

PREPARATION OF NI-MO CATALYSTS USING THE PILLARED CLAY AS A SUPPORT FOR HYDRODESULFURIZATION OF COKER NAPHTHA

HIDRODESULFURISASI COKER NAFTA DENGAN MENGGUNAKAN KATALIS NI-MO YANG BERPENYANGGA LEMPUNG BERPILAR

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ABSTRAK

Pada preparasi katalis Ni-Mo, salah satu syarat yang dibutuhkan adalah luas permukaan penyangga katalis yang besar untuk mendistribusikan logam Mo secara merata di permukaan penyangga. Adapun suatu cara yang menjanjikan adalah menggunakan lempung berpilar (pillared clay) sebagai penyangga katalis. Oleh karena itu, studi tentang preparasi katalis Ni-Mo dengan menggunakan lempung berpilar sebagai penyangga serta kemampuan katalis tersebut pada reaksi penghilangan senyawa sulfur Coker nafta dilakukan pada penelitian ini. Efek dari pH larutan impregnasi Mo juga diteliti. Hasil penelitian menunjukkan bahwa proses pilarisasi dengan menggunakan penyangga Al telah berhasil dilakukan. Hal ini ditunjukkan dengan kenaikan luas permukaan dan pergeseran ruang basal (d_{001}) dari lempung setelah dipilarisasi. Pada nilai pH-10 untuk larutan impregnasi Mo, aktivitas katalis Ni-Mo berpenyangga lempung berpilar menunjukkan kemampuan dua kali lebih aktif pada reaksi penghilangan senyawa sulfur Coker nafta dibandingkan pH-1, namun masih kurang aktif dibandingkan katalis komersial Ni-Mo. Hal ini disebabkan masih terbentuknya fasa MoO_3 pada katalis Ni-Mo yang dipreparasi.

Kata Kunci: Preparasi, Ni-Mo, Lempung berpilar, Penghilangan sulfur, Coker nafta

ABSTRACT

On the preparation of the Ni-Mo catalysts, a high of surface area of the support was needed in order to achieve the well dispersion of Mo on the support. One of the promising ways is the use of pillared clays as the support. Therefore, the preparation of pillared clay for a support of Ni-Mo catalyst and its effect on the hydrodesulfurization (HDS) reaction for sulfur removal of Coker naphtha were studied. The effects of pH of the Mo impregnation solutions were also studied. The results show that the pillarization process on clay using Al-pillared is significantly increased the surface area. Moreover, with the pH of the impregnation solution of 10, Mo is higher dispersed on the pillared clay support compared to pH-1, and thus the HDS activity of NiMo pillared clay catalyst of pH-10 is also more active. However, the HDS activity of the present catalysts is still not good enough compared to the commercial NiMo catalyst.

Keywords: Preparation, Ni-Mo, pillared clay, hydrodesulfurization, Coker naphtha

INTRODUCTION

Besides the environment protection to produce clean fuels by zero sulfur emission, the efficient utilization of limited natural resources are also the most urgent topic issues recently in petroleum industry. Catalysts based on molybdenum sulfide

promoted by nickel or cobalt are widely used in the refinery industry,¹⁻³ particularly for the hydrodesulfurization (HDS) reaction. Because of their importance, numerous research efforts have been accomplished in order to prepare advanced HDS catalysts, in particular highly active for deep hydrodesulfurization of oil refinery streams. It is

now well accepted that the active sites of these catalysts are the-so-called Co(Ni)-Mo-S phase, in which Co(Ni) atoms are located on the edge of MoS₂ particles.² Therefore, the preparation of a greater amount of Co(Ni)-Mo-S is a key step for attaining higher catalytic activity, such as by improving the dispersion of Co(Ni) and Mo on the support.¹⁻⁵

The well dispersion of Mo and promoter Co(Ni) on the support are depended on the specific surface area of the support.^{2,4-6} With the high surface area of the support, more amount of Mo could be dispersed on the surface support, and thus more amount of the active sites could be obtained. One simple and effective method to get the support with the higher surface area is to use the pillared interlayer clays (PILC).^{1,7-9} Pillared interlay clays have received attention due to the capability to modulate their surface area, porosity, acidity and thermal stability, and thus can be used as catalyst and/or as support of HDS catalysts.^{8,9} Moreover, PILC shows properties similar to those of the zeolites, which have shown that the HDS activity of 4,6-dibenzothiophene enhanced when they were combined with CoMo or NiMo as the active metals.^{3,10} However, detailed roles of Mo and promoted Ni on the PILC support remain still ambiguous because the literatures discussing about CoMo or NiMo sulfide supported on PILC are limited.

