TITLE: Surface Properties of Metal-Incorporated Al-Pillared Interlayered Clay Catalysts Analyzed by Chemisorption and Infrared Analysis

AUTHORS: Funda BASOGLU,Suna BALCI

PAGES: 215-225

G.U. Journal of Science
22(3): 215-225 (2009)

www.gujs.org

Surface Properties of Metal-Incorporated Al-Pillared Interlayered Clay Catalysts Analyzed by Chemisorption and Infrared Analysis

Funda Turgut BAŞOĞLU [1], Suna BALCI[1]♠

[1] *Gazi University, Faculty of Engineering & Architecture, Department of Chemical Engineering, 06570 Ankara, Turkey.*

Received: 06.02.2009 Revised: 19.03.2009 Accepted: 24.03.2009

ABSTRACT

Al-pillared interlayered clay (Al-PILC) was synthesized using bentonite from the Hançılı region of Central Anatolia in Turkey. Samples of Al-PILC were impregnated with Cu or Ag to produce Cu@Al-PILC and Ag@Al-PILC. Cu/Al-mixed PILCs were also obtained using mixed metal sources having (Cu/(Cu+Al)) atom percents as 5 and 10. The FTIR intensities of Lewis acidity peaks decreased whereas the intensity of Brönsted acidity remained nearly the same for pyridine sorbed PILCs after desorption at 150°C compared to those of pyridine sorbed PILCs at room temperature. These results confirmed the presence of both types of acidities within the matrix. Metal incorporation increased total (weak+strong) ammonia adsorption. Metal incorporation increased the total acidities of Al-PILC from 281.1 $\mu mol\ g^{-1}$ to 803-883 $\mu mol\ g^{-1}$ by NH_3 sorption at 50°C. The Cu/Al-mixed PILC(AP5) sample resulted 290 $\mu mol\ g^{-1}$ number of active sites at an NH_3 sorption temperature of 200°C, with the corresponding strong active sites as 44.6 $\mu mol\ g^{-1}$.

Key Words: *Pillared interlayered clay, Surface area, FTIR analysis, Ammonia sorption.*

---

1. INTRODUCTION

In recent years, research into applications of pillared interlayered clays (PILCs) as catalysts and catalyst supports has gained importance due to their molecular sieve properties and the effectiveness as catalysts. The principle behind PILC production is to insert voluminous foreign agents between the layers of clay to keep them apart. In this way, pore sizes can be increased, improving the porosity and surface properties. It is possible to produce a PILC with the desired pore dimensions by choosing the right pillar agent. The host clay should have a high swelling property, an expandable lattice structure, a high cation exchange capacity, and no sheet deformation. If such a clay material interacts with a pillar agent solution under conditions suitable for ion exchange, the resulting intercalated solid containing pillar ions can then be calcined to fix the pillar complex to the clay structure. The solid produced in this way has molecular sieve properties with no sheet deformation at relatively high temperatures. It also possesses numerous adsorption sites and active sites for catalysis, both of which are important structural properties for selective catalytic reduction and selective catalytic cracking [1-6].

Fourier Transform Infra Red (FTIR) is a method commonly used to analyse surface functional groups and surface acidity. The bands between 3000 and 4000 cm^{-1} in the spectrum are related to water and OH groups, while the bands within 400-1200 cm^{-1} are characteristic of metal bonded silica [7-9]. The metal oxide pillars, in addition to keep the clay layers apart, also provide an acidic character to the pillared structure. In fact, the surface of PILCs feature both Lewis and Brönsted acid sites [3, 7, 10-12]. The main source of Brönsted acidity is the separation of the lamellae by pillaring and consequent surface exposure of sylanol groups. The pillars themselves, on the other hand, contribute mainly Lewis acidity to PILCs. As a result of calcination, the excess aluminum oxihydroxide gives rise to coordinately

---

♠Corresponding author, e-mail: sunabalci@gazi.edu.tr.

unsaturated Al atoms, which are also a potential source of Lewis acids [7].

Active surface area values and chemically sorbed gas volumes are the indicators of acidity and the catalytic activity. Temperature-programmed ammonia desorption (NH_3-TPD), ammonia sorption and thermal gravimetric analysis (TGA) have also been used by several investigators to measure the acidity of PILCs [8, 10, 13-18]. In most of those studies, large quantities of the sorbed ammonia were desorbed at temperatures below 300˚C, indicating that the Al-PILCs possessed mainly physisorbed ammonia [7, 8, 10, 12, 15]. It was observed that incorporating of silver or copper into the Al-PILC structure in a post-synthesis step generally increased the amount of ammonia that could be chemically adsorbed [15, 19]. Upon heating to 500˚C, as usually occurs during calcination, the concentration of Brönsted acid sites dramatically decreased and the resulting PILCs exhibited mainly Lewis-type acidity [11, 12]. In order to modify the acidity of PILC samples, some authors applied acid activation prior to pillaring [20-22].

In this study, Al-PILCs impregnated with copper or silver and PILCs containing a mixture of copper and aluminum were synthesized using Hançılı White (HW) bentonite. The aim was to test the effect of metal incorporation on the acidity and on the other physicochemical properties. Crystal structures were examined by X-ray diffraction (XRD). The properties of the pore structures and catalytic activity were tested using nitrogen sorption, ammonia sorption, and FTIR.

2. EXPERIMENTAL

Table 1 summarizes some properties of Hançılı White bentonite samples from the region of Central Anatolia [23, 24]. In this study, calcium-presaturated Hançılı samples were used for the synthesis. For the synthesis of pillar complex, $AlCl_3.6H_2O$ was used as the aluminum source and NaOH was used for base hydrolysis. The copper and silver sources were $Cu(NO_3)_2$ and $AgNO_3$. All the chemicals were laboratory-grade and were purchased from Merck.

Table 1. Properties of the HW clay sample [23, 24].

