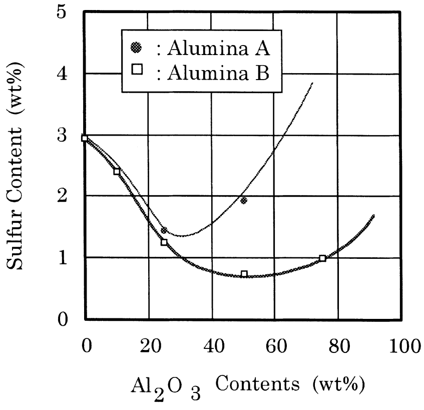

Fig. 8. Effect of alumina addition to the sepiolite catalyst for the desulfurization.

The results suggest that the dispersion of supported metal and micropore distribution of the catalyst were greatly improved by alumina blending with the sepiolite carrier. However, excess alumina blending decreased the activity. Hydrodesulfurization allowed higher alumina blending than asphaltene removal. The results imply that the blending of alumina with the sepiolite carrier affects diffusion into catalyst micro-

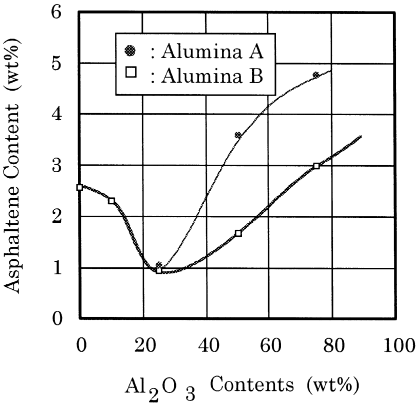

Fig. 9. Effect of alumina addition to the sepiolite catalyst for asphaltene removal.

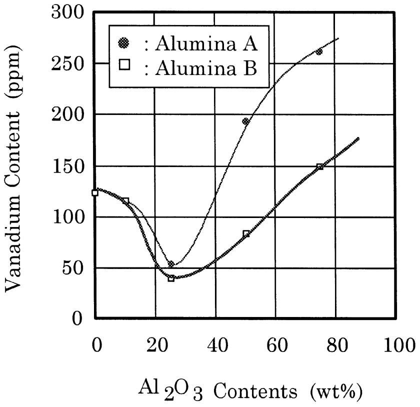

Fig. 10. Effect of alumina addition to the sepiolite catalyst for vanadium removal.

Table 1
Improved catalyst activity

Reaction	Reaction order, *n*	Relative rate constant (improved cat./original cat.) 25% alumina	50% alumina
Asphaltene cracking	2	1.7	1.5
Metal removal			
Vanadium removal	1	1.4	1.3
Nickel removal	1	1.4	1.5
Desulfurization	2	1.5	2.1
Denitrogenation	2	2.1	2.3
CCR reduction	2	1.5	1.2

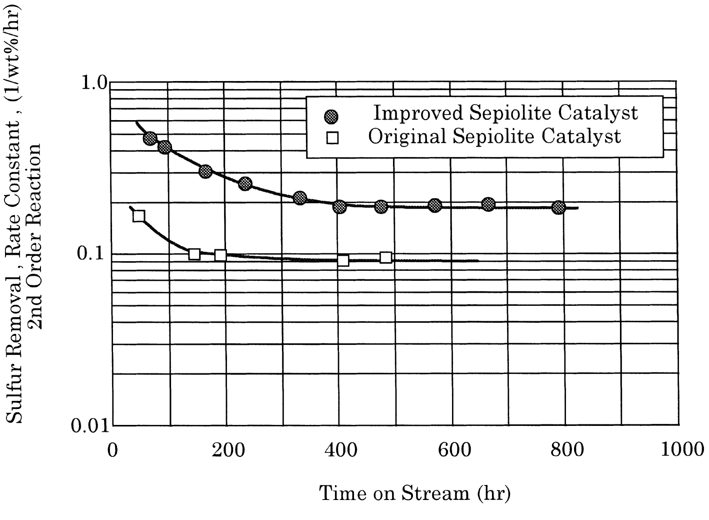

Fig. 11. Sulfur removal activity and stability of the improved sepiolite catalyst.

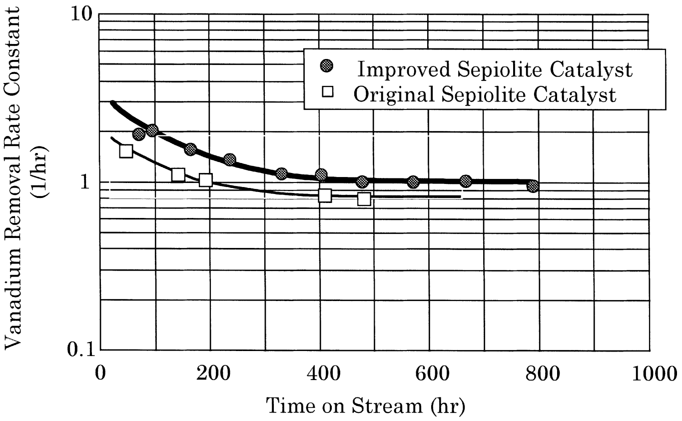

Fig. 12. Vanadium removal activity and stability of the improved sepiolite catalyst.

pores depending on reactant size. Alumina blending increases dispersibility of active metals but also increases microporosity, and thus, diffusional resistance.

