PILLARED BASED CLAYS AS CATALYSTS FOR WASTEWATER TREATMENT

[1]M. LAWAL, [2]I. A. NDANUSA, [3]I. MU AZU

Department of Chemical Engineering, Kaduna Polytechnic, Kaduna, Nigeria
E-mail - l.musa@kadunapolytechnic.edu.ng, [2]ibrahimndanusa3@gmail.com, [3]imuaz70@gmail.com

Abstract - Clays have been used extensively for a number of applications, ranging from traditional to professional. Because they are environmentally friendly, clay minerals have received considerable attention in recenttimes due to their low-cost, high selectivity, reusability and operational simplicity. Porosity and stability of these clay materials could be improved by a process known as pillaring, which leads to materials known as pillared interlayered clays (PILCs). Pillared clays results to enhanced pore volume, surface area, thermal and mechanical stability and improved catalytic activity when compared to the original clays. These enhancement makes them suitable for use as adsorbents and catalysts. Available literature recently has shown the great potential and viability of pillared clays as catalysts in a number of processes such as catalytic reactions and in waste water treatments.This review, therefore, focus on the use of pillared clays as catalysts for the treatment of wastewater containing different types of contaminants such as chlorophenols bearing effluents which are among the most hazardous pollutants in industrial wastewater and contaminated groundwater, being highly resistance to biodegradation. Their conversion into environmentally harmless species is a current need.

Keywords - Pillared Clays; Wastewater, Effluents; Chlorophenols, Biodegradation.

I. INTRODUCTION

Pillared interlayered clays (PILCs) are among the promising porous materials which can be utilized as catalysts in a number of reactions (Mishra, 2010). More than thirty years have passed since the first announcement of pillared interlayered clays.The preparative techniques have progressed remarkably with a wide variety of pillared solids being made (Sychevet al., 1997). Recent advances in the synthesis of PILCs have expanded considerably in the scope of their potential catalytic applications (Meloet al., 2000). PILCs are formed by intercalation of polymeric metal hydroxides or oligomeric hydroxyl cations into the interlamellar space of the cationic clays, followed by thermal treatment, allows pillaring of the clays, with a modification of the interlayer distance and typically also an increase of the thermal stability (Centi and Perathoner, 2008). The catalytic behaviour of PILCs is usually associated to the modification of the acidity (by substituting tetrahedral and octahedral sites), by active sites introduced during the pillaring process and by intercalation with organometallic complexes. The method of pillaring could largely affect the final characteristics and performances (Vgelset al., 2005). Moreso, anionic clays could be pillared (Gyftopoulouet al., 2005). These materials, particularly those having isopoly- and heteropoly-anions intercalated between the layers, show a quite interesting catalytic behaviour (Centi and Perathoner, 2008). Moreover, the transition metal oxide pillars can be modified by oxidation/reduction to become catalytically active and the pillars of the clay create specific and stable active sites. In these contexts first row transition metals like iron, titanium, vanadium and chromium-pillared materials are mostly studied. So there is enough scope of developing new catalytic materials for different applications by varying the transition metal oxide pillars only (Mishra, 2010). This area of research is still growing and need further exploration as potential catalyst which is very limited in the literature. Generally, it is also claimed that the pillaring procedure significantly improves the performances with respect to the starting clays. As a result there is now a renewed interest in the pillared material as polyfunctional catalysts and catalyst supports (Sychevet al., 1997).

Several research groups have investigated the characteristics of PILCs and their use as catalysts or catalytic materials (Ding et al., 2001). The general conclusion which may be derived from these studies that pillared clays are very interesting and promising catalysts in a broad range of applications, for example in acid-catalyzed reactions (Centi and Perathoner, 2008) , catalytic hydrotreating of heavy vacuum gas oil (Gyftopoulouet al., 2005), alkylation of aromatics (Belkhademet al., 2008), the synthesis of bulk and fine chemicals (a broad range of reactions such as dehydrogenation, hydroxylation, disproportionation, esterification, epoxidation, alkylation, isomerization, Fischer-Tropsch, methane reforming, hydrogenation, aromatization, etc (Ding et al., 2001). upgrading of lubricant oils and for the reduction of pollutants (selective catalytic reduction of NOx and catalytic removal of organic volatile compounds (Centi and Perathoner, 2008).