Metal oxide, % by mass							d_{001} value of clay sample (nm)	d_{001} value of clay sample calcined at 300˚C (nm)	Solid density of clay sample calcined at 300˚C (g cm^{-3})	Single point BET surface area of clay sample calcined at 300˚C (m^2 g^{-1})	C.E.C. ((meq) (100g)$^{-1}$)
SiO_2	Al_2O_3	Fe_2O_3	MgO	CaO	Na_2O	K_2O					
74.08	17.46	2.64	3.08	0.36	2.09	0.29	1.25	0.99	2.29	57	66

2.1. Al-PILCs Synthesis

Two different synthesis methods were used in this study [23]. In the first method, Al-PILC was synthesized as the support material using the recipe utilized by Tomul and Balci [25] and the OH:Al ratio was kept at 2.5 then calcined at 300˚C for 3 hours. Here after the sample was treated with nitrates of copper or silver using the procedure of Yang et al. [26] keeping “mmol metal/g clay” ratio as 2/1. After impregnation with metal, the clay suspension was centrifuged, washed several times, dried at room temperature, and calcined at 300˚C and 500˚C for 3 hours to obtain Cu@Al-PILC and Ag@Al-PILC. In the second method, copper and aluminum mixed-metal complexes were used together to produce Cu/Al-mixed PILC using the recipe suggested by Barrault et al. [27]. The pH value of pillar agent solution was adjusted to be below 3.8 using a few drops of NaOH solution [23].

Al-pillar complex was derived from 0.4 M solutions of metal and base. In mixed-metal pillar solution synthesis, 0.1 M stock solutions of each metal and 0.2 M of base were used. The metal solutions were mixed to yield atomic percents [Cu/(Cu+Al)] of 5 and 10. For production of both single- and double-metal PILCs, base hydrolysis was carried out at a titration rate of 30 mL hour^{-1}, followed by aging at 60°C for 18 hours. The resulting solution was added slowly (125 mL hour^{-1}) to a 2 % (w/w) clay suspension to produce Al-PILC synthesis. In mixed-metal PILC synthesis, HW clay pretreated with calcium ions was added to the pillar solution. For both types of PILCs, 10 mmol of pillar metal(s) were treated with 1 g of clay. Ion exchange was then conducted by leaving the suspension at 25°C for 4 hours. The intercalated solids were dried at room temperature for 5 days, then calcined [23, 24].

2.2. Characterization of Samples

X-ray diffraction patterns of PILCs calcined at 300°C were obtained at a 2θ (Bragg angle) = 4° -70° interval using a Philips PW 1840 diffractometer. Nitrogen sorption isotherms (77 K) of outgassed samples at 300°C for 6 hours were recorded on a Quantachrome Autosorp 1 C apparatus. FTIR spectra of the samples without and with pyridine adsorption and desorption were recorded in the range 400-4000 cm^{-1} using a Mattson 1000 spectrophotometer and the KBr disc method. Samples were exposed to pyridine vapor at room temperature for one week under a vacuum of 10^{-4} torr. Pyridine desorption was performed at 150°C for 3 hours. Ammonia sorption studies were carried out at 50 and 200°C using the Quantachrome Autosorb 1C apparatus. Before the sorption, samples were reduced with hydrogen using the procedure of Yang et al., 1998 [26]. Samples were brought to the desired adsorption temperature under atmospheric pressure, and ammonia was passed over them at a flow rate of 25 mL min^{-1} for 0.5 hour. Following sorption of ammonia, helium was passed over samples at a flow rate of 40 mL min^{-1} for 1 h to allow desorption of the physisorbed ammonia.

3. RESULTS AND DISCUSSION

Table 2 shows the basal spacing values (d_{001}) of PILCs calcined at 300°C, as determined from the first peak of XRD patterns using Bragg's law. The basal spacing d_{001} value of Al-PILC, originally 1.90 nm (2θ = 4.65°), decreased to 1.66 nm after silver incorporation and 1.59 nm after copper incorporation. The corresponding value for Cu/Al-mixed PILCs was 1.62 nm, ~2 % higher than the value in copper-impregnated Al-PILC. The settlement of copper or silver in the PILC matrix (interlamellar space and interpillar space) resulted in lower d_{001} values as consistent with the literature. It was observed that metal incorporation to PILC did not destroy the pillared structure.

Table 2. Basal spacing (d_{001}) and surface area values of PILCs.

Product code	Sample	d_{001} of sample calcined at 300°C (nm)	**Surface area ($m^2 g^{-1}$)**			
			Calcination temperature			
			300°C		**500°C**	
			S^a_{BET}	S^b_L	S^a_{BET}	S^b_L
Al-PILC	Al-pillared interlayered clay	1.90	296	469	269	431
Ag@Al-PILC	Silver-impregnated Al-PILC	1.66	188	301	137	217
Cu@Al-PILC	Copper-impregnated Al-PILC	1.59	110	179	107	169
Cu/Al-mixed PILC(AP5)	Copper and aluminum mixed PILC with Cu/(Cu+Al) atomic percent of 5	1.60	231	368	211	334
Cu/Al-mixed PILC(AP10)	Copper and aluminum mixed PILC with Cu/(Cu+Al) atomic percent of 10	1.62	271	431	249	396

[a] Specific surface areas from the Langmuir equation ($0.05 \leq P/P_0 \leq 0.30$, interval of relative pressure)

[b] Specific surface areas from the BET equation ($0.05 \leq P/P_0 \leq 0.30$, interval of relative pressure)

The nitrogen sorption isotherms given in Figure 1 showed Type II in BDDT (Brunauer, Deming, Deming and Teller) classification with hysteresis above relative pressure of 0.40 valid for micro-mesoporous structure [28]. Multi-point BET (S_{BET}) and Langmuir (S_L) surface areas were obtained from 77 K nitrogen adsorption isotherm data in the interval of $0.05 < P/P_0 < 0.30$. The results are summarized in Table 2. The Langmuir surface area values were higher than the BET values. The decrease in BET surface area of Al-PILC was more substantial with copper impregnation than with silver impregnation. Cu/Al-mixed PILC had a BET surface area similar to that of Al-PILC calcined at 300°C. With the increasing calcination temperature, BET and

Langmuir surface area values decreased in an agreement with the results obtained for 300°C.

