

A Review on the Importance of Pillared Interlayered Clays in Green Chemical Catalysis

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Abstract: In recent years, Pillared InterLayered Clays (PILCs) have been widely used in several applications; in particular in adsorption and catalysis. The research interest in this family of solids has increased considerably. Clay minerals provide distinct nanometer-scaled layers and interlayers for engineering them as active catalysts. As such, strategic design and preparation has led to a variety of catalysts, including ion exchanged catalysts, acidic activated clay catalysts, intercalated catalysts, pillared clay catalysts, clay-supported catalysts, inorganic and inorganic-organic composites and hybrids, and hierarchically structured solid catalysts. The clay-based heterogeneous catalysts have many practical and potential applications in green catalysis. The review is mainly focused on the importance and the applications of these Pillared Interlayered Clays,

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I. Introduction

Catalysis is one of the important tools for sustainability and profitability of chemical production processes. The total quantity of catalysts used all over the world in all the processes together exceeds several million tons per annum. Their handling during use in the chemical transformation and disposal after use is of great environment concern. Many heterogeneous catalysts used for organic transformations are either toxic or nonspecific or involve cumbersome procedures for their preparation and require a specialized care for their use, recovery and disposal which make the manufacturing process more and more energy intensive. There is obviously a continuous search for green catalysts which play a critical role in industrial reactions. An ideal green catalyst is a non-hazardous substance that can bring about a reaction at a faster rate and at lower temperatures than in the homogeneous conditions, yield maximum desired product with minimum waste, and which can be easily separated and recovered to be used more than once. Conventional heterogeneous catalysts such as metals, metal oxides, solid acids, low-dimensional solids and ion exchange resins are being used extensively in organic synthesis. Although very few of these fit into the definition of an ideal green catalyst, in the recent years there has been resurgence in the study of these catalysts, with or without modifications, reporting improved product yield and selectivity and reuse of the catalyst claiming green nature of the reaction. A recent trend in the chemical industry is to switch over to catalysts that are more benign to environment. Advantages associated with this are easy handling of the catalysts during life cycle and disposal after use. In this context one such material that is being tried in variety of reactions is the clay based material.

The discovery of functional solid materials of high catalytic performance is crucial to most chemical processes by allowing the replacement of polluting homogeneous catalysts by reusable heterogeneous catalysts [1] or by innovating the production of fuels and chemicals from sustainable resources like biomass and biomass-derived feedstocks [2,3]. To this goal, well-engineered solid catalysts offer excellent potential for minimizing the screening of catalysts which is usually time-consuming. In this context, clay minerals are just a class of inorganic layered compounds, which can be engineered into various functional solid catalysts due to their inherent features in composition and structure. Therefore, the rational design and preparation of novel catalysts based on clay minerals has received many a scholar's concern over the past four decades. Nowadays, there is a great need for creative strategies which should enable clay minerals to be engineered to "designer catalysts" for applications in green and sustainable catalysis, including chemical, photonic, electric, and biological processes.

II. Clays

Clays may be regarded as green catalytic materials as they are abundantly available in nature and can be used minimum processing. They are non-corrosive solid materials, have plasticity for easy fabrication into with desired shape and size for use in the reactor, could easily be separated from product stream, are disposable

relatively easily after use with no threat to ambience. Among the clays, the most used catalysts in chemical transformations are the montmorillonites. Several options for the surface modification of montmorillonite practiced by clay chemists are available. These include (i) ion exchange with multivalent inorganic cations and coordination complexes to incorporate red-ox species and simultaneously generating acid centres (ii) ion exchange with organic cationic species having long alkyl chains with bulky head groups and intercalation with organic compounds to swell the clay layers to variable extents (iii) treatment with inorganic hydroxyl-oligomeric species followed by thermal treatment to obtain pillared clays having Lewis acidity (iv) treatment with mineral and organic acids and surfactants to get acid clays with tunable porosities (v) dealumination of structural aluminum by mild acid treatment to generate porosity in the clay platelets as well as mixed Brønsted acids in the interlayer (vi) incorporation of polymeric hydrated species of metals along with alkylamine species in the interlayer followed by removal of the organic species by washing with organic solvents and thermal treatment to get porous clay heterostructures (vii) impregnation of metal salts followed by reduction to get supported metal and metal oxide catalysts and (viii) modification for microwave-assisted reactions as clays with their variety of bipolarity are excellent absorbers of microwaves. All these are simple methods of surface modification making use of non hazardous chemicals. Modified clays are invariably stable and do not lose their characteristics easily. There have been a number of reviews on the modification of clays in the recent years. Hundreds of publications are appearing every year on their applications in organic synthesis. Some of the reviews which have appeared recently have presented the ability of clay catalysts to bring about organic transformations such as addition, condensation, alkylation, rearrangement, isomerization, cyclization, ring-opening and closure, oxidation, hydrogenation and dehydrogenation, protection-deprotection, hydroboration and so on. But the reviewers have disregarded the role played by the modified surface. They do not relate the changed features of the modified clay surface with the performance characteristics.