The best clay base for pillaring is a high-swelling Na-montmorillonite (Issaadiet al., 2001). It is a mineral clay that can hold guest molecules between its layers (Choudharyet al., 1999). Many different cations, including hydroxy-aluminium, hydroxy-chromium, hydroxy-titanium and hydroxy-zirconium polycations have been used for the preparation of pillared

montmorillonite characterised by surface area of 200-400m^2/g, pore volume of 0.15-0.30 cm^3/g and interlayer spacing of 1-2 nm. Vaughan and Lussier (1980) demonstrated that montmorillonite interlayered with hydroxy-aluminium pillars will promote catalyticcracking and hydrocracking (Issaadiet al., 2001). Infrared spectra of adsorbed pyridine showed that both Brönsted and Lewis acid sites are present on the surface of the pillared clays.It was showed that the Brönsted acidity and the catalytic properties of Al-pillared montmorillonite could be improved by acid modification of the clay prior to its pillaring (Vaughan et al., 1980). Several studies on catalytic cracking are based on Al, Ga and Si-pillared clays. In some cases transition oxide-pillared clays are also studied for cracking reaction (Mishra, 2010). Cr-pillared laponite prepared using microwave irradiation is found to be a good catalyst for hydrocracking of heavy liquid fuels. Catalyst is found to be active even after 4 h of reaction regardless of high coke formation. The same catalyst can be reused without any decrease in the activity (Gyftopoulou et al, 2005). In addition, it was reported that by incorporating Al into Cr-PILC, both the thermal stability and surface acidity for the final mixed Al/Cr-PILC were improved, resulting in a higher activity in the catalytic cracking of cumene (Mishra, 2010).Various catalysts have been proposed as hydrodesulfurization (HDS) and hydrocracking (HC) catalysts (Kloproggeet al.,1993). In HDS and HC, transition metal sulfides catalysts supported on PILCs, possess some properties comparable to those of the zeolites, silica- alumina or alumina (Xiolinet al., 2011). Their pore structure and catalytic behavior can be varied over a wide range by changing the type of intercalate. Kloproggeet al. (1999) demonstrated that montmorillonite can be impregnated with nickel followed by sulfidation to provide catalysts exhibiting comparable and even higher thiophene HDS activities than alumina- and carbon-supported nickel sulfide catalysts (Yadav et al, 2004). The catalytic activity increased by raising the amount of Al13 pillars from 5.5 meq Al/g to 20 meq Al/g, whereas an increase in calcination temperature results in an activity loss. 5.5 meq Al/g is sufficient to saturate the montmorillonite (Zhenget al., 2005).

This study shows an overview of the different processes in which pillared clays are addressed to the abatement of water pollutants. In this way, pillared clays have been shown as catalysts for the treatment of wastewater containing different types of contaminants. Among them, the treatment of chlorophenols bearing effluent was highlighted. Chlorophenols (CPs) are among the most concerning pollutants in industrial wastewater and contaminated groundwater, being highly resistant to biodegradation. Their removal or conversion into enviromentaly harmless species is a current need. From chemical point of view, they can be removed by oxidative or hydrogenation treatment. On the whole this review highlighted the use of catalysts based on pillared clays for both pollutants treatment processes, specifically catalytic wet peroxide oxidation (CWPO) and catalytic hydrodechlorination (HDC).

Evolution of Catalytic Application of Pillared Clays

Pillared clays is process of smectic modification used to obtain materials that have found a wide range of applications in catalytic, adsorption and separation processes (Bankovicet al., 2009). The first industrial application of clays as catalysts dates back to 1915. Acid-treated smectites have been used for more than fifty years as catalysts for oil cracking being raplaced by zeolites due to their better activity and selectivity (Burch, 1988). Moreover, they have been extensively used as catalysts in organic and fine chemistry showing as main advantages the easy recovery and reused of the catalysts (Laszlo, 1986). Simple set-up and work-up, mild operation conditions and good yield and selectivity, all of them fairly useful features for developing environmentally friendly technologies (Cornelies and Laszlo,1994; Vaccari, 1998).