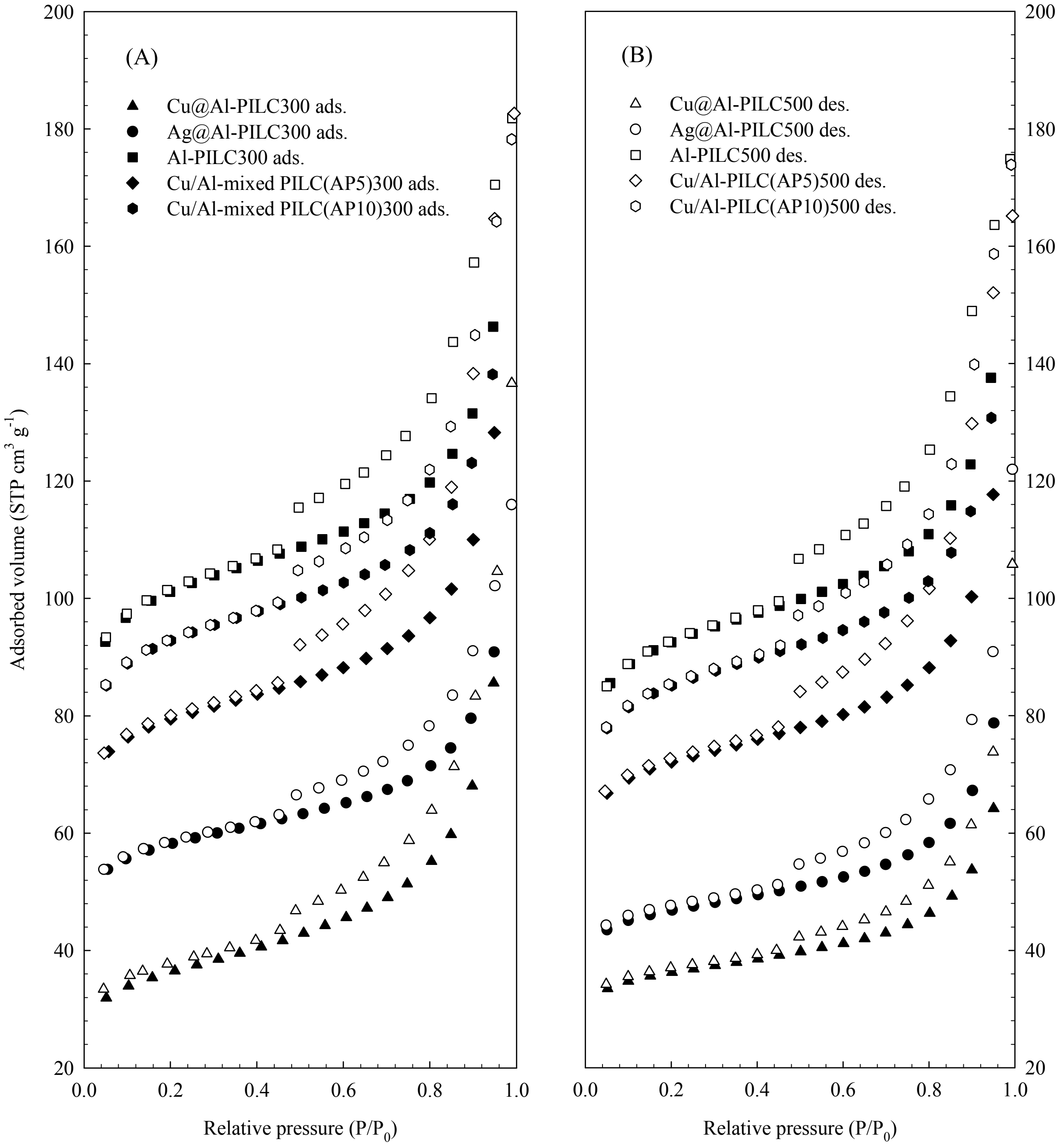

Figure 1. 77 K nitrogen adsorption/desorption isotherms of PILC samples calcined at (A) 300°C and (B) 500°C.

Figure 2 shows FTIR spectra recorded in transmission mode of the original clay and PILC samples calcined at 300°C and 500°C in the region of 400-4000 cm^{-1}. The spectrum of the host clay was in good agreement with the literature [7-9]. It showed two peaks at 3440 and 3660 cm^{-1} in the OH stretching region. This pattern was typical of water adsorption in montmorillonite. These peaks were due respectively, to hydroxyl groups involved in water-water hydrogen bonds and to the –OH stretching vibration in Al_2OH hydroxyl absorption of randomly oriented samples [7-9]. An intense peak at ~1020 cm^{-1} was observed as a result of the in-plane stretching vibration of the surface Si-O-Si when substitution of Si by Al was low. Small peaks were also observed at 910 cm^{-1} for Al_2OH libration and at 840 cm^{-1} for the Mg substitution for Al (in MgAlOH). The peaks at 720 cm^{-1}, 520, and 460 cm^{-1} could be due to Si-O bending vibrations. A decrease was observed in the intensity of the peak at 3660 cm^{-1} for Al-PILCs. Cu/Al-mixed PILCs also showed the same behaviour (Figure 2). The bands at 910 and 840 cm^{-1} decreased with pillaring, while no important differences were observed between the samples that showed a similar degree of exchange. The increase in calcination temperature to ~500°C did not cause significant changes in the overall spectra.