Clays are widespread, easily available and low-cost chemical substances. Both in their native state and in numerous modified forms, clays are versatile materials that catalyze a variety of chemical reactions. Just as they can be molded into any shape, their micro structure can be changed to suit chemists' needs to promote diverse chemical reactions. It is convincingly argued that clays initiated, supported and sustained the process of formation of small molecules on the earth millions of years ago, which gradually developed into more complex molecules. In the course of time, there emerged from the latter the self replicating assemblies that evolved into simple life forms and progressed to the present elaborate living world of plants and animals [4, 5, 6].

III. The Nature of Clays

Microscopically, naturally-occurring clay minerals are typically composed of ultrathin crystalline aluminosilicate layers (around 1.0 nm) superimposed on interlayer of hydrated ions. Therein, each aluminosilicate layer generally consists of one (for 1:1 type) or two (for 2:1 type) Si—O tetrahedral sheets and one Al—O (or Mg—O for some clay minerals) octahedral sheet. In other words, each layer in a 1:1 type clay mineral (T—O layer) is built by one octahedral sheet bonded to one tetrahedral sheet whereas each layer in a 2:1 type clay mineral (T—O—T layer) takes shape from one octahedral sheet sandwiched between two tetrahedral sheets through chemical bonds [7]. The interlayer and the T—O—T layers are bound together by both electrostatic and hydrogen-bonding forces. Isomorphous substitution by other metal ions of different valence readily occurs to the central metal ion either in the octahedral (e.g., Mg for Al) or tetrahedral sheets (e.g., Al for Si), thereby leading to negative charges on the layers [8]. Accordingly, positive-charged cations exist within the interlayer space necessary to compensate negative-charged aluminosilicate layers and such cations are hydrated like macro-counter anions. Besides, on either 1:1 or 2:1 clay minerals, the broken-edge of each layer acts as a second source of charge which is generally negative and pH dependent [9,10]. Consequently, clay minerals possess unique physicochemical properties such as large surface areas, swelling, ion exchange, and active broken-edge M—O— bonds. Therefore, clay minerals exhibit peculiar capacities for absorption, adsorption, and catalysis. Engineering clay minerals into catalysts primarily takes advantage of these characteristics, mainly arising from their layers and interlayer space. Thus, the formulations, structure, and surface properties of the resulting clay-based catalysts could be finely tailored. The clay-based catalysts could be categorized into seven types as follows: ion exchanged catalysts, acidic activated clay catalysts, intercalated catalysts, pillared interlayer clay catalysts, clay-supported catalysts, composites and hybrids, and hierarchically structured catalysts.

Clays are solid acidic catalysts which can function as both Brønsted and Lewis acids in their natural and ion-exchanged form. Clays are a class of soil with a particle size of <2 mm in diameter (which implies a surface area of about 23000 cm² per gram). Their characteristic physical features are, they are sticky and plastic

when moist, but hard and cohesive when dry. Structurally, they are crystalline hydrous aluminosilicates, and also contain various other cations. Their chemical composition and crystal structure are the basis on which they are divided into four main groups such as, illite, smectite, vermiculite, and kaolinite. Among these, the one that is found to be most useful as a catalyst to the synthetic organic chemist is a subgroup of the smectite clay, called montmorillonite, which is the main constituent of bentonites and Fuller's earth.

IV. The Structure and Properties of Montmorillonite Clay

The montmorillonite lattice is composed of a sheet of octahedrally coordinated gibbsite $[Al_2(OH)_6]$ sandwiched between two sheets of tetrahedral coordinated silicate $[SiO_4]^{4-}$ sheets. The three-sheet layer repeats itself, and the interlayer space holds the key to the chemical and the physical properties of the clay. An important and useful property of montmorillonite stems from its high degree of efficiency for M^+ cation exchange. This happens because of charge imbalances in its structure caused by exchange of Al^{3+} for Si^{4+} in the tetrahedral sheets, and of Mg^{2+} for Al^{3+} cations in the octahedral sheets. The defects at the edges of crystals also add to this imbalance. If approximately 20% of Al^{3+} positions are replaced by Mg^{2+} , montmorillonite will gain a cation exchange capacity of 100 millimoles of M^+ per 100 grams of clay. These balancing cations are presumably situated between the lattice layers. On wetting, the layers move apart by the entry of water molecules, thereby the clay swells and the existing interlayer cations become easily exchangeable. The catalytic properties of montmorillonite clay can be greatly manipulated to suit the needs of synthetic organic chemists. The interlayer in montmorillonite clay normally contains Na^+ , Ca^{2+} and Mg^{2+} as compensatory cations for the charge imbalance. When the clay is dry these cations reside in the hexagonal cavities of the silica sheets. However, when it is treated with water, the cations relocate themselves in the interlamellar region and become exchangeable by a variety of both metallic and nonmetallic cations, for example, H_3O^+ , NH_4^+ , Al^{3+} , Fe^{3+} , R_4N^+ , R_4P^+ , etc. One of the most useful properties of clay minerals lies in this fact.