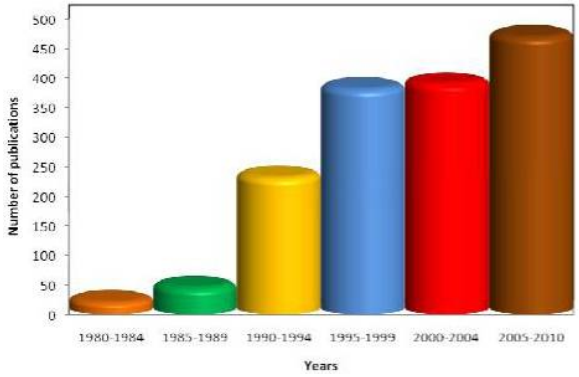


Figure 1: Evolution of pillared clays
Source: Molina et al. (2011)

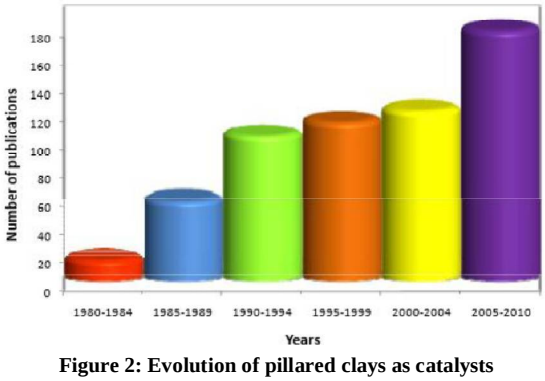


Figure 2: Evolution of pillared clays as catalysts applicationsSource: Molina et al, 2011

Pillaring improves the structural characteristics of the pattern clays, increasing the accessibility of the reactant molecules to the interlayer active sites, favouring in this way their catalytic properties (Kloprogge, 1998). These materials posses shape-selective properties due to their interlayer and inter

pillared distances which control the diffusion rates of reactants, reaction (Bergayaet al., 2006). The interest for pillared clays has suffered a dramatic increase in the last three decades (Gil et al., 2010). This great interest is reflected in Figure 1which shows the updated evolution of publications dealing with pillared clays. The use of pillared clays as catalysts is also gaining interest, with an average around 30papers/year, in the last decade as shown in Figure 2

Processes using pillared clays as catalysts

The catalytic activity of pillared clays can be controlled modifying their structure, textural properties and composition, making them suitable material for a large number of catalytic processes pointed out by (Beyer et al., 1995 and Pergheret al., 1999). Vaccari (1999), and Ding et al. (2001) submitted that the use of a variety of clays such as montmorillonite, beidellite, laponite, rectorite, pillared with different metals such as Al, Zr, Ga, Fe, Cr, Ti, Ce, La as catalysts for a diversity of reactions, like cracking of cumene and 1-butene, disproportional of propene and toluene, dehydration of glucose and alcohols, dehydrogenation of cyclohexane and cumene and Fisher-Tropsch synthesis among other. All these reactions can be group as acid- catalyzed reactions, synthesis of bulk and fine chemicals and pollutants removal, like NOx and organic volatile compounds (Centi and Perathoner, 2008).

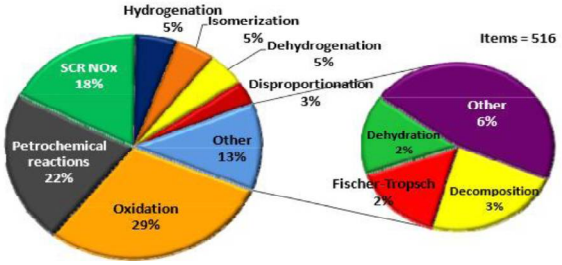


Figure 3: Processes using pillared clays as catalysts
Source: Molina et al. (2011)