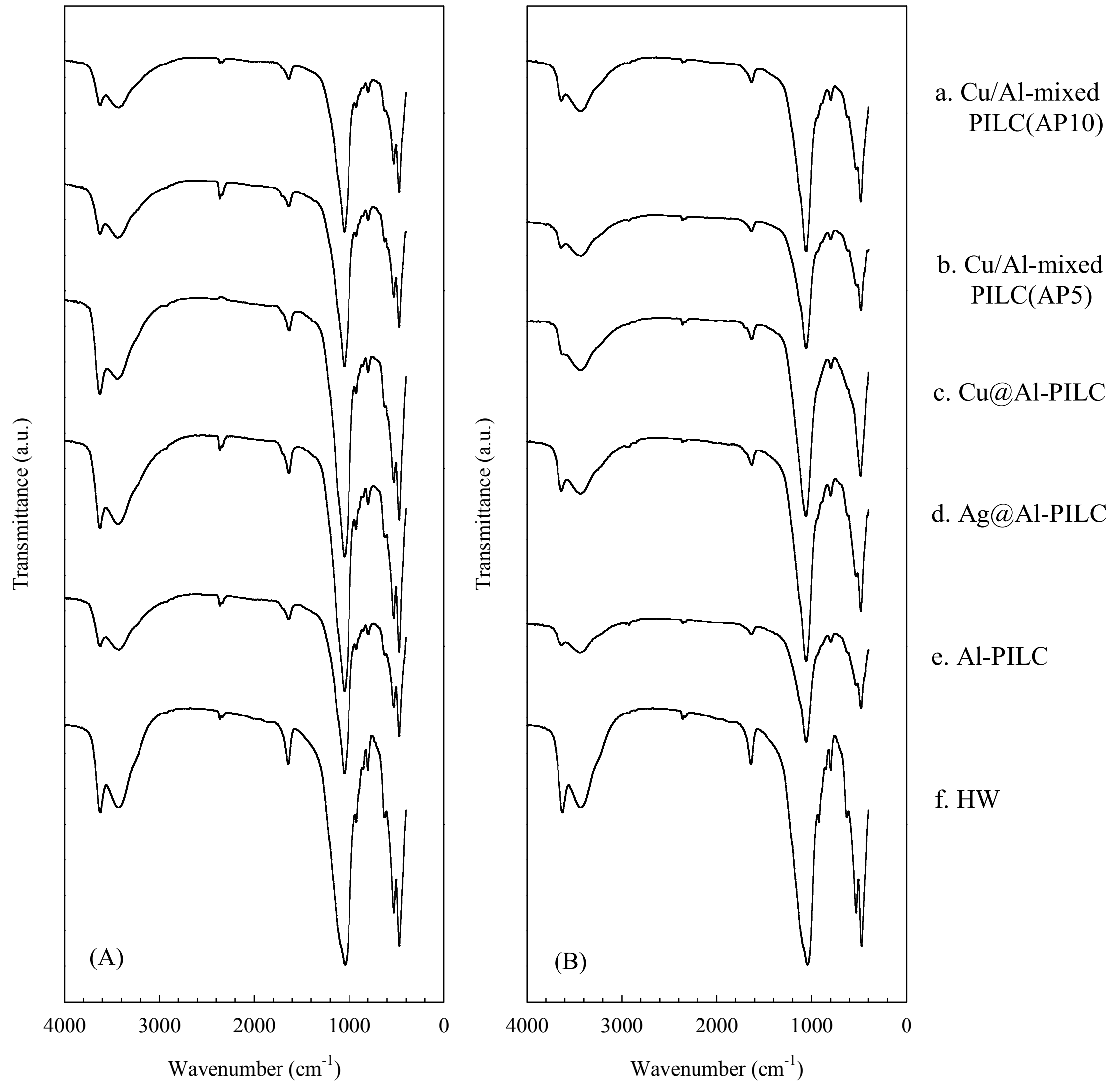

Figure 2. FTIR spectra of clay samples calcined at (A) 300°C and (B) 500°C.

Figure 3 shows the infrared spectra in the region of 1800-1300 cm^{-1} of the original clay and PILCs calcined at 300 and 500°C following exposure to pyridine vapor at room temperature and also shows the spectra after pyridine desorption at 150°C. The spectrum of the original clay showed bands at (i) 1448 cm^{-1} and a shoulder at ~1610 cm^{-1} assigned to Lewis-bound pyridine (L), (ii) 1490 cm^{-1} attributed to pyridine associated with both Lewis and Brönsted (L+B) acid sites, and (iii) 1638 cm^{-1} assigned to pyridine bound to Brönsted (B) acid sites [3, 10, 12]. For the PILCs, the spectra obtained showed bands at 1545 and 1638 cm^{-1} (B), and at 1610 and 1448 cm^{-1} (L). In particular, copper-impregnated PILC shows an intense peak at 1448 cm^{-1} and 1490 cm^{-1} (L+B). The broader bands at 1638 cm^{-1} on Al-PILC and on metal-incorporated PILCs could be taken as clear indications of enhanced Brönsted acidity in these samples. When pyridine-absorbed clay samples were desorbed at 150°C, the intensity of peaks at 1448 cm^{-1} (L) decreased, while the intensity of peaks at 1490 cm^{-1} (L+B), 1545 cm^{-1} (B), and 1638 cm^{-1} (B) did not change significantly (Figure 3).