In recent years, Pillared Interlayered Clays (PILCs) have been widely used in several applications; in particular in adsorption and catalysis. The research interest in this family of solids has increased considerably by the development of nanoscience and nanotechnology. Earlier works reported that pillared clays showed a significant modification effect in its porous structure and physicochemical properties [11]. Currently montmorillonite (M) clay is considered to be a most probable material in various catalysis reactions. A number of different cations, such as aluminium[12], titanium[13], iron [14], chromium[15], and zirconium [16,17] polycations have been used for the preparation of pillared M. The basic phenomenon used in the preparation of pillared clays is the ion exchange of interlamellar cations by the bulky cationic species (oligomer) that act as probes to keep the structure open. It is obvious that only the swelling clay minerals capable of cation exchange can be pillared [18]. To get a stable structure such as pillared clay, the intercalated solid has to be carefully processed further. Treatment of the solid at an elevated temperature is the next step after intercalation. This results in the dehydration and dehydroxylation of the polycation where it changes to stable oxide. Upon calcinations, the bond between the interlayer species and clay layers is thought to shift from ionic to near covalent, which results in the stabilization of the porous network by converting hydroxide pillars to stable oxides [19, 20]. Thus, pillared clays show a characteristic porous structure, influenced by the number and size of the pillars in the interlayer region, which is in turn influenced by the cation exchange capacity of the original clay mineral and the charge of each individual polycation, among other factors. The intense research on PILCs carried out in the last decades means that more than one thousand references can be found in the literature, including several review articles and books reporting synthesis procedures, and the characterization and applications of these solids [21, 22,23,24,25, 26, 27].

V. Ion Exchange Capacity

Cations in the interlayer space of clay minerals can be changed to various inorganic or organic cations via an ion-exchange reaction. Such a principle affords a facile way to prepare a clay-based catalyst with the desired ions as catalytically active species. The monovalent (Na^+) and divalent (Ca^{2+}) cations, which commonly occupy the interlayer region in natural mmt, for example, can be readily replaced by other ions. In this way, either homoionic or heteroionic mmt, in principle, can be produced. In this respect, cation exchange capacity (CEC) plays a leading role in an ion-exchange reaction. The CEC is mainly dependent on layer charge density. The larger the amount of cations in the interlayer, the more strongly the platelets of mmt are bound together. This might hinder catalytic efficiency by means of hampering intercalation of reactants between the platelets because most sites within the interlayer of mmt have been filled with cations (e.g., Na^+) [28]. Therefore, clay minerals with CEC in a certain range should be chosen and then treated under a set of proper conditions for the

ion exchange reaction. As a result, the ion exchanged clay catalysts might offer better catalytic performance for a specific reaction. Therefore, besides the selection of the parent clay minerals with a desired range of CEC and the conditions of ion exchange, CEC and subsequently the extent of ion exchange can also be controlled by pretreatments such as calcination [29]. Furthermore, hydrophilic clays can be changed into hydrophobic clays once the charge compensating interlayer cations sandwiched between the negatively charged aluminosilicate layers are exchanged with organic cations such as quaternary ammonium cations NR_4^+ , where R is an alkyl group or an aryl group [30]. Hence, the interlayer cations can be designed both qualitatively and quantitatively through a wide range of strategies for “designer catalysts.” Hydrogen ion exchanged clay minerals, which are generally produced by the treatment of clay minerals with acids, are an exclusive case among ion exchanged clay minerals. This is because such a process proves to be influential at least in three ways rather than merely in the way of ion exchange. The first is the ion-exchange reaction between interlayer cations with H^+ ; another is the part or thorough breakdown of the layers, leading to more broken-edge M—O— bonds and a reduced particle size of clay platelets; the third is the selective leaching of central atoms in tetrahedral and octahedral sheets [31]. Therefore, acid treatment might result in more acidic sites together with larger surface areas on the resultant products than the starting clay materials. Both outcomes are favorable for catalysis. Such clay-based materials treated by acids are often called acid activated clays. Of this type of clay-based catalysts, mmt K-10 is representative of a commodity product that has actual applications in some organic syntheses [32]. The concentration and the types of acid, and reaction time and temperature are major factors decisive to the physicochemical properties of the resultant acidified clay minerals. The use of concentrated inorganic acids, however, leads to environmental issues owing to the generation of a great deal of acidic wastewater, in addition to equipment corrosion and operational dangers. Organic acids such as carboxylic acids and sulfonic acids, instead of inorganic acids, can provide an alternative route to activated clay minerals. In addition, organic acid could lead to different degrees of changes in the layer, interlayer, and the edge compared with those attacked by mineral acids [33]