Centi and Perathoner, (2008), submitted that 85% of the publication deal with catalysis with 6% contribution of pillared clays stressing the fact that these materials are been still developed mainly at laboratory scale when compared with other materials as clays and hydrotalcites have already found a broad range of industrial applications.Vaccari, (1999) and Ding et al. (2001) pointed out that the main applications of pillared clays in catalytic processes are in oxidation reaction (152), petrochemical reaction (113) and selective catalytic reduction of NOx (91) as shown in Figure 3 Centi and Perathoner (2008), stated that in spite of the fact that pillaring can improve the catalytic properties of pattern clays, it is quite suprising the low relative presence of patents on pillared clays as catalysts. Pillared clays are being used as commercial catalysts only in few cases, this fact being due to the high cost of their synthesis versus natural clays, although natural clays do not present the textural and mechanical properties and thermal stability of pillared clays (Molina et al., 2011). Ding et al (2011), submitted that, although catalysts based on pillared clays have advantages over other materials commonly used for a number of reactions such as production of bio fuels, cracking of oil fraction, NOx abatement; these advantages are not sufficient to change a technology whose implementation at industrial scale requires long and costly implementation. There are some cases where pillared clays have shown promising short-term outlooks (Vaccari, 1999). That is the case of wastewater treatment by catalytic wet peroxide oxidation (CWPO), synthesis of methyl - buthyl (Manju and sugunan, 2005). Or ethyl benzene dehydrogenation to styrene (Huerta et al, 2003).The need of developing novel or improved cost effective technologies for the abatement of toxic water pollutants open interesting opportunities for catalysts process where pillared clays can play an important role (Lee et al., 2001).

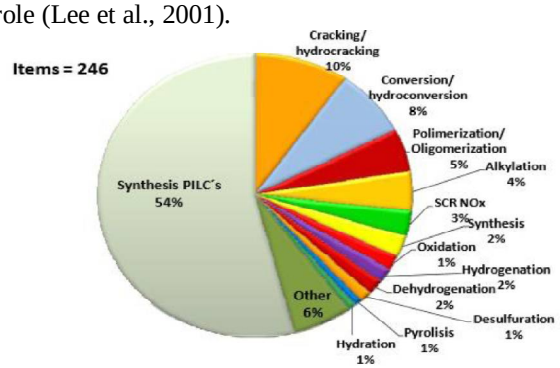


Figure 4: Patents on pillared clays
Source: Molina et al. (2011)

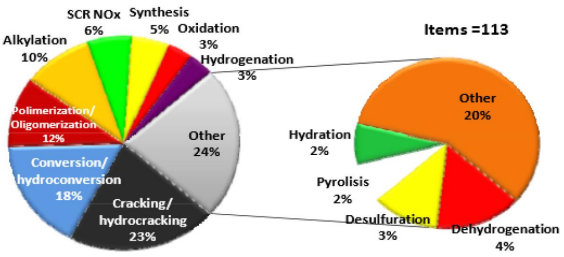


Figure 5: Patents on the use of pillared clays as catalysts
Source: Molina et al. (2011)

Application of pillared clays in oxidation processes

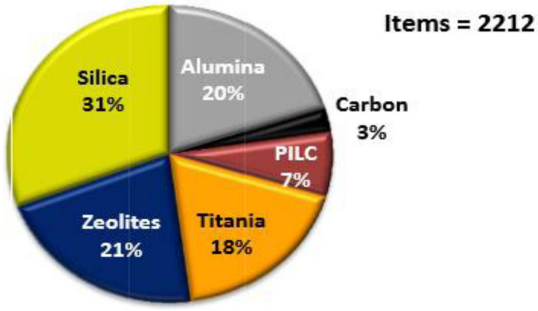


Figure 6: Material used as catalyst supports in oxidation process
Source (Moline et al., 2011).

Among the different materials used as support for oxidation reactions in liquid phase, pillared clays represent 7%, being silice, zeolites and almina the must studied. However, the interest for pillered clays has increased substantially in the last years (Molina et al., 2011).

As shown in Figures 6 and 7, pillered clays have been used in different oxidation (CWPO) and photo catalytic oxidation the most represented (Lee et al., 2001).

