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Article

Preparation and Characterization of Immobilized Molybdenum Complex on Pillared Montmorillonite K-10

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***Abstract*— This study was carried out to immobilize molybdenyl (VI) acetylacetonate ($MoO_2(acac)_2$) complex on alumina pillared montmorillonite K-10 (MMT K-10). Pillar MMT K-10 was produced by introducing MMT K-10 with a hydrolysis solution of NaOH with $AlCl_3$. Different concentrations of pillaring solution were prepared in terms of OH^- to Al^{3+} ratio (0.5, 1.0, 1.5 and 2.0) to observe the structural characteristics of MMT K-10. The pillared materials were then immobilized with 0.1 M $MoO_2(acac)_2$ and were characterized using X-ray diffractometry (XRD), scanning electron microscopy coupled in an energy dispersive X-ray spectrometer (SEM-EDX) and Fourier transform infrared spectroscopy with attenuated total reflection (FTIR-ATR) techniques. FTIR bands at ca. 890 – 930 cm^{-1} indicate that the Mo complex was immobilized on the surface of pillared MMT K-10 not in between the layers. This is supported by the SEM and XRD analysis where the SEM micrograph showed deposition of Mo on the surface of MMT K-10 as well as no modification of basal spacing was observed by XRD. Meanwhile, the d(001) spacing of the alumina pillared MMT K10 samples were seen to increase slightly as the concentration of OH^-/Al^{3+} increased.**

***Keywords*— Montmorillonite K-10; Molybdenum (VI) acetylacetonate complex; alumina pillaring.**

I. INTRODUCTION

Montmorillonite (MMT) is the major clay mineral of bentonite (2:1 smectite group clay) and have considerable potential as catalytic materials for various types of reaction due to their large surface area and cation exchange capacity [1],[2]. There are considerable methods which can be used to modify MMT to improve its catalytic properties, such of these methods include cation exchange [3], acid treatment [4] and organically modified MMT [5].

Montmorillonite was pillared in order to obtain catalyst supports or catalyst. Polyhydroxymetal ions were normally used as pillaring agent such as Al, Fe, Zn, Mn, Co, and Si [6],[7],[8]. These metal ions were able to separate the layer of clay and thus increasing the surface area, porosity, and acid sites of the clay. They were used in a wide range of catalysis reaction for example cracking [9], oxidation [6], methanol conversion [10] and hydrotreatment [11].

The pillaring solutions can be made by hydrolysis of aqueous solutions of NaOH and $AlCl_3$ to obtain $Al(OH)_3$, i.e. the polyhydroxyaluminium ion. The ratio of NaOH to $AlCl_3$ or OH^-/Al^{3+} is one of the important parameters in determining the incorporation of aluminium into the clay and consequently on the physicochemical properties of the clay [1]. The acidity of clay increases as the addition of pillaring solution. The process exposes the Brønsted and Lewis acid sites of the layers by propping up the clay layers. Moreover, the pillaring solution adds acid sites to the already existing hydroxyl groups and to aluminum. Today, the interests of many researchers are being focused on heterogenizing homogenous catalysts. This is because heterogeneous catalyst has some advantages over homogenous catalyst. It can facile separation and recovery of solid catalyst from the reaction mixture, while the homogeneous catalyst is difficult and expensive to recover. One of the technologies to produce heterogeneous catalyst is by the direct immobilization of metal complexes on montmorillonite K-10 (MMT K10) clay. It was stated that immobilization of the molybdenum complex on montmorillonite K-10 clay promotes oxidation reaction and this catalyst is highly reusable and could be used several times without any changes in its activity [2]. Because of the transition-metal complexes are often expensive to be purchased or prepared, the reusability of a support catalyst is the most important benefits of heterogeneous catalyst. Therefore, this study is focusing on immobilization of a liquid transition metal complex on pillared MMT K-10 clay and the produced materials were characterized their physical and chemical properties using XRD, SEM-EDX an FTIR analysis.

II. MATERIALS AND METHOD

A. *Preparation of Alumina Pillared MMT K-10*

Stock solutions of $AlCl_3$ for 0.4 M and NaOH at different concentrations (0.2, 0.4, 0.6, and 0.8 M) were prepared. Then pillaring solution was prepared by hydrolysis of aqueous $AlCl_3$ with NaOH solution at different OH^-/Al^{3+} ratio (0.5, 1.0, 1.5, and 2.0). NaOH (250 mL) at different concentration was added drop wise to $AlCl_3$ (0.4 M, 250 mL) with constant stirring and temperature was maintained at 80 °C during hydrolysis. After that, the pillaring solution was aged for 15 hours.