VI. Pillared Clays

A series of CuO supported Zr-pillared CeO_2 modified montmorillonite (MMT) catalysts have been successfully prepared by Rightor et al. [34] and has been considered for studying the total oxidation of toluene, acetone and ethyl acetate. It is believed that the new support of Ce–Zr/MMT is responsible for the enhanced catalytic performance for VOC combustion when it is used as support. Rachid et al. [35] reported sulfated zirconium montmorillonite supported 1 wt. % palladium is an active catalyst able to catalyse such reactions as hydroisomerization of light naphtha. Its relative high activity and selectivity can be related on one hand, to the relative strength of the acid sites and, on the other hand, to the hydrogenation power of palladium which avoids the (hydro) - carbon residues to block the active sites. Mishra et al [36] reported the preparation, characterization and catalytic activity of Zr-pillared clays with different pillar density, starting from Ni^{2+} exchanged clay. The physicochemical characteristics of the pillared clays have been evaluated using X-ray diffraction (XRD), thermogravimetric analysis (TGA), infrared (IR), UV–visible diffuse reflectance spectroscopy (UV–VIS–DRS) and sorptometric studies. The acidity of the pillared clays was calculated from TG analysis of the adsorbed n-butyl amine. Alkylation of phenol with methanol was carried out over these catalysts. Good correlation was observed between the alkylation activity and acidity of the pillared materials. Both O and C-alkylation was observed during the reaction. The pillared materials with lesser pillar density were found to be more selective towards anisole which can be attributed to the control in acidic properties of the materials. Bineesh et al. [17] were synthesized titania-pillared clay (Ti-PILC) and zirconia-pillared clay (Zr-PILC), and their catalytic performance was studied for the selective oxidation of H_2S to elemental sulfur. The good catalytic performance of the metal-oxide pillared clays may be due to the high surface area and the presence of Bronsted and Lewis acid sites. Ahmad et al [19] were studied Fischer- Tropsch (FT) synthesis over cobalt nanoparticles supported on modified Zr- pillared montmorillonite. The FT products obtained showed increased selectivity of C_2 - C_{12} hydrocarbons and decreased selectivity towards CH_4 and higher molecular weight hydrocarbons. S. Kavitha and S. Sugunan [37] prepared zirconium pillared and rare earth exchanged zirconium pillared montmorillonite and their catalytic performance was studied for the Friedel – Crafts Benzylation reaction. Zirconium pillared clays at room temperature was found to be very effective catalyst for the catalytic benzylation of benzene with benzyl chloride.

Pillared montmorillonites, i.e., Fe-Mt, Fe/Zr4:1-Mt, Fe/Zr1:1-Mt and Zr-Mt were synthesized by Zhou et al. [38] and applied to evaluate their feasibilities as adsorbents to remove Cr (VI) from solutions. These preliminary results indicate that Fe/Zr pillared montmorillonite can be applied as an effective adsorbent for the

treatment of Cr (VI)-rich wastewater. Pillared layer clays containing Fe,Al or Cr,Al mixed pillars were synthesized by Palinko et al. [39] and characterized with mid and far FT-IR and Mossbauer spectroscopies. Catrinescu et al. [40] attempted to identify the structure of iron-containing species in the AlFePILCs prepared from different clays, in order to analyze the catalytic properties in correlation with the nature of these active phases. M. Luo et al. [41] presents on the catalytic properties of Fe-Al pillared clay, which was used to promote the Fenton oxidation of phenol by hydrogen peroxide (H₂O₂). The effect of the Fe and Al present in the pillaring solution on the catalytic activity, the cause of induction period, and the kinetics of the catalytic reaction were investigated.

N. Bouchenafa-Saïb et al. [42] reported the preparation of a microporous material starting montmorillonite by pillaring it with chromium and aluminum and to study cadmium adsorption ability of these pillared clays and confirms that the Mont-Cr-Al is the better adsorbent for the cadmium, showing the interaction between Al and Cd. P. Yuan et al. [43] were synthesized iron pillared clays by the reaction of montmorillonite with base-hydrolyzed solutions of Fe(III) nitrate. In contrast with the classical microporous pillared structure, a novel meso-microporous delaminated structure containing pillared fragments in iron-pillared clay was obtained. These fundamental results are of importance in developing novel heterogeneous catalysts and adsorbents. J. Choy et al.[44] were prepared Chromia pillared clay by ion exchange type intercalation reaction between Na'-montmorillonite and the trimeric chromium oxyformate (TCF) salt in an aqueous solution. A solution of CrCl₃ and AlCl₃ in Na₂CO₃ was used by Zhao and others [45] to produce a CrAl PILC. Basal spacings of around 18 Å were achieved when calcined at 500°C with surface areas around 230 m²/g. The thermal stability was found to be greater than that of Cr PILC as well as possessing more acid sites.

