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SYNTHESIS AND CHARACTERIZATION OF MIXED Al,Cu-PILLARED AND COPPER DOPED Al-PILLARED BENTONITE

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Abstract. In this paper, mixed aluminum and copper pillared clays (Al,Cu-PILC$_s$) with different percentage of Cu and copper impregnated aluminum pillared clay (Cu@Al-PILC) were prepared using a bentonite sample. The samples were characterized by X-ray diffraction, N_2 adsorption-desorption and Fourier transformed infrared spectroscopy. The results showed bentonite had a main reflection of montmorillonite that characterized by basal spacing, increased by pillaring. The specific BET surface area, total surface area and micropore volume of Al-PILC decreased in Cu@Al-PILC but increased in the case of mixed metal pillars and the maximum of these parameters related to Al,Cu15-PILC. Maximum weight percentage of copper was in Cu@Al-PILC therefore it contained higher percent of copper and its catalytic properties increased. FTIR result of samples confirmed the successful intercalation of Cu.

Keywords: aluminum, bentonite, copper, pillared clays.

1. Introduction

Recently metal oxides have been incorporated into different solid supports such as activated carbon, carbon nanotube, clays, *etc*. Clays have been reported to be a good candidate as catalysts support because they are natural, cheap, abundant and are easy to process [1-4].

The pillared interlayered clays (PILC$_s$) are one of the porous materials which can be utilized as catalyst in a number of reactions. These microporous materials are prepared by exchanging the charge compensating cations between the clay layers with large hydroxycations followed by calcination. On heating the hydroxycations undergo dehydration and dehydroxylation, forming stable metal oxide clusters which act as pillars keeping the silicate layers separated and creating interlayer space of molecular dimensions. The resultant material has small pores and a large surface area with high thermal stability [1]. In addition, appropriate modification of the chemical nature of pillars enables modeling of the materials acid-base and redox properties. All these properties make them ideal as potential adsorbents, catalysts and/or catalyst support [5-9].

Interlayering of clays with single species of copper have also received much attention by researchers because of their catalytic potential. Their results show that the inclusion of Cu into a clay is giving rise to an expanded product similar to PILC$_s$ but it collapsed after calcination and therefore is not becoming pillar at all. Due to the reason described, copper was incorporated in the interlayer space of clay by means of mixed polycations and or by Cu-doping on a clay previously pillared. The Al-polyoxocation (*i.e.* keggin ion Al_{13}) pillar agent has been commonly employed due to its well-defined structure and chemical composition. The modification of aluminum pillared interlayered clay (Al-PILC) with copper improves the catalytic activity and result in high conversion in catalytic reaction such as CO oxidation, NO reduction, wet peroxide oxidation of phenol, *etc*. [10-15]. Copper ion impregnation of Al-PILC generally decreases the specific surface area and micropore volume, while the use of mixed Cu and Al pillars results in higher surface area value and better ordering of the intercalated structure but it should be noted in this case that smaller amount of copper are included in PILC$_s$.

In the present study, synthesis and characterization of mixed Al,Cu-PILC, and Cu doped Al-PILC was investigated and compared. Unlike prior researches where up to 10 % copper was mixed in pillared solution [7, 11, 16-19], in this work percentage of copper in mixed pillared solution was increased up to 20 %. Therefore, PILC$_s$ contain higher percentage of copper and predicted their catalytic properties increased.

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2. Experimental

2.1. Materials

Bentonite sample from Kheirabad mine (Kerman, Iran) was used in this work. In order to increase the percentage of montmorillonite, bentonite purification was done on the basis of particle size. The starting material for the pillaring procedure was the sodium form of this bentonite. Its cation exchange capacity (CEC) was determined by the adsorption of copper ethylenediamine complex to be 115 meq/100g clay and its BET surface area was 33 m^2/g. Sodium hydroxide, aluminum and copper chloride were used in Merck grade.