Therefore, the objective of the present study was to investigate the Ni-Mo catalysts using a PILC as the support for the HDS reaction of Coker naphtha. A pillared interlayer clays using Al as a pillaring agent (Al-PILC) was prepared, and then the Al-PILC support was impregnated to active metal Ni-Mo by the double impregnation method to prepared Ni-Mo/PILC catalysts. We also investigated the effect of pH of the Mo impregnation solution on Ni-Mo/PILC catalysts related to the structure as well the HDS activity. The prepared catalysts were characterized by means of a variety of physicochemical techniques, and the catalytic activity was measured on the HDS reaction of Coker naphtha, then correlation between structure and activity were discussed. The catalytic activity of commercial Ni-Mo catalyst (BASF M8-24) was also measured for comparison.

EXPERIMENTAL

Materials and the preparation methods of the PILC as the support and Ni-Mo/PILC catalysts are explained in this section as well the characterizations of those prepared catalysts. Moreover, sulfidation process and the HDS activity of Coker naphtha are also included.

Preparation of Al-PILC support and Ni-Mo catalyst

The starting material for the Al-pillared clay (Al-PILC) used as support was a montmorillonite from Sigma Aldrich. This clay is a dioctahedral with chemical formula (Na,Ca)_{0.3}(Al,Mg)₂Si₄O₁₀(OH)₂•n(H₂O), high purity and Ca-rich mont-morillonite. Ca, Mg, and Na is the main exchangeable cation on montmorillonite with the specific surface area (S_{BET}) around of 210 m²g⁻¹. The pillaring method was carried out in the present study according to the procedure of Salerno et al.⁸ using the pillaring agent of 91% aqueous solution of Al₁₃ Keggin cation type. The synthesized procedure of Al₁₃ Keggin cation was detailedly described by Hsu et al.¹¹ This pillaring solution was added drop-wise carefully to 10 wt% suspension of the natural clay under stirring until pH of the solution mixtures about 4.1, then continued the stirring for 24 h. The amount of aluminium was used around of 10 meq Al g⁻¹ clay. The final suspension was centrifuged to separate the solution, then was washed by dialysis with distilled water until free of ions, dried in oven at 373 K and finally calcined at 673 K for 6 h. The Al-pillared clay thus prepared is designed as PILC hereinafter.

Two catalysts containing only Mo and Ni-Mo catalysts supported on the PILC were prepared by double impregnation method (Mo first and then Co) using (NH₄)₆Mo₇O₂₄•4H₂O (AHM) and Ni(NO₃)₂•6H₂O (Ni nitrate) aqueous solutions, followed by drying at 383 K over night and calcined at 773K for 5 h after each step. The Ni and Mo were fixed at 3 wt% Ni and 8.7 wt% Mo with respect to PILC, respectively. In the present study, pH of the Mo impregnation solution was adjusted to pH 1 and pH 10 by using 0.1 M HNO₃ and NH₄OH solution. The catalysts thus prepared hereinafter are denoted as Mo/PILC and NiMo/PILC.

Characterizations

The textural properties of Al-PILC support (specific surface area) prepared by the pillaring method was evaluated on a Quantosorb (Quantachrome, US) nitrogen physisorption apparatus. Prior to the measurements, the sample was degassed at 673 K for 5 h under He gas. Surface areas were determined by physical adsorption of N₂ at a liquid nitrogen temperature, using the BET equation.¹² Moreover, X-ray powder diffraction (XRD) measurements of the support of PILC and the calcined Mo/PILC and NiMo/PILC catalysts were carried out on a X-ray Diffraction apparatus (X'Pert – Phillips, Netherlands) with 30 kV and 15 mA, equipped with an automatic divergence slit. The radiation source was Cu K_{α1,2} ($\lambda = 1.541841$ Å) with a Ni filter.