M. Kurian et al.[12] reported the use of cleaner, shape selective iron pillared clay catalysts for Friedel-Crafts alkylations. Presence of surface acid sites as well as its nature influences the catalytic activity. A free radical mechanism has been suggested for the reaction. P. Kar et al. [46] prepared Cr-pillared montmorillonite clay (Cr-PM) by the intercalation of the chromium oxyhydroxy cationic clusters into the clay interlayer and subsequent thermal activation. The Cr-PM material was used as an efficient heterogeneous catalyst for the synthesis of octahydroxanthenes by the condensation of dimedone with aryl aldehydes. Structurally diverse octahydroxanthenes were synthesized under solvent free conditions and microwave irradiation using Cr-PM as heterogeneous catalyst. Thomas et al. [47] describe metal cation exchanged mmt prepared by an ion exchange reaction of K-10 mmt with Ce³⁺, Fe³⁺, and Al³⁺ for one pot acetalization of carbonyl compounds (cyclohexanone, acetophenone, and benzophenone) with methanol under ambient conditions. Compared with Y- zeolites, SiO₂, and γ-Al₂O₃, such clay-based catalysts were found to be more active. Paranjape et al. [48] reported Friedel–Crafts acylation of arenes by using chloroacetyl chloride on Fe³⁺-exchanged montmorillonite K10 in liquid phase .The yields are good only with polymethylated benzene derivatives, namely, durene, mesitylene, p-xylene and m-xylene. Nissam Ellias and S. Sugunan [49] were prepared Aluminium pillared clay and Iron –Aluminium pillared clays by ion exchange method and cerium was loaded in pillared clays by wet impregnation method. The catalytic activities of the prepared catalysts were evaluated for the hydroxylation of phenol. Incorporation of cerium enhances the selectivity of hydroquinone by the formation of metaloxo peroxide intermediate. These catalysts can be effectively used as green catalyst for the abatement of phenol on waste water.

New chromium pillared clays of basal spacing 2.45 nm were synthesized and characterized by M. Roulia et. Al [50]. The chromium oligomers used for intercalation were prepared by quick addition of base and acid to Cr(III) monomeric solutions followed by reflux. The synthesized clays exhibit increased BET surface area and higher micropore volume compared to clays with lower galleries, pillared either by smaller Cr(III) oligomers or by Cr(III) monomers. Important parameters affecting the *d*₀₀₁ basal spacing were studied, e.g. the pH of the pillaring solution, the intercalation time, the chromium concentration and the counter-anion present in the chromium solutions. Scanning electron micrographs were acquired to demonstrate changes of the clay texture before and after pillaring. The thermal behavior of the synthesized clays was also examined. C. H. Zhou [51] reported the use of Clays and modified clays in various types of organic reactions such as addition, Michael addition, carbene addition and insertion, hydrogenation, allylation, alkylation, acylation, pericyclic reactions,condensation reactions, aldol formation, imine synthesis, diazotization reactions, synthesis of heterocycles, esterification reactions, rearrangement/isomerization reactions, cyclization reactions, oxidation of alcohols, dehydrogenation, epoxidation and several more.

VII. To The Future

In the years ahead, it is expected that the strategic design and preparation of clay-based catalysts could be directed to catalytic conversion of biomass-based and biomass-derived feedstocks [52]. The stimulus comes from the fact that diminishing fossil fuels as finite resources and increasing amounts of planet-warming greenhouse gases like CO₂ and NO_x and SO_x in the atmosphere require the green production of renewable transportation fuels. Although current biofuels, such as corn-based ethanol and lipids and fatty oils-based biodiesel, have the capacity to some extent to mitigate worldwide dependence on petroleum and coals, new processes using lignocellulosic biomass must be developed to produce sustainable fuels to meet the continuously increasing worldwide need. Ideal drop in hydrocarbon-based fuels are expected to be made from grass, wood, or algae biomass through efficient chemocatalysis, including liquefaction, pyrolysis, or gasification. Still, besides fuels, modern life also depends on the petrochemical industry because most drugs, paints, and plastics are currently derived from oil. Hence, current processes for fine chemicals and materials are also not sustainable in terms of resources and environmental impact. Therefore, to tackle this problem, a second future focus of clay-based catalysts could be on their function as active catalysts for producing fine chemicals from bioderived feedstocks, like lignocellulose J. [53,54] and saccharide [55], lactic acid and glycerol[56].

The clay minerals can catalyze a variety of organic reactions occurring on their surface and interstitial space. Synthetic organic chemists have been attracted to their tremendous potential as catalysts only relatively recently. Modification of their properties by incorporating different metal cations, molecules or complexes, can lead to catalysts that are useful in effecting even more varieties of reactions and higher selectivity in product structure and yield. There is a theory that the molecules of life actually developed in sedimentary clays. As the organic chemist is becoming more aware of the clay's efficacy, its uses in organic synthesis are bound to increase, especially because it helps in developing eco-friendly chemical processes. The dark clay has a bright future in the area of organic synthesis.