2.2. Synthesis of Al-PILC and Al,Cu-PILC

The process of pillaring was carried out according to the following process. The pillaring solution was prepared by adding 0.2M NaOH into 0.1M $AlCl_3$ and 0.1M $CuCl_2$ to maintain hydrolysis molar ratio OH/Me^{n+} of 2 where Me^{n+} = Al^{3+} or Al^{3+}+Cu^{2+}. The pillaring solutions had $Cu^{2+}/(Al^{3+}+Cu^{2+})$ molar ratios 0, 0.05, 0.1, 0.15 and 0.2. The $PILC_s$ obtained were noted as Al-PILC; Al,Cu5-PILC; Al,Cu10-PILC; Al,Cu15-PILC and Al,Cu20-PILC, respectively. The procedure included continues stirring at 333 K for 2 h followed by stirring at room temperature overnight. In the next step the pillaring solution was slowly added into 2 wt % clay suspension (Me^{n+}/clay = 4 mmol/g). The dispersion was stirred for 20 h at room temperature. The intercalated clay was separated by centrifugation, washed with distillated water several times to remove chloride ions (silver nitrate test) and then dried for 3 days at ambient temperature. The dried samples were ground and calcined at 673 K for 2 h.

2.3. Synthesis of Cu@Al-PILC

Impregnation was carried out by reacting 1 g of Al-PILC calcined at 673 K with 100 ml of 0.02M copper nitrate solution while adjusting the pH to 6 by adding ammonia solution. The dispersion was stirred for 24 h at 323 K. The solid material was removed from solution, washed with distillated water 5 times and dried at room temperature. The ground samples were calcined at 673 K for 2 h.

2.4. Characterization

X-ray diffraction (XRD) patterns of samples were obtained using Bruker D8 advance X-ray diffractometer with Cu radiation (λ = 0.15404 nm) and recorded with a scanning rate of 1°/min. Nitrogen adsorption-desorption measurement was carried out with Belsorp mini II, surface area and pore size analyzer. Before each measurement the samples were first degassed at 573 K for 3 h under vacuum. The adsorption-desorption isotherm was run at $0 < P/P_0 < 1$ by use of nitrogen at 77 K. Using the nitrogen adsorption data, the specific BET surface area (S_{BET}) was estimated at relative vapor pressure values(P/P_0) between 0–0.5. The Fourier transformed infrared spectroscopy (FTIR) analyses were performed using Tensor II (Bruker company) in the range of 4000–400 cm^{-1} with KBr pellet technique.

3. Results and Discussion

3.1. Characterization of the Bentonite

The X-ray diffraction pattern of the purified bentonite is given in Fig. 1. X-ray diffraction comparison of raw and purified bentonite showed that in the purified bentonite, minerals such as illite, hematite and calcite have been removed and only cristobalite remained, which might be due to the large amount of cristobalite in the raw bentonite. The reflection at diffraction angle 2θ of 23° revealed cristobalite. The main reflection of montmorillonite occurred at 2θ of basal (d_{001}) reflection between 2–10°. One of the determining reflections of montmorillonite was observed near 8°, which corresponded to *d*-spacing of 11 Å. The specific BET surface area of the purified bentonite was 33 m^2/g.

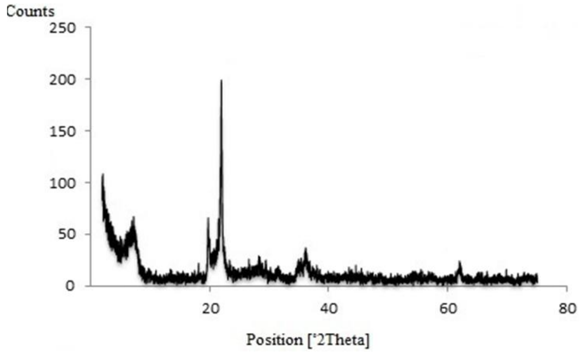

Fig. 1. XRD of purified bentonite

3.2. Characterization of the $PILC_s$

The X-ray diffraction of Al-PILC, Cu@Al-PILC and Al,Cu-$PILC_s$ with different percentage of copper are shown in Fig. 2. Upon pillaring process, the d_{001} reflection shifted to the lower 2θ values, corresponding to the increase in d_{001} values. Table 1 summarized the results of d_{001} value. The d_{001} value of all samples increased significantly after pillaring, which indicated aluminum and copper were efficiently intercalated into the interlayer space of clay. X-ray diffraction comparison of different samples showed that the basal (d_{001}) reflection in Al, Cu10 and Al,Cu15 were sharper than the other samples and also had more height. This indicated that in these samples the clay's crystalline structure has preserved better. Adding copper to the Al-PILC sample did not affect the XRD pattern of the initial pillared clay. No copper oxide phase was observed in the XRD pattern of the doped sample, which indicated high dispersion of copper in the Al-PILC.