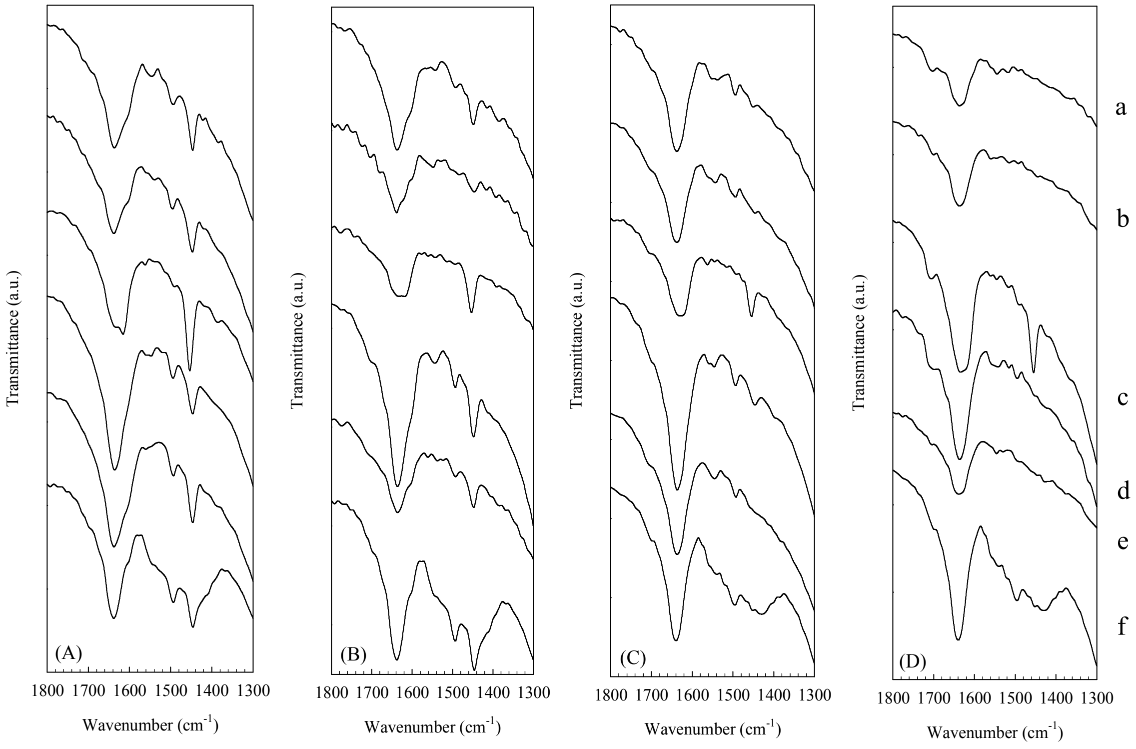

Figure 3. FTIR spectra of clay samples calcined at (A) 300˚C (B) 500˚C after pyridine adsorption at room temperature and FTIR spectra clay samples calcined at (C) 300˚C (D) 500˚C after pyridine desorption at 150˚C (Sample notation is same as the one in Figure 2).

Figure 4-5 shows the ammonia sorption isotherms used for the determination of the monolayer coverage (surface acidity) at 50˚C and 200˚C of Al-PILC, of silver-impregnated Ag@Al-PILC, and of Cu/Al-mixed PILCs pre-calcined at 500˚C. The amount of strongly sorbed ammonia was calculated from the difference between the total and the weakly sorbed quantities, both at the same adsorption temperatures. The amount of strongly sorbed material might give an idea of the number of active sites available for catalytic reactions at these temperatures, while the weakly sorbed quantities might reflect the sites available for physisorption. The strongly sorbed ammonia gas volumes of PILC samples were close to one another but much less than the volumes of weakly sorbed gases at both adsorption temperatures. Hence, it might be that active sites available for catalytic reactions were almost the same at both low and high temperatures. Metal incorporation caused a >2-fold increase in total and weak sorption amounts at low temperature, while these values did not change to a great extent at high sorption temperatures. Thus, most of the totally sorbed ammonia at low temperature could be strongly sorbed to the surface by increasing the temperature.

Although adsorption points deviated from the linearity at low pressure, they showed the linearity above 0.3 bar; especially the total, weak, and actual chemical adsorption points. The plateau did not occur at pressures above 0.85 bar. Hence all isotherms given in Figures 4 and 5 produced quite nice linear extrapolations above 0.3 bar, and monolayer coverage could be estimated by the extrapolation technique [28]. In determination of monolayer coverage, straight line was drawn through adsorption points above 0.3 bar and from the intersection point through y axis of that line, monolayer coverage was estimated hereafter acidity (the numbers of adsorbed gas molecules) and corresponding active surface area values were calculated [28]. Active site properties - monolayer capacity, acidity, and active surface area - of PILCs pre-calcined at 500˚C are given in Table 3.