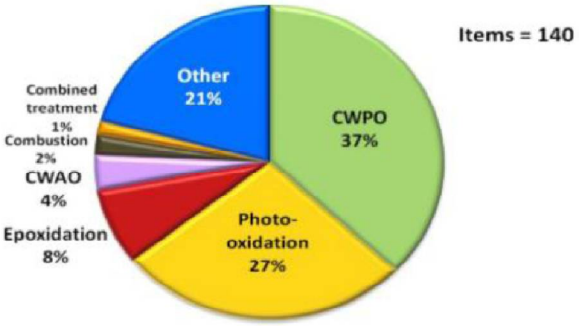


Figure 7: Different oxidation techniques using pillered clays as catalysts
Source (Molina et al., 2011).

Bovtunet al., (2005), pointed out that almost all the studies deal with the abatement of water pollutants whose distribution are shown in Figure 8. A diversity of raw clays has been used for the preparation of these pillered materials corresponding around 80% to bentonite-montmorillonite (Figure 9). Fe is by far the metal most frequently used as active phase although many others have been also tested (Boukunet al., 2005).

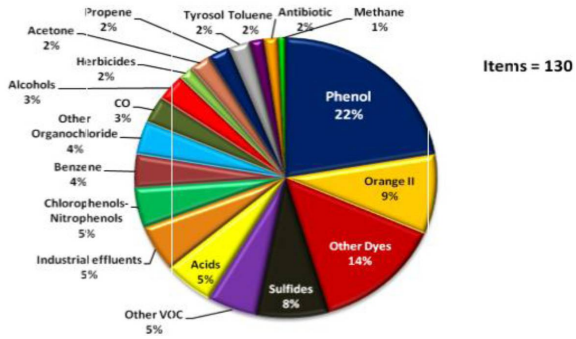


Figure 8: Water pollutants on use of pillared clays in oxidation processes
Source (Moline et al., 2011).

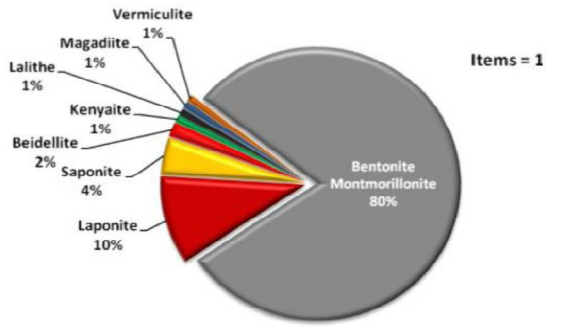


Figure 9: Types of clays used as PILLS for oxidation catalysts.
Source (Moline et al., 2011).

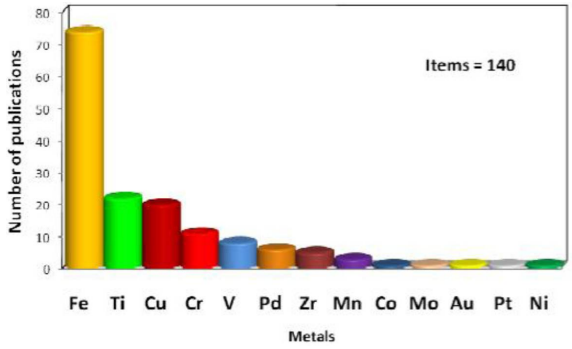


Figure 10: Metlas used as active phase in clays for oxidation with pillared catalyst.
Source (Moline et al., 2011).

Application of pillared clays in Advance oxidation processes

Hoke et al., (1992); Zinovgeret al., (2007), revealed that among the methods developed for the treatment of waste water with none or low biodegradable organic compound advanced oxidation process (AOPs) appear as a promising technology which has been reported to be effective for the degradation of soluble organic contaminants in water and soils, providing an almost complete degradation under mild operating conditions.

AOPs have been defined those aqueous phase oxidation processes based primarily on the intermediacy of the hydroxyl radical in the mechanism (Ollis, 1993). AOPs not only achieve the chemical transformation of the pollutants but present other advantages such as complete mineralization of some species allowing their oxidation at very low concentrations, the improvement of the organoleptic properties of the treated water and a low energy consumption compared with other methods (Herney-Ramirex et al 2010). Primo et al., (2008), pointed out that these processes can be developed by the use of a combination of oxidants, such as ozone, oxygen or hydrogen peroxide and different types of metals catalysts.