The amounts of oxides content on PILC and the calcined NiMo/PILC catalysts were determined by means of X-ray Fluorescence (XRF) analysis at Research Center for Metallurgy, Serpong. The FTIR spectra of the calcined Mo/PILC catalysts were recorded in a transmission mode at room temperature on a single-beam FTIR spectrophotometer (JASCO, Japan). After cooling to room temperature, the IR spectra were measured and background spectrum was subtracted. The detailed procedures have been described elsewhere.¹³

Reaction procedure

In order to evaluate the initial activity of the freshly prepared catalyst, we conducted the activity of the catalysts in Coker naphtha HDS was simultaneously measured in a high-pressure fixed-bed flow micro-reactor (MCB-890, Vinci Tech., France) with catalyst volume 2 ml (particle size 0.2–0.5 mm). The operation condition was conducted at H₂ pressure 3 MPa; LHSV 10 h⁻¹; H₂/liquid ratio of 72 and at temperatures around of 583 K. The feedstock was Coker naphtha containing of S enriched with 400 ppm and the reaction was carried out for 15 h. Before the HDS reaction, the fresh catalyst was sulfided insitu with 1.5 wt% dimethyl disulfide/diesel mixtures at 3 MPa and 503 K for 2 h. The contents of S in the feed and products were analyzed by means of XRF analysis at Pertamina UP.III, Balongan. From fractional

conversion, the HDS activity of the catalysts was calculated in terms of first order respect to the S concentration, k_{HDS} .¹⁴ The reproducibility of the HDS activity test was better was $\pm 4\%$.

RESULTS AND DISCUSSION

In order to explain the characterization and catalytic activity data of the prepared catalysts were obtained after measurements, we divided into three parts in this section, which are detailed described about the physicochemical properties of the pillared clay, Mo dispersion and Ni-Mo/PILC catalysts characterization, and the HDS activity of the prepared catalysts.

Physicochemical properties of the pillared clay (PILC)

In the present study, we prepared of the PILC support by the pillaring technique using Al in two times (PILC-1 and PILC-2), and the textural properties (specific surface area) of montmorillonite and the PILC supports derived from the N₂ adsorption-desorption isotherms are depicted in Figure 1. The specific surface area of PILC is considerably increased after the pillaring technique, in particular for PILC-1 (277 m²g⁻¹). It is evident that the pillaring process on montmorillonite is obtained using the Al pillaring agent. The increase of specific surface area of clay after the pillaring process is one of methods to get information that the pillarization was done successfully.^{7,15,16} Moreover, the increase of specific surface area using Al as pillaring agent is around of 200–400 m²gr⁻¹.^{7,16} However, Figure1 also shows that the surface area of PILC-2 is not notably increased. We suggest that is due to sensitivity in adjusting the pH of the solution mixtures on the preparation step of the pillaring process of montmorillonite, according to the procedure of Salerno et al.,⁸ PILC-1 will be used as the support in the present study afterward.

Another method for obtaining an information about the pillared clay process was well occurred, is by calculation of the basal spacing (d_{001}) of clay from XRD measurement at small range of 2-theta (2θ) around of 0°–10°. ¹⁵⁻¹⁷

The XRD patterns of clay before and after the pillaring process are shown in Figure 2. It is clearly shown that the basal spacing (d_{001}) of the original clay (Figure 2a) changed from 7.04° becomes 6.24° and 6.56° after pillaring followed by drying and calcinations, respectively (Figs. 2b,c). Moreover, the intensity of clay diffraction peak at 8.81° is also decreased after the pillaring process. The changed of basal spacing (d_{001}) and decreasing of the diffraction peak intensity at 8.81° ascribed that Al was interacted with the clay between the phyllosilicate layers of clays to form pillared after calcinations,¹⁵⁻¹⁷ and thus the pillaring process was well occurred.

Table 1 shows the oxides composition of clay before and after the pillaring process. The amount of CoO was significantly decreased and almost zero while the Al content was drastically increased. This result can be explained that all the Ca^{2+} cation between the phyllosilicate layers of clays are exchanged with Al by the pillaring technique, thus becomes the pillared after calcinations,¹⁵⁻¹⁷ in agreement with the changed of the surface area and the basal spacing of clay (Figs 1 and 2) after the pillaring process. It is concluded

that the pillaring process of clay (montmorillonite) in the present study is successfully obtained.