Nitrogen adsorption-desorption isotherms of PILCs are shown in Fig. 3. These isotherms resembled the type IV isotherm in the BDDT (Brunauer, Demming, Demming Teller) classification that indicated the presence of both micropores and mesopores [20, 21]. The hysteresis interval in Al, Cu20 was more than other samples that showed this sample had larger pores. Decrease in the hysteresis interval of Cu@Al-PILC could be caused by smaller pore dimensions that showed copper particles were adsorbed into the pores. The initial slope of adsorption-desorption isotherms showed that in low P/P0 adsorption amount increase drastically, which is related to the micropores. Approximately 40 % of the volume of nitrogen adsorbed by PILCs occurred at $P/P_0 < 0.1$. The total pore volume (V_T) of Al-PILC was 0.204 cm^3/g and addition of copper increased total pore volume. *V-t* plots resembled the nitrogen adsorption isotherm curve as expected (Fig. 4). The *t*-plots had two different slopes, indicating that the PILCs had homogenous sized micropores. At the early stage of adsorption, adsorption amount increased drastically due to adsorption into micropores, but the thickness of adsorption did not increase so much, as the result the slope of t-plot became sharp. When adsorption into micropores was completed, adsorption happened only on the surface and the slope of the curve became gradual. The *V-t* plot of Cu@Al-PILC had deviation from the linear curve, that was due to capillary condensation [20, 22, 23]. Micropore volumes ($V_{\mu,t}$) of PILCs are summarized in Table 1. The micropore volume of Al-PILC was 0.0668 cm^3/g and decreased by 29.6 % after impregnation. Micropore blocking and micropore volume decrease for Al,Cu-PILCs did not occur. As can be seen, micropore volume in Al,Cu-PILCs increased and maximum micropore volume was observed in Al,Cu15-PILC.

The specific surface areas calculated by the different models are given in Table 1. The specific BET surface area (S_{BET}) of Al-PILC was 227 m^2/g and use of mixed metal pillars increased this value by about 20 %. In the doped sample during the impregnation method a part of the copper species is deposited outside the interlayer space. Upon calcinations, these species produced external mesoporous copper particles that could increase external surface area while blocking the internal surface. As the result, BET surface area of the Cu@Al-PILC decreased. The total specific surface area ($S_{T,t}$) and external surface area ($S_{ext,t}$) measured from the slope of first linear segment and second linear segment of *t*-plots, respectively, are summarized in Table 1. Approximately 80 % of total specific surface area was related to the micropore surface area in Al,Cu-$PILC_s$, as calculated by the difference between total and external specific surface area, but this percentage reduced to 70 % in Cu@Al-PILC.

The average pore diameter (*d*) of all samples was between 3.12 and 3.82 nm (Table). As can be seen, the average pore diameter of Al,Cu20-PILC was higher than in the others, similarly with the result mentioned in the adsorption-desorption isotherm section. Weight percentage of copper (Cu, wt %) measured in samples is reported in Table 1. As can be seen weight percentage of copper in Cu@Al-PILC is much higher than in other samples.