A homogeneous slurry of MMT K-10 was made by stirring a suspension containing 10 g of clay in 500 mL of distilled water. Then, this slurry was added into pillaring solution prepared as above and the mixture was stirred for six hours at 80 ºC. After that, the ion exchanged dispersion was filtered by using Buchner funnel. Then the filtrate was washed from free chloride ion and undergoes chloride test using $AgNO_3$. At the end, the clay was air-dried and then calcined at 400 ºC for 5 hours and identified as Al-MMT K-10 (*x*) where *x* represents OH^-/Al^{3+} ratio (0.5, 1.0, 1.5, 2.0).

B. Immobilization of Molybdenum Complex On Al-MMT K-10 (x)

9 g of Al-MMT K-10 at different OH^-/Al^{3+} ratio (0.5, 1.0, 1.5, and 2.0) was immersed in a solution of 0.1 M molybdenyl acetylacetonate ($MoO_2(acac)_2$) in toluene under magnetic stirring for 18 hours at room temperature and inert atmosphere. After that, the mixture of Al-MMT K-10 and $MoO_2(acac)_2$ was filtered and thoroughly washed with hot toluene in order to remove any unreacted metal complex. Finally, the obtained solid was dried at 110 ºC in a drying oven for 5 hours. Samples were labeled as Mo-Al-MMT K10 (*x*).

C. Characterization of Catalyst

X-ray diffraction (XRD) patterns were taken at ambient temperature by the use of a Siemens D500 diffractometer using Ni filtered Cu Kα radiation ($\lambda = 1.5418$ Å; 40 kV and 40 mA). Bragg's law, defined as $n\lambda = 2d \sin\theta$, was used to compute the crystallographic spacing (d) for the examined samples. For morphology determination, the micrographs from scanning electron microscopy (SEM) were accomplished on a JEOL JSM- 6300F microscope with an acceleration potential of 20 kV coupled in a Noran System Instruments EDX energy dispersive X-ray spectrometer (EDS). SEM images were taken using a back-scattering detector. IR spectra of the samples were recorded on a Varian 3100 FTIR Excalibur Series system equipped with MCT/A detector in the region 4000–700 cm^{-1} in ATR methods at a resolution of 16 cm^{-1} with 32 numbers of scan.

III. RESULTS AND DISCUSSION

A. XRD Analysis

X-ray diffraction patterns of the unmodified MMT K10 and the modified clays are given in Figure 1. Clearly, the crystalline structures of the clay samples were retained even after being modified through pillaring and immobilization processes. The diffraction peaks of MMT K10 detected were compared with previous work [12]. The diffraction peaks of d(001), d(003), d(110), d(130 – 200) and d(060) can be observed at 2θ 9.1º, 17.8º, 19.8º, 34.8º and 61.8º with the distances of 9.75 Å, 4.96 Å, 4.48 Å, 2.66 Å and 1.72 Å respectively. The MMT K10 structure can be confirmed with the presence of the d(060) peak located at 61.8º with the distance of 1.72 Å. Based on Srodon et al. [13], this can be concluded that the structure of MMT is an Al-rich 2:1 dioctahedral. Further analysis on the diffractogram reveals the existence of impurities of clay, i.e. muscovite and quartz [14].

As can be seen from the shift of the characteristic peak corresponding to d(001) spacing and the intensity of the peak, it is evident that some pillaring has taken place. The d spacing and intensity of the peaks of the samples are given in Table 1. The d(001) spacing of the alumina pillared MMT K10 samples were seen to increase slightly between the unmodified MMT K10 and pillared MMT K10 from 9.70 Å to ca. 10.10 Å. The result confirmed the slight enlargement in the interlayer of the MMT K10. The effect of concentration of OH^-/Al^{3+} was not clearly seen where the change of d values was significantly small. The introduction of Mo complex after pillaring step did not show any evidence of the change in d(001) spacing. This is in agreement with the previous works where it was stated that complex immobilization did not induce any structural modification in the clay matrix [2],[15].