Heterogeneous catalysis is an interdisciplinary area and modern industries are learning more and more about the applications and benefits of catalysts. Catalyst technologies generally involve less capital investment, lower operating costs, higher purity products and reduced environmental hazards. Friedel-Crafts alkylation is a very important tool for introducing alkyl substituents into the aromatic ring system and hence is a key reaction in chemistry. Conventionally, homogeneous acidic catalysts are used for the reaction. This presents several problems like tedious work up, use of corrosive chemicals, moisture sensitivity, decreased regioselectivity etc. The use of solid acids to replace waste generating soluble Lewis acids for the alkylation of arenes facilitates improved procedures. The partial oxidation of organic molecules (typically hydrocarbons) is another diverse and widely used area of chemistry with applications in almost all of the important fine and speciality chemicals industries including the manufacture of pharmaceuticals, agrochemicals and monomers. The oxidation products are intermediates in perfumery, pharmaceutical and agrochemical Industries. The use of hydrogen peroxide and heterogeneous catalytic systems in oxidation reactions has received some attention in the last years. Glycerol is produced as a by-product in the transesterification of vegetable oils and animal fats in biodiesel production, or by fermentation of biomass, and while a number of established uses for this glycol exists, the large quantities of glycerol produced during biodiesel manufacture in particular cannot be absorbed by these existing markets. Glycerol is therefore an ideal candidate as a renewable and highly flexible feedstock chemical, given its wide availability and biosustainable production, its rich chemical functionality, and its low toxicity and biodegradability. It is therefore unsurprising that processes for the valorisation of glycerol have attracted considerable recent interest. The generation of acetals and ketals, derived from glycerol is an emerging area of importance that has attracted considerable recent attention, given the potential of these materials as fuel additives and surfactants. Approaches employing transacetalisation protocols are an attractive route to access these materials, since the exchange process produces methanol as the only by-product of the reaction.

VIII. Conclusion

The continuing advances in clay-based catalysts have provided the path for new strategies to produce “designer catalysts” from layered clay minerals. Without a doubt, a rather extensive territory can be explored if one considers the great versatility originating from the 2D layered structure of clay minerals and guest molecules. Stereochemistry, block design, quantum dot, and nanoscale architecture entail limitless strategies involving the clay matrix. Besides the further expansion of their use in green catalytic processes because of the environmentally friendly credentials, future developments of clay-based designer catalysts are worthwhile being focused on the production of fuels and fine chemicals from renewable bioresources and on solar-driven syntheses. Tough challenges currently confronting researchers in the sciences of applied clay minerals,

materials, and catalysis are just the upcoming opportunities for them to strategically invent clay based “designer catalysts” ahead.