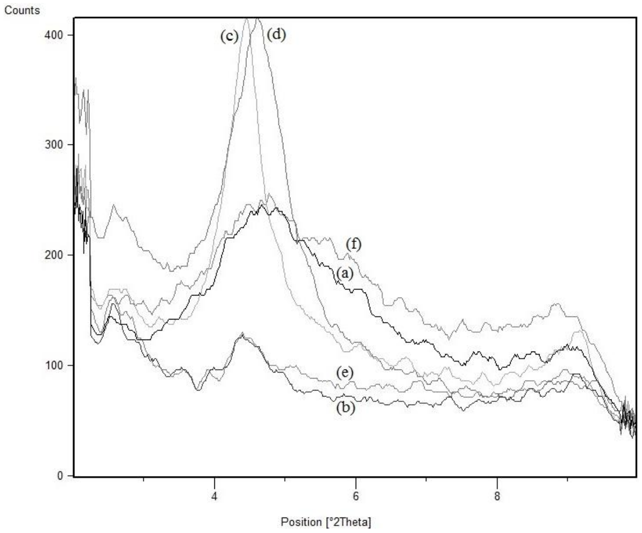

Fig. 2. XRD of Al-PILC (a); Al,Cu5-PILC (b); Al,Cu10-PILC (c); Al,Cu15-PILC (d); Al,Cu20-PILC (e) and Cu@Al-PILC (f)

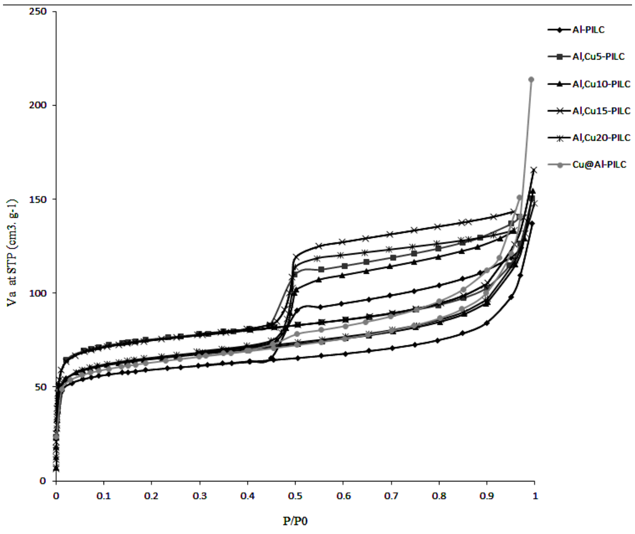

Fig. 3. 77 K nitrogen adsorption-desorption isotherms of PILCs

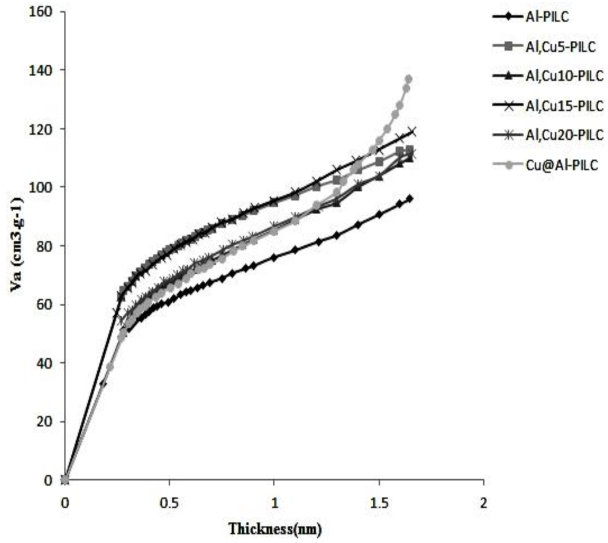

Fig. 4. *V-t* plot of PILCs

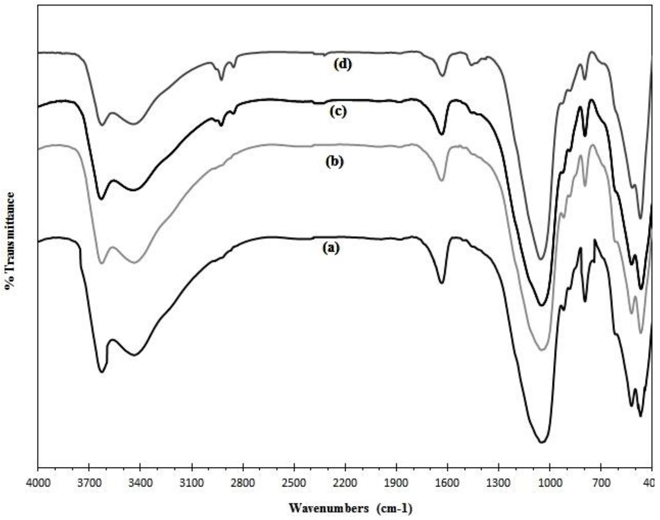

Fig. 5. FTIR of purified bentonite (a); Al-PILC (b); Al,Cu15-PILC (c) and Cu@Al-PILC (d)