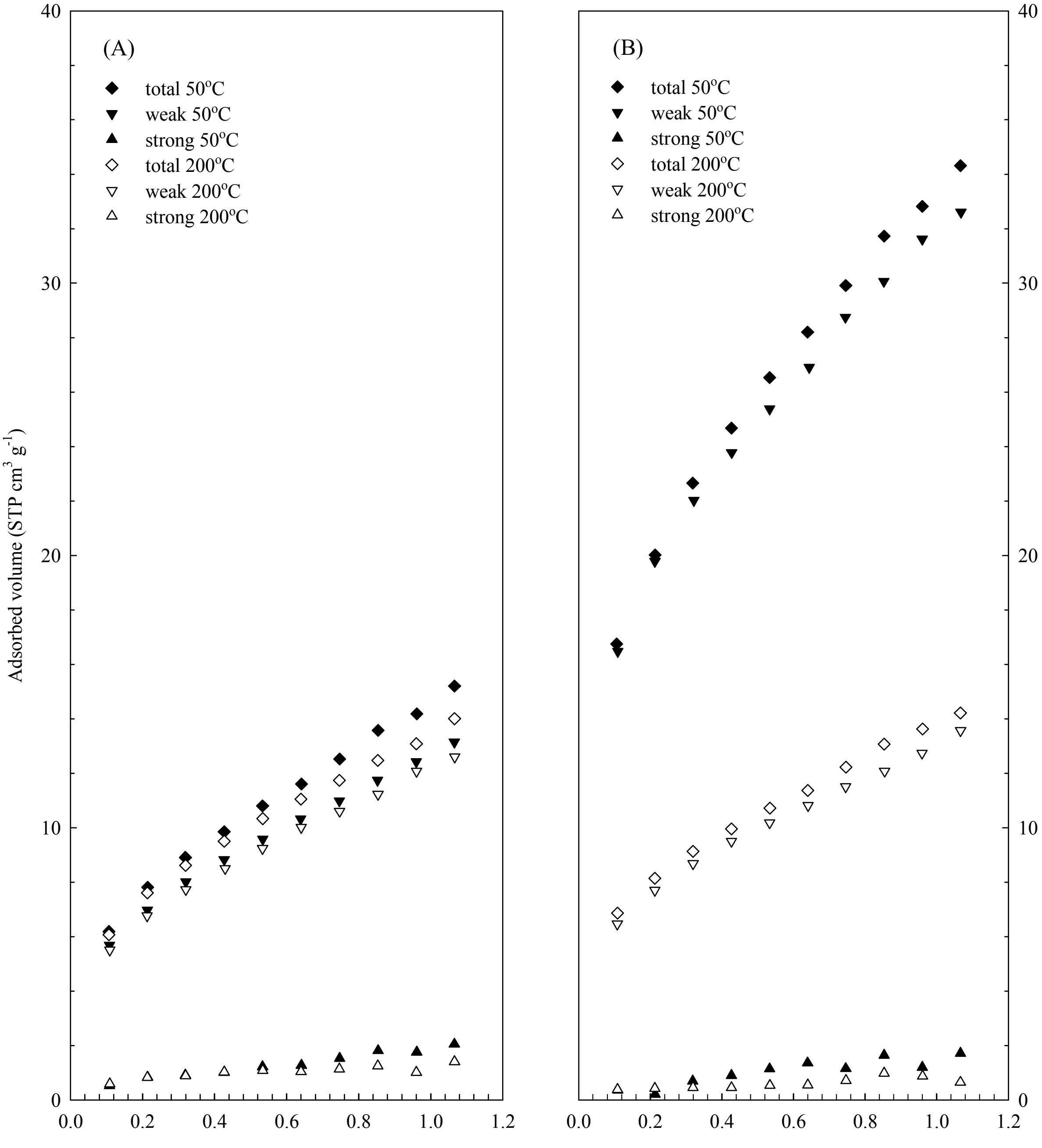

Figure 4. Ammonia sorption isotherms at 50°C and 200°C of (A) Al-PILC and (B) Ag@Al-PILC calcined at 500°C.

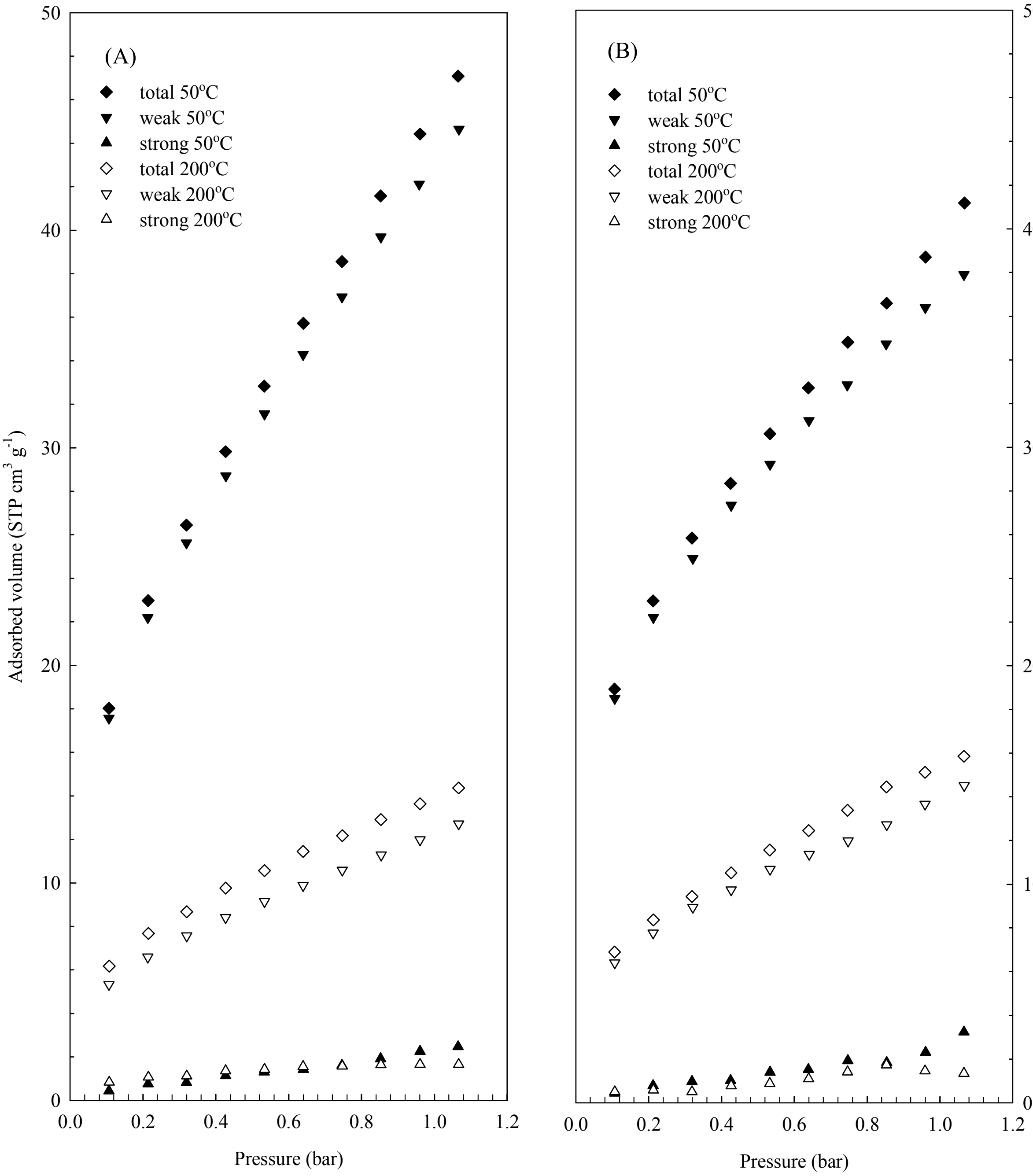

Figure 5. Ammonia sorption isotherms at 50˚C and 200˚C of (A) Cu/Al-mixed PILC(AP5) and (B) Cu/Al-mixed PILC(AP10) calcined at 500˚C.