Mo dispersion and Ni-Mo/PILC catalysts characterization

Figure 3 shows the XRD patterns of Mo/PILC catalysts as a function of pH of the Mo impregnation solution. The XRD patterns in Figure 3 showed MoO_3 diffraction peaks at 2-theta around of 23.3° , 27.3° and 49.2° are observed even at pH-1 or pH-10 (Figs. 3b,c).⁶ It is indicated that some of Mo was not well dispersed on the PILC support. However, if the diffraction peaks of MoO_3 between pH-1 and pH-10 were compared, in particular at 23.3° , we observed that the intensity of MoO_3 diffraction peak at pH-10 was weaker compared to pH-1, indicating that the amount of MoO_3 phases was low at pH-10. The formation of MoO_3 phases is not wanted due to decreasing the active phase Ni-Mo-S after sulfidation.⁶ Therefore, we suggest that the Mo/PILC catalysts at pH-10 is more active compared to pH-1. Moreover, the FTIR spectra of the Mo/PILC catalysts as a function of pH of the Mo impregnation solution

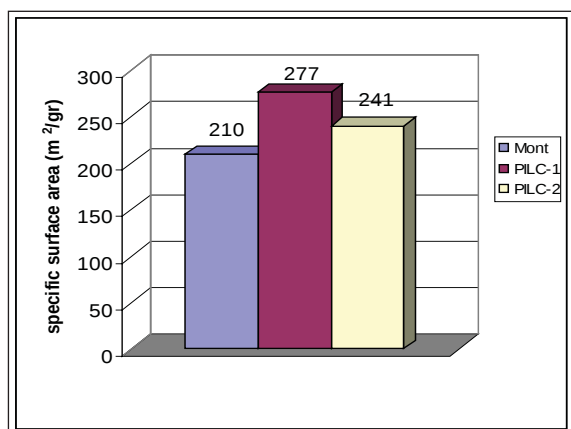


Figure 1. Surface area of clay before and after the pillaring technique.

Table 1. The oxides composition of clay before and after the pillaring process from XRF measurement.

Oxides Composition (wt%)	Clay	PILC-1
CaO	0.167	0.006
SiO ₂	65.599	57.142
Al ₂ O ₃	26.550	35.599

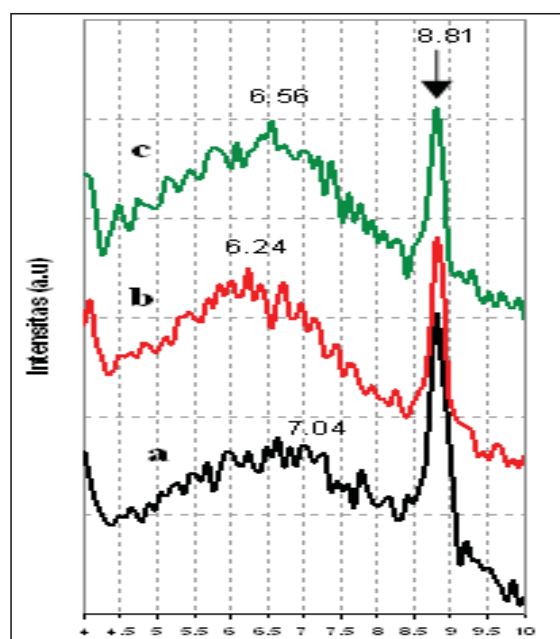


Figure 2. XRD patterns of the clay prepared by the pillaring process using the Al_{13} Keggin cation type solution (PILC-1). (a) before the pillaring, (b) after the pillaring and drying and (c) after the pillaring and calcinations.