References

- [1]. M Poliakoff, P Licence, Sustainable technology: green chemistry. *Nature* 450,2007, 810–812.
- [2]. M S Holm, S Saravanamurugan, E Taarning, Conversion of sugars to lactic acid derivatives using heterogeneous zeotype catalysts. *Science* 328 (5978), 2010, 602–605.
- [3]. C H Zhou., Emerging trends and challenges in synthetic clay-based materials and layered double hydroxides. *Appl. Clay Sci.* 48,2008., (1–2), 1–
- [4]. R Saladino, C Crestini, U Ciambecchini., F Ciciriello,G Costanzo ,E Di Mauro., Synthesis and degradation of nucleobases and nucleic acids by formamide in the presence of montmorillonites. *Chembiochem* 5,2004, 1558–1566.
- [5]. R Stern, M J Jedrzejak., Carbohydrate polymers at the center of life's origins: the importance of molecular processivity. *Chem. Rev.* 108, 2008, 5061–5085.
- [6]. F Ciciriello, G Costanzo, S Pino, E Di Mauro, Spontaneous generation revisited at molecular level. In: Pontarotti, P. (Ed.), *Evolutionary Biology: Concept, Modeling, and Application*. Springer, Berlin, 2009, pp. 3–22.
- [7]. F Bergaya, B K G Theng, G Lagaly, *Handbook of Clay Science: Developments in clay Science*, vol. 1. Elsevier,2006, Amsterdam. and references therein.
- [8]. C I Sainz-Diaz,V Timon, A Botella, A Hernandez-Laguna, Isomorphous substitution effect on the vibration frequencies of hydroxyl groups in molecular cluster models of the clay octahedral sheet. *Am. Mineral.* 85, 2000,1038–1045.
- [9]. S V Churakov, S.V, Ab initio study of sorption on pyrophyllite: structure and acidity of the edge sites. *J. Phys. Chem. B* 110 (9),2006, 4135–4146.
- [10]. C Tournassat, A Neaman, F Villieras, D Bosbach, L Charlet, . Nanomorphology of montmorillonite particles: estimation of the clay edge sorption site density by low-pressure gas adsorption and AFM observations. *Am. Mineral.* 88 (11–12), 2003,1989–1995.
- [11]. A. Gil, L.M. Gandia, M. A. Vicente, Synthesis and catalytic application of pillared clays,” *Catalysis Reviews—Science and Engineering*, 42, 2000, 145-212.
- [12]. M. Kurian, S. Sugunan,Catalytic activity of iron pillared montmorillonite for benzylation of benzene with benzyl chloride. *Bulletin of the Catalysis Society of India* 4,2005, 88-100.
- [13]. J. Bovey, F. Kooli, W Jones, Preparation and Characterization of Ti-Pillared Acid-Activated Clay Catalysts,*Clay Minerals*, 31 (1996) 501.
- [14]. M. A. Leon, J. Castiglioni, J. Bussi, M. Sergio, Catalytic activity of an iron-pillared montmorillonitic clay mineral in heterogeneous photo-Fenton process. *Catalysis Today*, 133-135, 2008, 600-605.
- [15]. G. Mata, R. Trujillano, M. A. Vicente, C. Belver, M. Garcia, S.A.Korili, A.Gil, Chromium-saponite clay catalysts: Preparation, characterization ,*Applied Catalysis A General*, 327, 2007, 1-12.
- [16]. B. G. Mishra, G. R. Rao, Physicochemical and catalytic properties of Zr-pillared montmorillonite with varying pillar density. *Microporous and Mesoporous materials* 70 ,2004, 43-50.
- [17]. K.V. Bineesh, D.K.Kim, H,J,Cho, D. W. Park, Synthesis of metal-oxide pillared montmorillonite clay for the selective catalytic oxidation of H₂S. *Journal of Industrial and Engineering Chemistry* 16 ,2010, 593-597
- [18]. M. Chen, L. Qi, L. Fan, R. Zhou, X. Zheng, . Zirconium-pillared montmorillonite and their application in supported palladium catalysts for volatile organic compounds purification. *Materials Letters* 62 ,2008, 3646-3648.
- [19]. N. Ahmad, S. T. Hussain, B. Muhammed, N. Ali, S.M. Abbas, Z. Ali, Zr-pillared montmorillonite supported cobalt nanoparticles for Fischer–Tropsch synthesis . *Natural Science: Materials International* 23, 2013, 374-381.
- [20]. J. Zhou, P.Wu, Z. Dang, N. Zhu, P. Li,J. Wu, X. Wang, Polymeric Fe/Zr pillared montmorillonite for the removal of Cr(VI) from aqueous solutions. *Chemical Engineering Journal* 162 ,2010, 1035–1044.
- [21]. A Gil, L M Gandia, M A Vicente, Recent advances in the synthesis and catalytic applications of pillared clays. *Catal. Rev.* 42,2000, 145–212.
- [22]. A Gil, S A Korili, M AVicente, Recent advances in the control and characterization of the porous structure of pillared clay catalysts.. *Catal. Rev.* 50,2008, 153–221.
- [23]. Gil, A., Korili, S.A., Trujillano, R., Vicente, M.A. (Eds.),. *Pillared Clays and Related Catalysts*. Springer.
- [24]. Z Ding, T J Klopogge, R L Frost, G Q Lu, G.Q.,H Y Zhu, . Porous clays and pillared clays-based catalysts. Part 2: a review of the catalytic and molecular sieve applications. *J. Porous Mater.* 8,2001, 273–293.
- [25]. E M Serwicka, K Bahrnowski, Environmental catalysis by tailored materials derived from layered minerals. *Catal. Today* 90,2004, 85–92.
- [26]. J T Klopogge, L V Duong, R L Frost, A review of the synthesis and characterisation of pillared clays and related porous materials for cracking of vegetable oils to produce biofuels. *Environ. Geol.* 47,2005, 967–981.
- [27]. F Bergaya, A Aouad, T Mandalia, Pillared clays. In: Bergaya, F., Theng, B.K.G.,Lagaly, G. (Eds.), *Handbook of Clay Science*. Elsevier, Amsterdam, .2006, 393–422.
- [28]. P C Joshi, M F Aldersley, J W Delano, J P, Ferris, Mechanism of montmorillonite catalysis in the formation of RNAoligomers. *J.Am. Chem. Soc.* 131 (37),2009, 13369–13374.
- [29]. O M Sadek, W K Mekhamer., Ca-montmorillonite clay as thermal energy storage material. *Thermochimica Acta.* 363 (1–2),2000, 47–54.
- [30]. G J Churchman, Formation of complexes between bentonite and different cationic polyelectrolytes and their use as sorbents for non-ionic and anionic pollutants. *Appl. Clay Sci.* 21 (3–4),2000, 177–189.
- [31]. K Okada, N Arimitsu, Y Karneshima, ANakajima, K J D MacKenzie, . Solid acidity of 2:1 type clay minerals activated by selective leaching. *Appl. Clay Sci.* 31 (3–4), 2006,185–193
- [32]. P S Baran, T J Maimone, J M Richter, Total synthesis of marine natural products without using protecting groups. *Nature* 446,2007 404–408.
- [33]. A Studel, F L Fatenburg, H RFischer ,P G., Weidler, K Emmerich, . Alteration of swelling clay minerals by acid activation. *Appl. Clay Sci.* 44 (1–2),2009, 105–115