One of the more promising AOPs is based on the use of Fentons reagent where Fe^{2+} reacts with H_2O_2 to generate hydroxyl radicals (Herney – Ramirez et al., 2010). H_2O_2 as oxidizing agent is much more efficient that gaseous oxygen for the mineralization of pollutants at near ambient condition and with lower reaction times (Ukisa and Miyadera, 2003). Letacefet al., (2003), suggested that Fe^{3+} can also be used due to the reaction cycle involved fenton like mechanism. This side reactions compete with this catalytic cycle oxidation of the reduced transition metal fow by O_2 dissolved in water and complexation of the transition metals ion by some intermediate oxidation product as oxalic acid (Centiet al., 2000). The loss of iron, which has to be removed before discharge, make necessary additional separation stage and sludge disposal, being a major drawback which has limited in practice a more extended application of

the technology (Carriozoet al., 2003). A solution to this problem can be the used of stable solid catalysts in a heterogeneous version of the Fenton process. Catalytic wet peroxide oxidation (CPWO), which can be operated in a broad range of pH values and can be effectively applied on waste water treatment (Barraoiltet al., 2003). Different materials base on clays have been described as Fenton-type catalysis for the treatment of different organic and species in aqueous media CU^{2+} containing montmorillinites (Barrenet et al 1998) and Fe^{+3} or Cu^{+3} – containing pillered clay (Catrinescuet al., 2003), have fileds high phenol and Toc conversion with good reaction rates and very low metal leaching, mailaining their activiety in successive runs (Molina et al., 2006; Guelonet al., 2003 and Parathoner, 2008).

Navalonet al. (2010) and Garriidet al. (2010) have reviewed the use of pillered clays as catalysts in heterogeneous Fenton and Fenton like processes. In addition Soon and Hammed (2010), have reported on the application of these catalysts in Fenton and photo-Fenton processes for the treatment of synthetic dyes. Furthermore Parathonor and Centi (2010) submitted that pillered clays can be used for wastewater treatment through Fenton like processes and other AOPs.

Application of pillared clays in hydrogenation processes

Pillared clays with different metals have studies as catalysts in number of hydrogen reaction (Moline et al., 2006). Some of them are of potential interest in wastewater treatment, most in particular hydrodechlorination (HDC) which append as an emerging technology for the abatment of highly toxic-organic chlorinated pollutants (Moline et al., 2011). A wide variety of metals have been used as active phase Ni has been used for benzene hydrogenation, while other metals like Co and Mo, have been employed for Fisher- Tropach synthesis and hydrosulfuration, but precious metals (Pt, Pd or Rh) are the most extensively studied for hydrogenation (Calvoet al, 2005).

Types of pollutants in hydrodechlorination

Catalytic hydrodechlorination (HDC) non-destructive chlor-waste treatment that involves hydrogen cleavage of C-Cl bonds (Satakrishna and Keana, 2010). Application in the environmental field is of current main interest since it reduces dramatically the toxicity of waste streams bearing chlorinated pollutant (Gupta et al., 2002). HDC shows main advantages operation at low temperature and pressure, high conversion, no occurrence of more harmful side products, and low sensitivity to pollutants concentration (Keane et al., 2004). Orderiez et al (2002), revealed that this technique has been applied to a diversity of chlorinated components in water and gas phase. Felis et al (1999) and Boukunet al. (2005) pointed out that almost one half of the HDC studies relative to water pollutants abatement deal with cholobenzener and chlorophinols but a wide diversity of other species have also been used as target compounds.

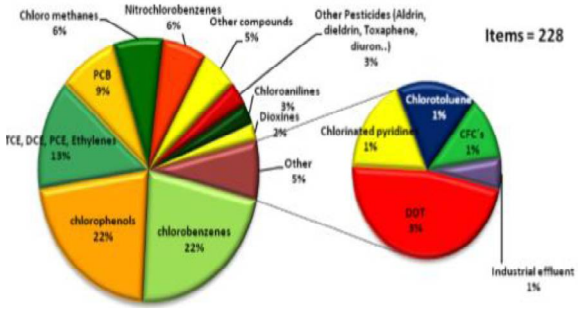


Figure 11 Type of pollutants in HDC
Source (Molina, et al, 2011).