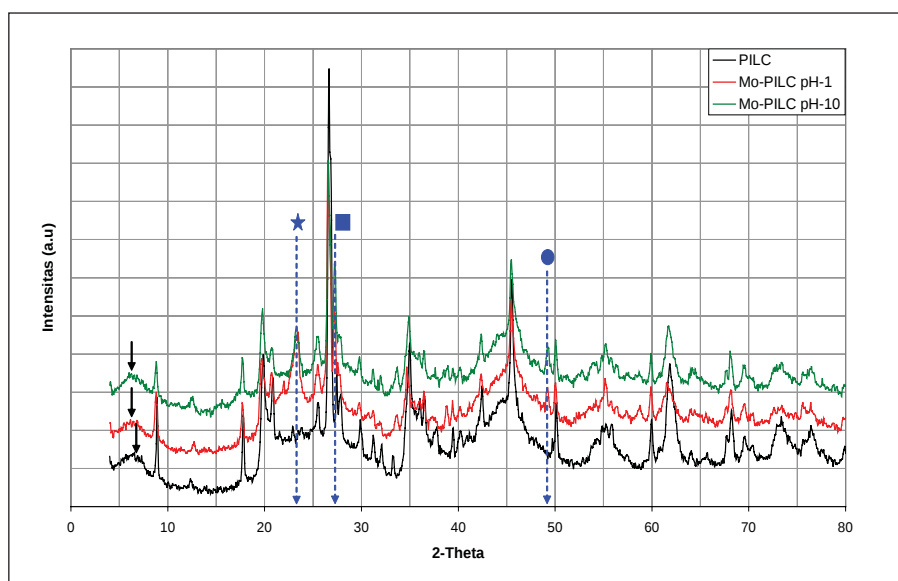


Figure 3. XRD pattern of the Mo/PILC catalysts as a function of pH of the impregnation solution. (a) The PILC support, (b) Mo/PILC at pH-1 and (c) Mo/PILC at pH-10. ★▲● = MoO₃ and ▼ = d₀₀₁.

are depicted in Figure 4. It shows that the spectra of Mo/PILC catalysts were observed at the bands 665, 707, 800, 894, 944 and 1055 cm⁻¹ even at pH-1 and pH-10. The bands at 944 cm⁻¹ was assigned as the FTIR spectra of MoO₃,¹⁸ while for the MoO₄²⁻ spectra was observed at band of 894 cm⁻¹,¹⁸⁻²⁰ and the remains of bands at 1055, 800, 707 and 665 cm⁻¹ were corresponded to $\nu_s(\text{Si}=\text{O})$ stretching vibration mode of the PILC support. Although the spectra of MoO₃ and MoO₄²⁻ were observed on the Mo/PILC catalysts at pH-1 and pH-10, the intensity of MoO₃ spectra at pH-10 in Figure 4c was weaker compared to pH-1 (Figure 4b) together with the high intensity of MoO₄²⁻ at pH-10, indicating that Mo was slightly well dispersed on the support at pH-10 than of pH-1. Thus, the Mo/PILC catalyst at pH-10 is more active compare to pH-1,⁶ in agreement with the XRD result (Figure 3). Nevertheless, from Figs 3 and 4, we still observed the formation of MoO₃ phases in spite of MoO₄²⁻ phases for both pH.

The dispersion of Mo on the support is depended on the isoelectric point (pH_{ZCP}) of the support.^{2,6-8} A well dispersion of Mo will be obtained if pH of the Mo impregnation solution is same with the pH_{ZCP} of the support. For example, Mo will be well dispersed on the Al₂O₃ support if pH of the Mo impregnation solution of pH-5 as

similar of the isoelectric point of the Al₂O₃ support.⁶ In case of the PILC support, the isoelectric of PILC is depended on the kinds of clay, which were used as the starting material, and still no accurately information about the pH_{ZCP} of PILC. Lo'pezCordero et al.²¹ showed that pH_{ZCP} of PILC using Al is around of 3.0 as similar to that of silica. However, due to the presence of free alumina (from some excess of hydroxyl-aluminium polycations used in pillaring) on the PILC surface, they also showed that the excess of Al may give rise of the pH_{ZCP} of PILC in which about of 8,9 in their worked.²¹ But, still no detailed information of pH_{ZCP} for montmorillonite is obtained.

Therefore, two pH values of the Mo impregnation solution were used in the present study, such as pH-1 and pH10, in order to get information about the well dispersion of Mo on the PILC support. With Figs 3 and 4, we still observed the formation of MoO₃ phases in the Mo/PILC catalysts, suggesting that the pH values of the impregnation solution, which were used in this present, was not accurate with the isoelectric (pH_{ZCP}) of montmorillonite, and thus unwell dispersed of Mo was still occurred on the PILC support (Figs. 3 and 4).