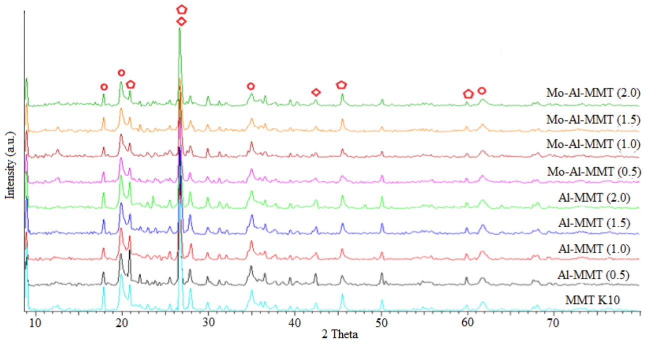

Fig. 1 XRD patterns of unmodified and modified MMT K10. Symbols ο – montmorillonite, □ – muscovite and ⬠– quartz.

TABLE I
XRD DATA OF RAW MMT K10 AND MODIFIED MMT K10 FOR d(001) PEAK

Sample	d spacing (Å)	Intensity (scan)
MMT K10	9.70	365
Al-MMT (0.5)	9.97	300
Al-MMT (1.0)	9.97	252
Al-MMT (1.5)	10.08	221
Al-MMT (2.0)	10.08	198
Mo-Al-MMT (0.5)	9.97	275
Mo-Al-MMT (1.0)	9.97	242
Mo-Al-MMT (1.5)	10.10	195
Mo-Al-MMT (2.0)	10.10	195

B. SEM Analysis

The surface integrity of MMT K10, Al-MMT K10 and Mo-Al-MMT K10 samples were evaluated from scanning electron microscopy (SEM). SEM micrographs (magnification 1000x) show changes in morphology between MMT K-10, Al-MMT and Mo-Al-MMT. The surface of MMT K-10 is smoky rather than Al-MMT which is finer and smooth in its surface structure. This could be due to the increasing in surface area of the montmorillonite clay.

For sample with the presence of Mo complex, it can be seen that the surface of Al-MMT were deposited or agglomerated with the Mo complex. The presence of pieces of Mo complex deposited on the surface of Al-MMT suggest that molybdenum might not be intercalated between the Al-MMT layer structure. This finding is in agreement with the XRD data where the d spacing values were remains unchanged after the modification with Mo complex as shown in Figure 2.

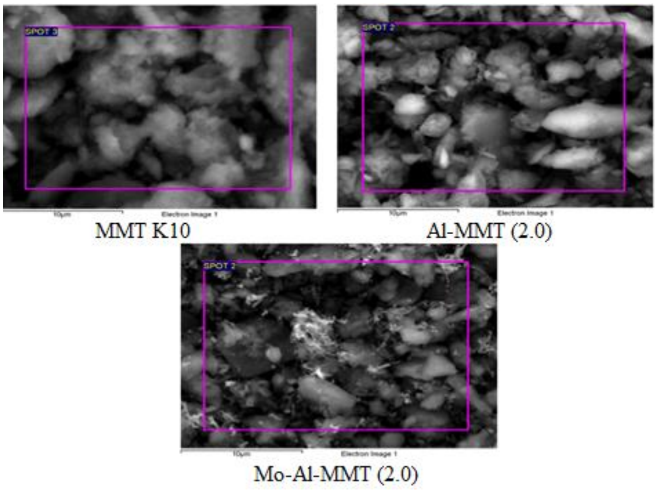
MMT K10
Al-MMT (2.0)
Mo-Al-MMT (2.0)

Fig. 2 Scanning electronic microscopy analysis (SEM) of MMT K-10, Al-MMT (2.0) and Mo-Al-MMT (2.0) in the same magnification (1000x)

Figure 3 shows the average weight percentage of Mo (calculated from EDX analysis) was slightly increased from OH^-/Al^{3+} ratio 0.5 to 1.5. However, for OH^-/Al^{3+} = 2.0 the average weight of Mo was decreased. As mentioned earlier, pillaring increases the acidity of the clay. The process exposed the Brønsted and Lewis acid site when the clay layer's was propping up and the pillars added acid site to the already existing hydroxyl group and to Al. Alumina is known to increase the Lewis acidity, while hydroxyl group is known to increase the Brønsted acidity.