Wet air oxidation as well as AOPs have been used for the removal of that type of pollutants, although they show some limitations such as large reagents, consumption and complex equipment, depending on the type of process (Santos et al., 2002 and Zazo et al, 2005).

Metals and catalytic supports used for Hydrodechlorination (HDC).

The catalyst tested in HDC consist mainly of precious metals, mostly Pd, over different supports, most in particular carbon and alumina (Molina et al., 2009). Molina et al.,(2010), tested different precious metals supported on Al-pillared clays for the abatement of chlorophenols using formic acid and the results are promising.

Molina et al., (2010) further stated that most of the HDC studies using direct H_2, its low solubility in water can be a drawback for its application in wastewater treatment, especially as the pollutant concentration become higher. Formic acid in liquid at room temperature, which from an engineering point of view provide some advantages as an easier shipping and handling (Molina et al., 2009). Kepiakeet al., (2004), reported its use in HDC of chlorobenzenes.

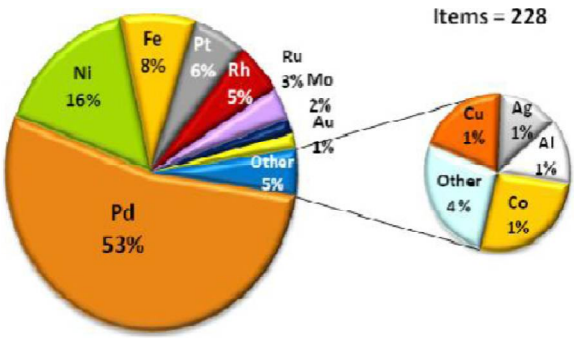


Figure 12: Metals used in HDC catalysts
Source (Moline et al., 2011).

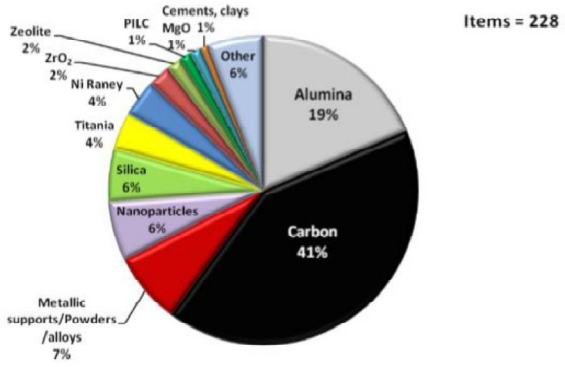


Figure 13: Catalytic Supports used for HDC catalystsSource (Moline et al., 2011).

CONCLUSION AND RECOMMENDATION

The use of pillared clays as catalysts for wastewater treatment had been reviewed. From the findings, there are growing advances in research within the last years which proves that pillared clays are promising catalysts or catalyst supports in different processes, including catalytic wet peroxide oxidations (CWPO) and catalyticalhydrodechlorination (HDC), both of interest for wastewater treatment in particular for the abatement of hazardous pollutants from industrial effluents. From the findings, Fe–Containing Al and Zr–pillared clays have potential application in CWPO while Pt, Pd and Rh on Al pillared clays have potential application in HDC. The results of the finding allow considering pillared clays catalysts as promising emerging technologies for the abatement of hazardous and recalcitrant water pollutants.

Therefore, there is need for more research on pillared clays as catalyst in wastewater treatment especially in developing nations like ours with goal of finding appropriate solutions for socio-economic problems and environmental protection.

REFERENCES

[1] Barama, S., Dupeyrat, L. Capron, M. and Bordes-Richard E. (2009)Buletin of catalyst today 141 (3-4) 385 – 392.

[2] Belkhadem F, Clacens J-M, Bengueddach A, &Figueras F. (2008) journal of Applied Catalysts: 298: 188

[3] Bovkun, T.T.,Sasson, Y. and Blum, S. (2005) Journal of molecular catalysts 242, 68 -73.

[4] Burch, R. (1988) Buletain of Catalyst today.