Monolayer coverage values from strong adsorption data were found to be nearly the same for all PILCs and they were lower than the ones calculated from the weak data at both temperatures (Table 3). Incorporation of either silver or copper caused significant increases in total and weak sorption coverages at low adsorption temperature, though a significant increase was not observed at high adsorption temperatures. Increase in sorption amounts was due to increase in numbers of physical/chemical active sites by metal incorporation although the BET surface areas of metal incorporated PILC samples were found lower than that of Al-PILC.

Table 3. Active site properties of PILCs calcined at 500°C obtained from ammonia sorption data.

Product code	Monolayer coverage (STP cm^3 g^{-1})			Acidity (μmol g^{-1})			Surface area (m^2 g^{-1})		
	Total sorbed ammonia gas volume	Weakly sorbed ammonia gas volume	Strongly sorbed ammonia gas volume	Total active sites	Weak active sites	Strong active sites	Total sites' surface area	Weak sites' surface area	Strong sites' surface area
Adsorption temperature 50°C									
Al-PILC	6.3	5.9	0.4	281.1	263.2	17.8	11.8	11.1	0.7
Ag@Al-PILC	18.1	17.6	0.5	807.5	785.2	22.3	42.3	41.1	1.2
Cu/Al-mixed PILC(AP5)	18.0	17.9	0.1	803.1	798.6	4.5	32.9	32.7	0.2
Cu/Al-mixed PILC(AP10)	19.8	19.6	0.2	883.4	874.5	8.9	36.2	35.8	0.4
Adsorption temperature 200°C									
Al-PILC	6.5	5.7	0.8	290.0	254.3	35.7	12.2	10.7	1.5
Ag@Al-PILC	7.0	6.7	0.3	312.3	298.9	13.4	16.4	15.7	0.7
Cu/Al-mixed PILC(AP5)	6.5	5.5	1.0	290.0	245.4	44.6	11.9	10.1	1.8
Cu/Al-mixed PILC(AP10)	6.9	6.6	0.2	307.8	294.5	8.9	12.6	12.1	0.4

Total acidity of the Al-PILC, measured as 281.1 μmol g^{-1} at a sorption temperature of 50°C, jumped to 883.4 μmol g^{-1} for Cu/Al-mixed PILC(AP10). Metal-containing pillared samples possessed much more total active sites caused by weak active sites than the corresponding samples without metals. Silver impregnation increased the strong active sites of Al-PILC, estimated as 22.3 μmol g^{-1}, by 25 % increase at adsorption temperature of 50°C. Increasing the adsorption temperature to 200°C reduced the difference in total acidities between Al-PILC and metal-containing PILCs. Strong active sites of Cu/Al-mixed PILC(AP5) were obtained 25 % higher than ones of Al-PILC at high adsorption temperature. Total sites surface area, 97-99 % of which was weak sites surface area increased by metal incorporation at low adsorption temperature. At high adsorption temperature these values were observed as close to ones of Al-PILC ranging nearly 12-17 m^2 g^{-1} (Table 3). At high adsorption temperature, weak sites surface area percent of total sites was ranged between 85-96 in metal corporated PILCs.

4. CONCLUSIONS

The basal spacings (d_{001}) and the BET and Langmuir surface areas of Al-PILC decreased when metals were incorporated into the clay. Increasing the calcination temperature also reduced the values of the BET and Langmuir surface areas. Pillaring, in contrast, increased both Lewis and Brönsted acidities. An increase in calcination temperature did not cause any distinct changes in transmittance peak positions, either in pyridine-sorbed or -desorbed samples. The intensity of peaks showing Brönsted acid sites remained nearly constant at a desorption temperature of 150°C, while Lewis acidity peak intensities decreased. Increasing the ammonia sorption temperature caused a decrease in the amount of weakly sorbed material relative to the amount of strongly sorbed material. Metal incorporation increased the total acidity. In addition, Cu/Al-mixed PILCs and silver-impregnated Al-PILC could support a nearly similar amount of weakly or strongly sorbed material. For the metal-incorporated PILCs tested, the numbers of molecules of adsorbed ammonia gas necessary for monolayer coverage were very close to one another. The Cu/Al-mixed PILC(AP5) sample was synthesized with the total number of active sites as 290 µmol g^{-1} at an adsorption temperature of 200˚C, with the corresponding strong active sites as 44.6 µmol g^{-1}.

ACKNOWLEDGEMENTS

The authors wish to express their gratitude and appreciation for financial support from the Scientific Research Projects Department of Gazi University (project codes BAP 06/2003-69 and BAP 06/2005-43) and the Scientific and Technological Research Council of Turkey (project code MİSAG 172).

REFERENCES

[1] Grim, E.R., “Clay Minerology”, ***Mc Graw-Hill***, Newyork, 27-42, 55-64 (1953).

[2] Bekkum, H., Van Flarigen, E.M., Jansen, J.C., “Introduction to zeolite science and practice studies in surface science and catalysis”, ***Elsevier***, Newyork, 203-236 (1991).

[3] Figueras, F., “Pillared clays as catalysts”, ***Catal. Rev.***, 30(3): 457-499 (1988).

[4] Kloprogge, J.T., Duong, L.V., Frost, R.L., “A review of the synthesis and characterization of pillared clays and related porous materials for cracking of vegetable oils to produce biofuels”, ***Environ. Geol***., 47: 967-981 (2005).