Moreover, the increased OH^-/Al^{3+} ratio has improved the Brønsted acidity [16] and it reached the maximum for the sample with OH^-/Al^{3+} = 1.5. Obviously, OH^-/Al^{3+} ratio = 1.5 is the optimum concentration for the Al-MMT in immobilization of Mo. The higher the Brønsted acid sites on the clay layers, the higher molybdenum can be deposited on then Al-MMT surface. This could be due to the OH- on the surface of Al-MMT is bonded strongly to the Mo complex via hydrogen bond between acetylacetonate ligand and the OH^- on the surface [17].

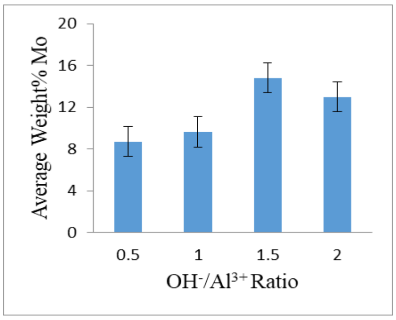

Fig. 3 The average weight% molybdenum complex on the surface of Al-MMT with different ratio of OH^-/Al^{3+}

C. FTIR Analysis

The FTIR spectra of MMT K-10, $MoO_2(acac)_2$, Al-MMT (1.5) and Mo-Al-MMT (1.5) are shown in Figure 4. Complex of $MoO_2(acac)_2$ exhibits two v(O=Mo=O) vibrations at about 930 cm^{-1} (υ_{sym}) and 895 cm^{-1} (υ_{sym}) which is confirming the presence of a cis-MoO_2 structure. Furthermore, the peaks for acac ligand, i.e. v(C=O) and v(C-O) appeared at about 1580 and 1260 cm^{-1}.

The MMT K-10 spectrum in the region 3700-3000 cm^{-1} and peak at 1630 cm^{-1} show two components associated with -OH stretching and bending vibration respectively. The band observed at ca. 3600 was assigned to -OH stretching vibration that originated from the Al-Al-OH stretch. Peak at around 1010 cm^{-1} was detected in all IR spectra of MMT samples. It represents the complex Si-O stretching vibration band [12].

Similar band patterns were observed for the IR spectra of MMT K10, Al-MMT (1.5) and Mo-Al-MMT (1.5). Importantly, bands indicating the free $MoO_2(acac)_2$ were not also detected in Mo-Al-MMT (1.5). Interaction of Mo complex with the clay showed that a broad band in the –OH region at 3700-3000 cm^{-1} and the major Si-O stretching remained unreacted. This indicates that the complex reacted with the clay via hydrogen bonding [2].

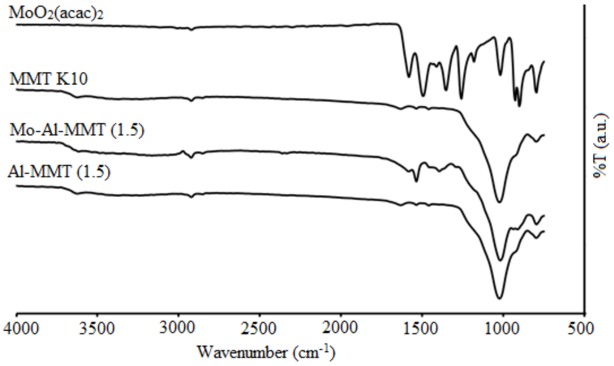

Fig. 4 FTIR spectra of MMT K10, Al-MMT (1.5), Mo-Al-MMT (1.5) and $MoO_2(acac)_2$

IV. CONCLUSIONS

In this study, alumina pillared MMT (Al-MMT) materials were synthesized using a different ratio of OH^-/Al^{3+} as the pillaring solution. Then the $MoO_2(acac)_2$ complex was successfully immobilized on the surface of pillared MMT. The materials produced (Al-MMT and Mo-Al-MMT) were characterized using XRD, SEM-EDX and FTIR analyses. It was found that pillaring gave the effect towards the structure of the MMT K10 where the d spacing of d(001) peak increase moderately when the concentration of pillaring solution changed. When Mo complex introduced to the Al-MMT, the complex was bound with the silanol groups on the surface of MMT layers via hydrogen bond.

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