- [34]. E G Rightor, M S Tzou, T J Pinnavaia, J. Catal. 1991,130, 29.
- [35]. I Rachid, G Franc, E C Chems, Palladium-sulfated zirconium pillared montmorillonite: Catalytic evaluation in light naphtha hydroisomerization reaction, Catalysis Today 113,2006, 174-177.
- [36]. B. G. Mishra, G Ranga Rao, Physicochemical and catalytic properties of Zr-pillared montmorillonite with varying pillar density., Microporous and Mesoporous Materials 70 ,2004, 43-50 .
- [37]. S. Kavitha and S. Sugunan, Benzylolation of benzene over rare earth exchanged zirconium pillared montmorillonite, IOSR-Journal of Applied Chemistry, 2278-5736,2014,12-20.
- [38]. J. Zhoua, P. Wua, Z. Danga, N. Zhua, P. Li, J. Wua, X. Wanga, 2010. Polymeric Fe/Zr pillared montmorillonite for the removal of Cr(VI) from aqueous solutions., Chemical Engineering Journal 162, 2010, 1035-1044.
- [39]. K. Palinko, I. Lazar, Kiricsi., Cationic mixed pillared layer clays: infrared and Mossbauer characteristics of the pillaring agents and pillared structures in Fe,Al and Cr,Al pillared montmorillonites, Journal of Molecular Structure 410-411 (1997) 547-550.
- [40]. C Patrinescu, D Arsene, C. Teodosi, Catalytic wet hydrogen peroxide oxidation of para-chlorophenol over Al/Fe pillared clays (AlFePILCs) prepared from different host clays, Applied Catalysis B: Environmental 101 ,2011, 451-460.
- [41]. M. Luo, D. Bowden, P. Brimblecombe, Catalytic property of Fe-Al pillared clay for Fenton oxidation of phenol by H₂O₂, Applied Catalysis B: Environmental 85, 2009, 201-206.
- [42]. N. Bouchenafa-Saïb, K. Khoulî, O. Mohammedi, Preparation and characterization of pillared montmorillonite: application in adsorption of cadmium; Desalination 217,2007,282-290.
- [43]. P.Yuan, H. He, F. Bergaya, D. Wu, Q. Zhou, J. Zhu, Synthesis and characterization of delaminated iron-pillared clay with meso-microporous structure., Microporous and Mesoporous Materials, 88,2006, 8-15.
- [44]. J. Choy, J. Kim, D. Yoon, D. Kim;1998, crystalline Structure of Chromium Oxide-Cluster Pillar in Montmorillonite : Mol. Cryst. Liq. Cryst., Vol. 31, 1998, pp. 315-320.
- [45]. D. Zhao, Y. Yang, X.Guo: Synthesis and characterization of hydroxy-CrAl pillared clays. Zeolites 15,1995, 58-66.
- [46]. P. Kar, S.Samantaray, B. G. Mishra; Catalytic application of chromia-pillared montmorillonite towards environmentally benign synthesis of octahydroxanthenes, Reac Kinet Mech Cat 108, 2013,241-251.
- [47]. J.M. Thomas, J. Klinowski, Systematic enumeration of microporous solids: towards designer catalysts. Angew. Chem. Int. Ed. 46 ,2007, 7160-7163.
- [48]. T. B.Paranjape, G. D. Gokhale, S. D. Samant, Chloroacetylation of arenes using chloroacetyl chloride in the presence of FeCl₃ modified montmorillonite K10. Indian J. Chem. 47 ,2008, 310-314.
- [49]. N. Ellias, S. Sugunan, Wet peroxide oxidation of phenol over cerium impregnated Aluminium and Iron- Aluminium Pillared Clays, IOSR- JAC,5 ,2014, 80-85
- [50]. M. Roulia, Synthesis and characterization of novel chromium pillared clays, Materials Chemistry and Physics, 91,(2005),281-288.
- [51]. C. H. Zhou, An overview on strategies towards clay-based designer catalysts for green and sustainable catalysts, Applied clay science,53, (2011), 87-96.
- [52]. M. Stocker, Biofuels and biomass-to-liquid fuels in the biorefinery: catalytic conversion of lignocellulosic biomass using porous materials. Angew. Chem. Int. Ed. 47, 2008, 9200-9211.
- [53]. J. Q. Bond, D. M. Alonso, D.Wang, R. M. West, J. A.Dumesic, Integrated catalytic conversion of γ -valerolactone to liquid alkenes for transportation fuels. Science, 327,2010, 1110-1114.
- [54]. E. L. Kunkes, D. A. Simonetti, R. M.West, J. C.Serrano-Ruiz, C. A.Gartner, J. A. Dumesic, Catalytic conversion of biomass to monofunctional hydrocarbons and targeted liquid-fuel classes. Science 322, 2008,417-421.
- [55]. J. R. Regalbuto, Cellulosic biofuels—got gasoline? Science 325,2009, 822-824.
- [56]. Y. X. Fan, C. H. Zhou, X. H. Zhu, Selective catalysis of lactic acid to produce commodity chemicals. Catal. Rev. 51 (3),2009, 293-324.