[5] Caluo, L, Mohedano, A. F and Casses (2005). Journal of Indian Engineering Chemical Research 44: 6661 – 6667.

[6] Carriazo J Guelon E. and Barranlt, J. (2005)Buletain of Catalysts Today 107 – 108.

[7] Centi G, &Perathoner S. (2008), Journal of Microporous and Mesoporous Materials, 107: 3

[8] Choudhary V, &Mantri K. (1999) Procedure of Indian Academic of Science: 111(5): 669

[9] Cornelies and Laszto, (1994) Journal of Syntheses Catalyst.

[10] Ding Z, Kloprogge J T, Frost R L, Lu G Q & Zhu H Y. (2001) Journal of Porous Materials: 273

[11] Gyftopoulou M E, Milian M, Bridgwater A V, Dugwell D, Kandiyoti R, &Hriljac J A. (2005), Journal of Applied Catalysts : 282: 205

[12] Heney-Ramirel J. Vicentel, M. A. And Madira E.(2010) Journal of Applied Catalysts and Environment 98, 10 – 26.

[13] Hoke, J.B., Gramillion, G.A. and Balko E.N. (1992).Journal of Applied Catalysts. 1, 285 – 296.

[14] Huerta, L. Meyer E., and Choren, E. (2003)Jouranal of Microporous and mesoporous materials 57, 219 – 227.

[15] Issaadi R, Garin F, Chitour C E, &Maire G. (2001), Journal of Applied Catalysts:207: 323

[16] Kloprogge J T, Welters W J J, Booy E, de Beer V H J, van Santen R A, Geus J W, & Jansen J B H. (1993), Journal of Applied Catalysts 97: 77

[17] Laszto, P. (1996). Accademic of chemical Research 19, 121 – 127.

[18] Lee C. W., Tatarchuk A, and Wang B. (2001). Journal of microporous and mesoporous material. 44 – 45.

[19] Manju, K. And Sugnnan, S. (2005) Journal of porous molecules 12, 323 – 336.

[20] Melo D M A, Ruiz J A C, Melo M A F, Sobrinho E V, &Schmall M. (2000), Journal of Microporous and Mesoporous Materials, 38: 345

[21] Mishra T. (2010), Pillared clays and related catalysts. Springer, New York, 99

[22] Mollna, C. B. Zazo, J.A. and Monsaho, V. M. (2010) Journal of Water Science Technology 61(8) 2161.

[23] Navalon, SAluan M. and Garcia H., (2010) Journal of Applied Catalysts 99, 1 – 28.

[24] Ollis, D. (1993) Buletain of Emerging Technology is Waste Management II 518. Washington DC.

[25] Parathoner S, and Cent (2008). Journal of pillared clays and related catalysts New York 167 – 200.

[26] Perghar, S. D.,Corma, A. and Quimila E (1999) Journal of Clays catalyst 22(5) 693 – 709.

[27] Pure Appl. Chem., Vol. 71, No. 12, pp. 2367±2371, 1999.

[28] Sychev M,(San) de Beer V H J, Kodentsov A, van Oers E M, & van Santeny R A. (1997), Journal of molecular Catalysts, 168: 245

[29] Ukisu, Y. Miyadara, J. (2003) Journal of Applied Catalysts and Environment.

[30] Vaccari, (1999) Journal of Applied Science. 141: 161 – 198.

[31] Vaccarki (1998)Buletain of catalysts Today 41, 53 -71.

[32] Vaughan D.W. &Lussier R. (1980), Proceedings of 5th International Conference on Zeolites, Naples Heyden Press, London.

[33] Vogels R J M J, Kloprogge J T &Geus J W. (2005), Journal of molecular Catalysis, 231(2): 443

[34] Xiaolin T, Zheting L, & Li S. (2011) Journal of China Petroleum Processing and Petrochem Technology, 13(3): 16

[35] Yadav M K, Chudasama C D, &Jasra R V. (2004), Journal of Molecular Catalysts: 216: 51

[36] Zheng S, Sun S, Wang Z &Gao X (2005), Bulletin of Catalysts Society India, 4: 30

★★★