4.2. *Increasing the amount of active metals*

The activity of the original sepiolite catalyst could be remarkably improved by increasing amounts of active metals with an optimum blending ratio of alumina.

The activity of improved sepiolite catalyst compared with the original catalyst, when manufactured in semi-commercial equipment, is shown in Table 1 for two types of catalysts with different alumina and active metal contents. The improvements of the relative rate constants for a catalyst aged by 5 wt% metals deposition are shown for the reactions of asphaltene, vanadium, sulfur, nitrogen removal and CCR reduction against the original sepiolite catalyst. The degree of activity improvement for various kinds of reactions depends on the amount of catalyst

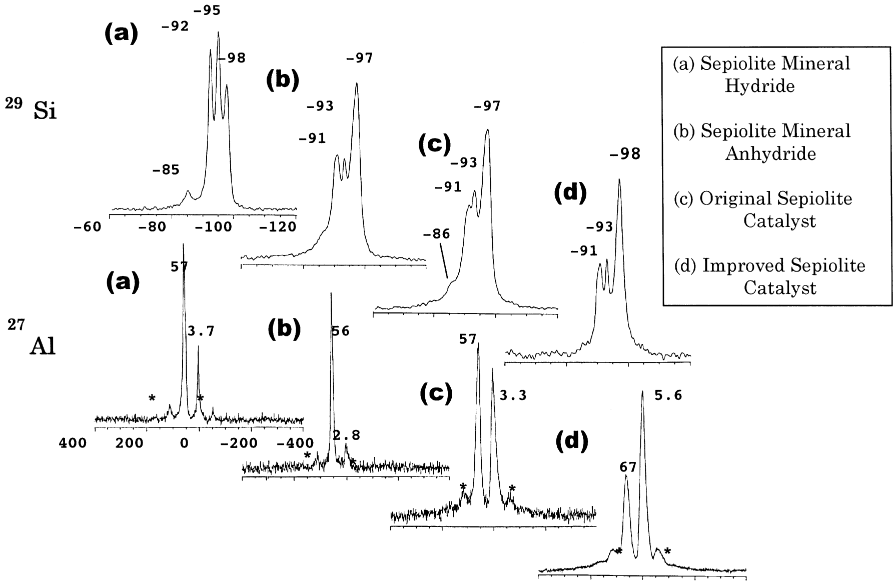

Fig. 13. MASNMAR spectra of sepiolite catalyst.

metal and the blending ratio of alumina to sepiolite. Fig. 11 shows that the improved catalyst has much higher hydrodesulfurization activity and activity maintenance than that of the original catalyst. The hydrodesulfurization activity is stable after 400 h on stream, while the activity is twice as high as that of the original sepiolite catalyst. Fig. 12 also shows that the activity for vanadium removal is also highly stable.

The catalyst is expected to maintain activity for at least 1 year from the data accumulated for the original sepiolite catalyst.

5. Properties of modified sepiolite catalyst

5.1. Solid-state NMR

^{29}Si-MASNMR spectra for (a) sepiolite mineral, (b) sepiolite mineral calcined at 723 K, (c) original sepiolite catalyst and (d) improved sepiolite catalyst obtained without cross polarization (CP) are shown in Fig. 13. All spectra exhibit three major signals at −91 to −92, −93 to −95 and −97 to −98 ppm. Barron et al. [8] have reported and assigned the resonance peak at −97 to −98 ppm to the edge silica