[5] Bergaya, F., Theng, B.K.G., Lagaly, G., “Pillared Clays and Clay Minerals. In Handbook of Clay Science”, ***Elsevier***, Newyork (2006).

[6] Gil, A., Korili, S.A., Vicente, M.A., “Recent Advances in the Control and characterization of the Porous Structure of Pillared Clay Catalysts”, ***Catal. Rev.***, 50(2): 153 – 221 (2008).

[7] Salerno, P., Asenjo, M.B., Mendioroz, S., “Influence of preparation method on thermal stability and acidity of Al-PILCs”, ***Thermochim. Acta***, 379: 101-109 (2001).

[8] Trombetta, M., Busca, G., Lenarda, M., Storaro, L., Ganzerla, R., Piovesan, L., Lopea, A.J., Alcantara-Rodriguea, M., Rodriguez-Castellon, E., “Solid acid catalysts from clays Evaluation of surface acidity of mono-and bi-pillared smectites by FTIR spectroscopy measurements, NH_3-TPD and catalytic tests”, ***Appl. Catal. A-Gen***., 193: 55-69 (2000).

[9] Kurian, M., Sugunan, S., “Characterization of the acid-base properties of pillared montmorillonites”, ***Micropor. Mesopor. Mat***., 83: 25-34 (2005).

[10] Chae, H.J., Nam, I., Ham, S.W., Hong, S.B., “Physicochemical characteristics of pillared interlayered clays”, ***Catal. Today***, 68: 31-40 (2001).

[11] Gil, A., Gandìa, L.M., Vicente, M.A., “Recent advances in the synthesis and catalytic applications of pillared clays”, ***Catal. Rev***., 42(1&2): 145-212 (2000).

[12] Issaadi, R., Garin, F., Chitour, C-E., “Study of the acid character of some palladium-modified pillared clay catalysts:Use of isopropanol decomposition as test reaction”, ***Catal. Today***, 113: 166-173 (2006).

[13] Sapag, K., Mendioroz, S., “Synthesis and characterization of micro-mesoporous solids: pillared clays”, ***Colloid Surface A***, 187-188: 141-149 (2001).

[14] Occelli, M.L., Biz, S., Auroux, A., Iyer, P.S., “Physicochemical properties of some metal supports for hydrotreating catalysts preparation”, ***Appl. Catal. A-Gen***, 179: 7-129 (1999).

[15] Chmielarz, L., Zbroja, M., Kustrowski, P., Dudek, B., Rafalska-Lasocha, A., Dziembaj, R., “Pillared montmorillonites modified with silver”, ***J. Therm. Anal. Calorim***., 77: 115-123 (2004).

[16] Sohn, J.R., Lee, S.H., “Effect of TiO_2-ZrO_2 composition on catalytic activity of supported $NiSO_4$ for ethylene dimerization”, ***Appl. Catal. A-Gen***., 321: 27-34 (2007).

[17] Olszewska, D., “Ammonia and water sorption properties of the mineral-layered nanomaterials used as the catalysts for NOx removal from exhaust gases”, ***Catal. Today***, 114: 326-332 (2006).

[18] Damjanovic, L., Rakic, V., Mioc, U.B., Auroux, A., “Influence of cations on active sites of the alkaline earth salts of 12-tungstophosphoric acid: microcalorimetry study”, ***Thermochim. Acta***, 434: 81-87 (2005).

[19] Chmielarz, L., Kustrowski, P., Zbroja, M., Gil-Knap, B., Datka, J., Dziembaj, R., “SCR of NO by NH_3 on alumina ot titania pillared montmorillonite modified with Cu or Co. Part II. Temperature programmed studies”, ***Appl. Catal. B- Environ***., 53: 47-61 (2004).

[20] Mishra, T. Parida, K., “Transition metal pillared clay 4. A comparative study of textural, acidic and catalytic properties of chromia pillared montmorillonite and acid activated montmorillonite”, ***Appl. Catal. A-Gen***., 166(1): 123-133 (1998).

[21] Bovey, J., Kooli, F., Jones, W., “Preparation and characterization of Ti-pillared acid activated clay catalysts”, ***Clay Miner***., 31(4): 501-506 (1996).

[22] Kooli, F., Jones, W., “Al- and Zr-pillared acid activated saponite clays: characterization and properties”, ***J. Mater. Chem***., 8(9): 119-2124 (1998).

[23] Turgut, F., “Katalizör ve Katalizör Desteği Olarak Kullanılmak Üzere Al-Sütunlandırılmış Kil Sentezi ve Karakterizasyon Çalışmaları”, Doktora Tezi, ***Gazi Üniversitesi Fen Bilimleri Enstitüsü***, Ankara, 58-90 (2004).

[24] Basoglu, F.T., Balci, S., “Micro-meso pore analysis of Cu or Ag incorporated Al-PILCs and application to Cr removal from aqueous solution”, ***Appl. Clay Sci***., submitted (2008).

[25] Tomul, F., Balci, S., “Synthesis and Characterization of Al-Pillared Interlayered Bentonites”, ***G.U. J. Sci***., 21(1): 21-31 (2008).

[26] Yang, R.T., Tharappiwattananon, N., Long, R.Q., “Ion-exchanged pillared clays for selective catalytic reduction of NO by ethylene in the presence of oxygen”, ***Appl. Catal. B-Environ***., 19: 289-304 (1998).

[27] Barrault, J., Bouchoule, C., Echachoui, K., Frini-Srasra, N., Trabelsi, M., Bergaya, F., “Catalytic wet peroxide oxidation (CWPO) of phenol over mixed (Al-Cu)-pillared clays”, ***Appl. Catal. B-Environ***., 15: 269-274 (1998).

[28] Lowell, S., Shields, J.E., Thomas, M.A., Thommes, M., “Characterization of Porous Solids and Powders: Surface Area. Pore Size and density”, ***Kluwer Academic Publishers***, 213-228 (2004).