Table

Properties of PILC$_s$

Samples	d_{001}, nm	V_T, cm^3/g	$V_{\mu,t}$, cm^3/g	S_{BET}, m^2/g	$S_{T,t}$, m^2/g	$S_{ext,t}$, m^2/g	*d*, nm	Cu, wt%
Al-PILC	1.91	0.204	0.0668	227	280.9	58.93	3.59	0
Al,Cu5-PILC	1.95	0.226	0.077	248	309.4	57.5	3.46	0.45
Al,Cu10-PILC	1.92	0.227	0.096	287	357.4	52.12	3.64	0.75
Al,Cu15-PILC	1.98	0.242	0.097	296	369.1	50.94	3.3	1.65
Al,Cu20-PILC	1.94	0.217	0.071	244	277.9	58.1	3.82	2.9
Cu@Al-PILC	1.9	0.317	0.047	204	245.8	69.49	3.12	10.7

FTIR spectra of purified bentonite, Al-PILC, Al,Cu15-PILC and Cu@Al-PILC are given in Fig. 5. All the samples exhibit bands around 3625 and 3440 cm^{-1}, the band at 3625 cm^{-1} is assigned to the metal –OH in the octahedral layer and the other band is associated with adsorbed water in the interlayer. In Al,Cu15-PILC and Cu@Al-PILC the new bands at 2926 and 2855 cm^{-1} can be assigned to the Cu–Si–O bond and confirmed the successful intercalation of Cu. Band at 1630 cm^{-1} represent water molecules on the surface of clay, after pillaring and calcinations at 673 K this peak decreased in PILC$_S$. New band at 1460 cm^{-1} in Cu@Al-PILC is attributed to CuO. Band corresponding to the Si–O–Si stretching vibration is located at 1050 cm^{-1} with no change by pillaring, but there occurred small decrease in band width. Aluminum and copper pillaring agent had caused a decrease in the free silica peak intensity, which occurred at 794 cm^{-1}. Bands at 522 and 470 cm^{-1} originate from Si–O bending and Al–O stretching vibration, respectively. There is a decrease in Si–O bending but a small increase in Al–O stretching intensity by pillaring [8, 16, 23-27].

4. Conclusions

Impregnation of Al-PILC with Cu^{2+} ions or the use of mixed metal pillars did not affect the basal spacing, which indicated copper was efficiently dispersed into the interlayer space. Specific BET surface area, total surface area and micropore volume of Al-PILC decreased in Cu@Al-PILC but increased in the case of mixed metal pillars and the maximum of these parameters related to Al,Cu15-PILC. In the Cu@Al-PILC total pore volume and external surface area increased due to external mesoporous copper particle. N_2 adsorption-desorption demonstrated a significant increase in surface area and volume of pillared samples relative to bentonite. FTIR result of samples confirmed the successful intercalation of Cu. Maximum weight percentage of copper was related to Cu@Al-PILC.

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СИНТЕЗ ТА ХАРАКТЕРИСТИКА СУМІШІ Al,Cu-ЗШИТОГО І ПРОМОТОВАНОГО МІДДЮ БЕНТОНІТУ

Анотація. *З використанням зразка бентоніту одержано суміші глин, зшитих алюмінієм та міддю (Al, Cu-PILCs) з різним відсотком Cu та імпрегнованих алюмінієм (Cu@Al-PILC). Характеристику зразків проведено за допомогою рентгенівської дифракції, адсорбції-десорбції* N_2 *та Фур'є-спектроскопії. Визначено, що площа поверхні за БЕТ, загальна площа та об'єм мікропор Al-PILC зменшуються в Cu@Al-PILC, проте збільшуються у випадку змішаних металів і досягають максимуму для Al, Cu-PILCs. Встановлено, що найвищий вміст міді є в Cu@Al-PILC, тому його каталітичні властивості покращуються. Фур'є-спектроскопією підтверджено введення міді в структуру Al, Cu-PILCs.*

Ключові слова: *алюміній, бентоніт, мідь, зшиті глини.*