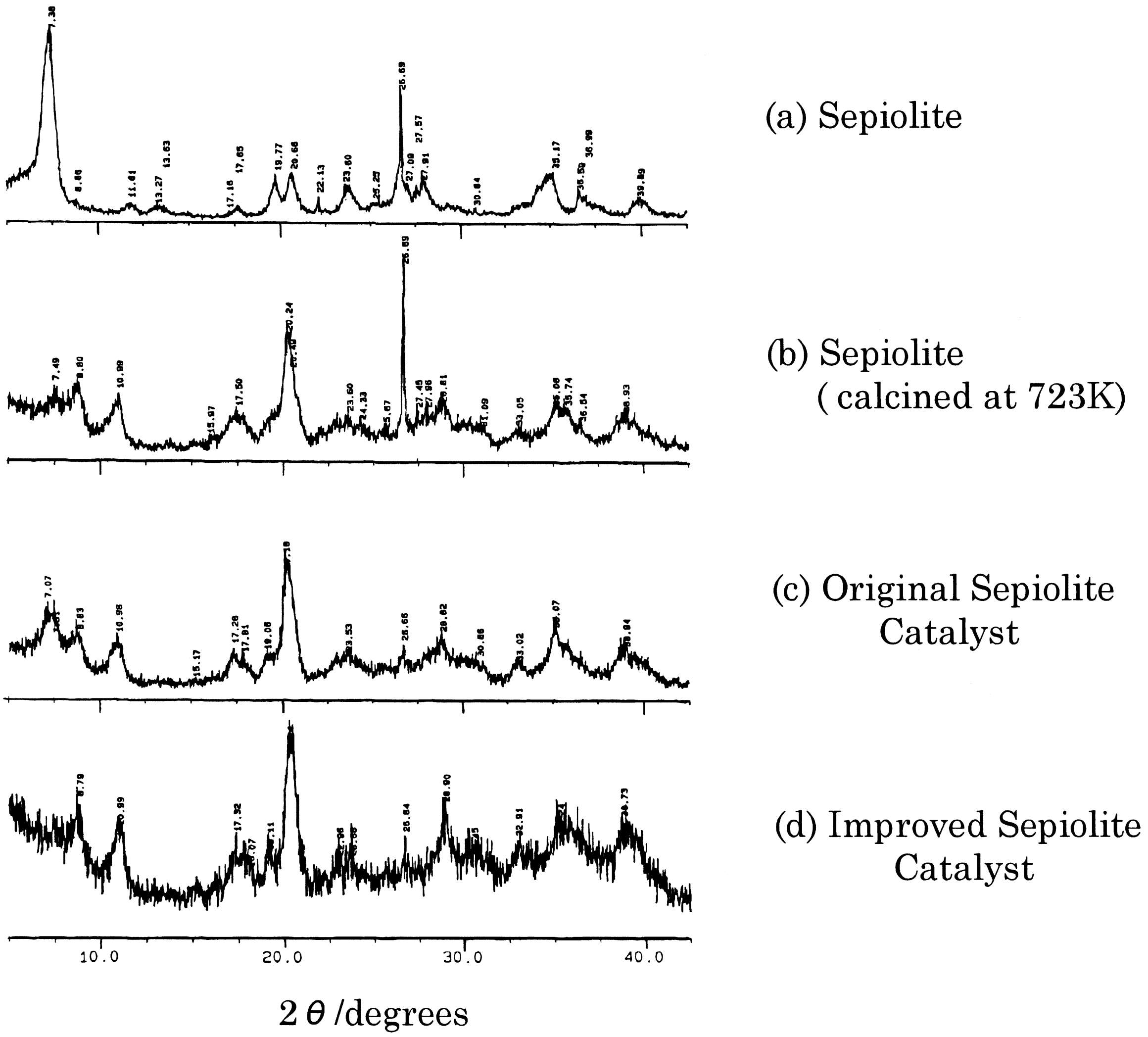

Fig. 14. XRD patterns of sepiolite catalyst.

in the ribbon structure and two other peaks to the near edge silica. The weak resonance line at -85 ppm is attributed to the terminal SiOH (Q3 (Si–1OH)) in the micropores. There is no appreciable difference in ^{29}Si-MASNMR spectra among (b)–(d), indicating no changes in the short range ordering on silicon atoms of sepiolite crystal structure among them in spite of the contents of physically mixed alumina.

The resonance lines at 56–57 ppm in ^{27}Al–MASNMR spectra are assigned to Al atoms in the tetrahedral layer substituted for Mg atoms, while the line resonating at 3–4 ppm are attributed six fold Al atoms at the edge of the layer generated as $AlO_4(OH)_2$. It is impossible to observe directly the Al components in the sepiolite crystal structure, for the ^{27}Al resonance lines due to physically mixed alumina are obtained in the same chemical shift ranges.

5.2. XRD patterns

Fig. 14 shows XRD patterns of sepiolite and catalysts. The patterns for sepiolite catalysts, physically mixed with even 50% alumina (d), show diffraction peaks attributed to crystalline sepiolite indicating that the crystal structure is maintained.

6. Conclusion

1. The activity of sepiolite catalyst was improved by optimum blending of suitable alumina to the sepiolite carrier.
2. A further improvement of catalytic activity was obtained by increasing the amount of active metals because the dispersibility of active metals was improved by the optimum blending of the best suited alumina.
3. The sepiolite catalyst is expected to be widely employed with the new technology of controlling its hydrodesulfurization activity by alumina blending; either in a high conversion process for residual bottoms with a relatively low hydrogenation activity, or in the front–end reactor of a deep desulfurization process with a high hydrodesulfurization activity.

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