The Mo/PILC catalysts, then, were impregnated by Ni without adjusting of pH, and the XRD

patterns of NiMo/PILC catalysts are depicted in Figure 5. The XRD patterns of commercial catalyst are also included. After impregnation, the intensity MoO_3 spectra were decreased or even vanished, in particular at 2-theta of 23.3° , 27.3° and 49.2° (Figs. 5c and e). It is considered that when Ni was impregnated on the Mo/PILC catalysts, Mo was redispersed and thus the dispersion of Mo become increased,^{2,13} although some MoO_3 phases were still observed. Moreover, with the commercial catalyst (Figure 5f), no diffraction peaks were observed except the Al_2O_3 spectra, describing that Mo and Ni were well dispersed on the Al_2O_3 support, resulting large amount of active site, Ni-Mo-S, after sulfidation.²

Table 2 shows the oxides composition of the calcined NiMo/PILC catalysts as well the commercial catalyst from the XRF analysis. The NiMo/PILC catalyst at pH-10 showed large amount of Mo and Ni oxides compared to pH-1.

Although the amount of Mo oxides in Table 2 was not described the active site formation directly, at least we consider that more amount of Mo could be impregnated on the PILC support by using pH-10 of the impregnation solution than of pH-1, suggesting that large amount of the active site could be formed at pH-10. However, the amount of Mo and Ni oxides on the NiMo/PILC catalysts is lower than that of the commercial catalyst, indicating that the commercial catalyst is more active than the prepared catalysts.

Catalytic activity of Ni-Mo/PILC catalysts

The catalytic activity of fresh NiMo/PILC catalysts on the HDS reaction of Coker naphtha is described in Figure 6. After 15 h reaction time, the rate constant of the NiMo/PILC at pH-10 (Figure 6B) showed twice more active compare to pH-1. It is considered that the large amount of Mo was well

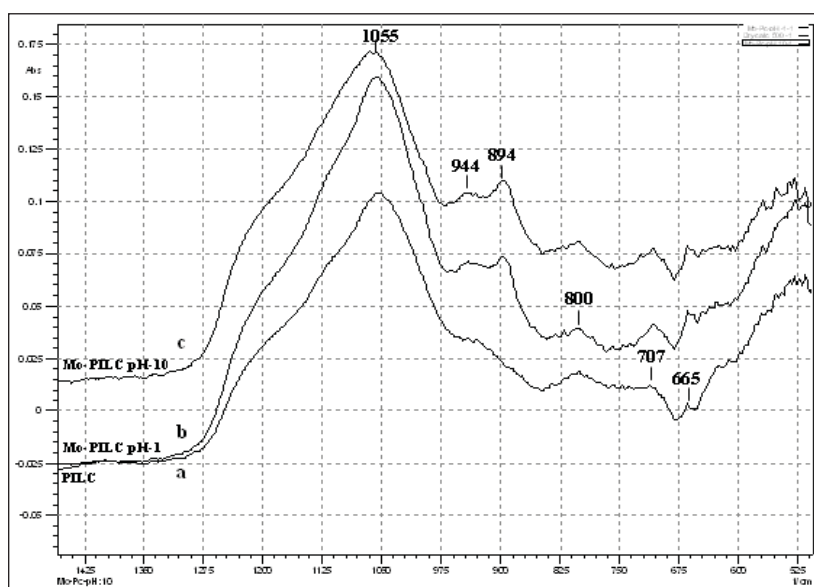


Figure 4. FT-IR spectra of the Mo/PILC catalysts as a function of pH of the impregnation solution. (a) the PILC support, (b) NiMo/PILC at pH-1 and (c) NiMo/PILC at pH-10.

Table 2. The oxides composition of the NiMo/PILC catalysts by the XRF measurement.

Catalyst	MoO_3 (wt%)	NiO (wt%)
NiMo/PILC pH-1	11.797	1.391
NiMo/PILC pH-10	12.031	1.459
Commercial Catalyst (BASF M8-24)	14.50	4.0

dispersed on the PILC support at pH of the Mo impregnation solution of 10 compared to pH-1, resulting large amount of active site, Ni-Mo-S, after the Ni impregnation and sulfidation at pH-10 although the MoO_3 phases were still observed. This is in agreement with the results in Figs. 3–5.

However, the HDS activity of the NiMo/PILC catalysts was less active compared to the commercial catalyst (Figure 6A). The difference between the both catalysts could be clearly explained not only due to the large amount of Mo on the commercial catalysts (Table 2), also the well dispersion of Mo is obtained on the

commercial catalyst compared to the NiMo/PILC catalysts (Figure 5). Thus, the formation of active site was larger on the commercial catalyst and more active than that of the prepared catalysts.

CONCLUSION

The pillaring process of Montmorillonite using Al_{13} Keggin cation type solution could be obtained from the increase of the surface area and the basal spacing (d_{001}) of the clay. With the pH of the Mo impregnation solution of 10, the dispersion of Mo on the PILC support is larger that that of pH-1, therefore the HDS activity of Coker naphtha on

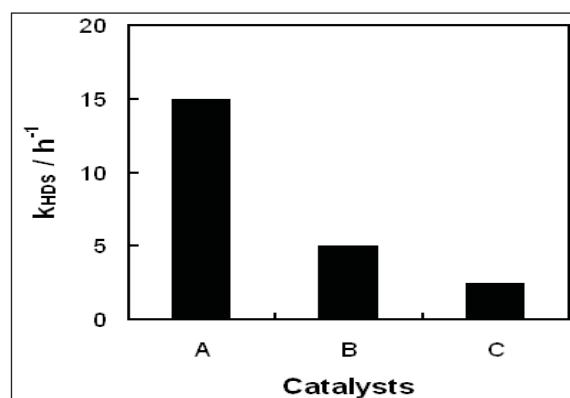


Figure 6. HDS activity of the Ni-Mo/PILC catalysts as a function of pH of the Mo impregnation solution. (A) Commercial Ni-Mo, (B) NiMo/PILC pH-10 and (C) NiMo/PILC pH-1.

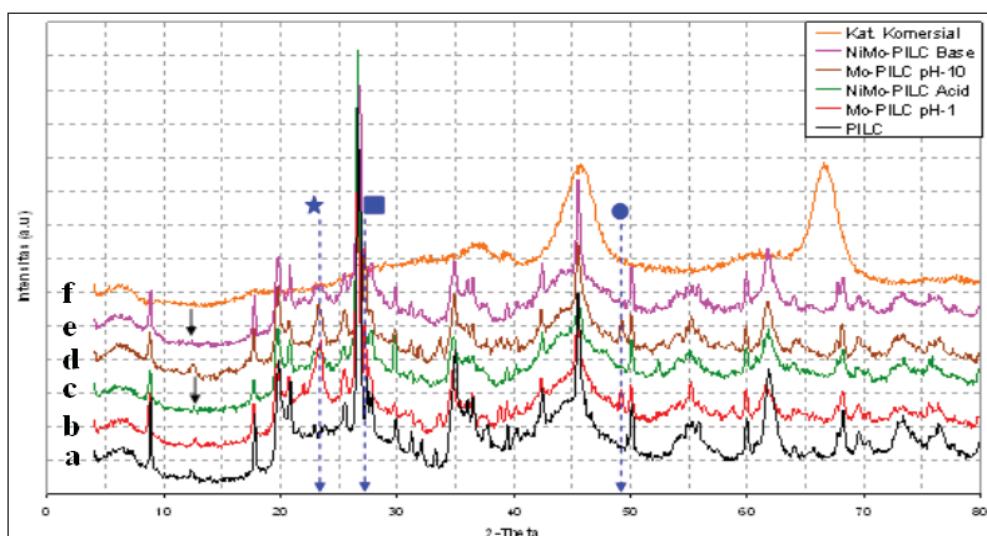


Figure 5. XRD pattern of the Ni-Mo/PILC catalysts as a function of pH of the Mo impregnation solution. (a) The PILC support, (b) Mo/PILC at pH-1 and (c) NiMo/PILC at pH-1, (d) Mo/PILC at pH-10, (d) NiMo/PILC at pH-10 and (f) commercial catalyst. ★▲● = MoO_3 .

the NiMo/PILC catalyst at pH-10 was twice active compared to pH-1, but still less active than the commercial Ni-Mo catalyst. We suggest that is due to the dispersion of Mo on the support. In the present study, the MoO_3 spectra were still observed for both pH systems, ascribing that the pH values of the Mo impregnation solution are not accurate with the pH_{ZCP} of the PILC support. Moreover, the PILC is one of promising materials to use as the support of HDS catalysts.

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