Synthesis, Characterization and Application of Transition Metal-based Layered Double Hydroxides

ABSTRACT

With increase demand of the materials important for daily life as well as for industrial purpose, new catalytic processes have been developed day by day. A number of more than 90% of chemical processes in various chemical, petrochemicals, energy, and food industries are carried out through catalytic route. In heterogeneous catalysis, the catalyst is present in a phase differ from the reactants and products. Owing to various advantages such as cost, catalyst separation, regeneration, and reusability, heterogeneous catalysts are preferred over the homogeneous one for commercial application in the production of value added fine chemicals, fuel and also pharmaceuticals. Thus, heterogeneous catalysis plays vital role in the modern economy and for the development of environmentally and economically benign future industries by improving the existing processes.

The main contents of this thesis have been divided into six chapters. **Chapter 1** includes the introduction and literature survey about layered double hydroxides that have been used as heterogeneous catalysts. **Chapter 2** describes experimental section which includes the details of the materials preparation, characterization techniques, and experimental methods. The results and discussion are presented in **Chapter 3**, **Chapter 4** and **Chapter 5**. **Chapter 6** deals with the conclusion and future scopes of the thesis.

Chapter 1: Introduction

This chapter includes the general introduction of catalysis, types of catalysis, importance of heterogeneous catalysts and their application in the field of catalysis. General introduction of an important heterogeneous catalyst, namely layered double hydroxide (LDH) is included along with structure, synthetic procedures, properties and application in various fields. It focuses on the application of LDHs in two important area of interest on which present investigation has been carried out, i.e. waste water treatment and organic reaction transformations.

Layered double hydroxides (LDHs) are inorganic layered compounds with positive residual charges arising due to the partial isomorphous substitution of Mg^{2+} cation of $Mg(OH)_2$ brucite sheets with divalent and trivalent cations. This excess residual charge can be compensated by incorporation of various anions in the interlayer region. These are commonly known as the hydrotalcite-like compounds. Due to their layered structure with tunable properties by changing the metal cations and interlayer anions, they have drawn considerable attention in the research areas all over the globe. The structural and physicochemical properties of these compounds can be easily modulated by varying the synthesis procedures. Besides, the possibility to synthesize these compounds in a large scale under laboratory conditions makes them more suitable for the researcher. The layered structure with surface hydroxyl group, anion exchange properties and high surface area make LDHs as suitable candidate in the area of adsorption and photocatalysis. Moreover, owing to their basic properties, these compounds displays excellent catalytic activity for various base catalyzed organic transformations. Moreover, the thermal treatment improves the basicity and surface area of these compounds by converting them to mixed metal oxides.

The aforesaid heterogeneous catalyst has been employed as adsorbent and photocatalyst in the waste water treatment. The adsorption is the sorption process widely adopted for waste water treatment due to its simplicity, ease of operation, low cost and effectiveness. The general introduction to adsorption process, its importance with literature reviews are described elaborately in this thesis. Herein, we have also included another important technique for waste water treatment i.e. photocatalysis. In general, photocatalysis is a reaction accelerated by a catalyst in presence of photon or light. The general mechanism and importance of photocatalytic process along with literature reviews are described. The general introduction of organic contaminants such as dyes and phenolic compounds along with their adverse effect on environment are elaborated in this thesis. The history and classification of dyes are also included in this part of the thesis.

The catalytic activity of the heterogeneous catalyst has been checked through base catalyzed nitro-aldol (Henry) reaction. It is the classical C–C bond formation reaction between a nitroalkane containing α-hydrogen and a carbonyl compound (aldehyde or

ketone), in presence of a base catalyst to yield *β*-nitroalkanol or 2-nitroalkanol. The nitro-aldol product has attained significant interest since the very early days with its synthetic utility to obtain various chemically and biologically important compounds. The mechanism and importance of the reaction are included with literature reviews. Finally, we have highlighted the objectives of the present investigation.

Chapter 2: Materials and details of experimental methods

This chapter comprises the details of the chemicals and solvents used in this study. Synthetic procedures of the LDH and LDH-derived mixed oxides are described in details. This chapter also includes the detailed procedures of adsorption, photocatalytic as well as the nitro-aldol (Henry) reaction. Details of the various characterization techniques are also described herein.

Chapter 3: Binary and ternary layered double hydroxides (LDHs) for adsorptive removal of various organic dye pollutants

This chapter describes the synthesis of various binary and ternary LDHs and their application as adsorbents for removal of various organic dye pollutants from aqueous solution. The chapter has been further divided into three sections: section 3A, section 3B and section 3C.

Section 3A: Efficient removal of anionic organic dye pollutants from aqueous solution by NiMgAl layered double hydroxides

This section demonstrates the synthesis of NiMgAl LDH with various Ni/Mg molar ratios using co-precipitation method and effect of Ni on the structural as well as on the adsorption properties for removal of anionic organic dye pollutants from aqueous solution. The complete characterization of synthesized materials using various analytical techniques has been explained thoroughly. NiMgAl LDH with Ni/Mg molar ratio 1:1 possessing high BET surface area and pore volume, exhibits high adsorption capacity for removal of anionic methyl orange (MO) from aqueous solution. The optimization of adsorption process has been studied thoroughly by considering various reaction parameters such as

contact time, adsorbent dosage, initial dye concentration and solution pH. Adsorption kinetics has been analyzed by various kinetic models and the adsorption process follows pseudo second-order kinetics. The adsorption isotherm analysis reveals that Langmuir isotherm model was best fitted to the adsorption data thereby confirming a monolayer adsorption. Adsorption interaction of the dye onto the LDH surface has been investigated using XRD, SEM and FTIR spectroscopy.

Section 3B: Preferential adsorption of various anionic and cationic dyes from aqueous solution over ternary CuMgAl LDH

This section comprises of complete characterization of a series of CuMgAl LDHs with varying molar ratio of Cu/Mg synthesized via simple co-precipitation route. The preferential adsorption of various anionic dyes such as methyl orange (MO), bromothymol blue (BTB), erichrome black-T (EBT) and congo red (CR); and cationic dyes such as methylene blue (MB) and rhodamine B (RhB) from aqueous solution have been tested over the synthesized materials. The anionic dyes are preferentially adsorbed over the adsorbents in higher amount compared to the cationic dyes. Adsorption kinetics and isotherm analysis are also discussed in details. The influences of various parameters such as contact time, adsorbent dosages, initial dye concentrations and solution pH on the adsorption process have been studied thoroughly. The interaction of dyes with LDH structure was also investigated through FTIR, PXRD and SEM.

Section 3C: Adsorptive removal of congo red from aqueous solution by sonochemically synthesized NiAl layered double hydroxide

This section deals with the complete characterization of NiAl-LDHs synthesized via co-precipitation method followed by ultrasonic irradiation for various time. The activity of the synthesized LDHs as efficient adsorbent has been discussed herein for removal of congo red (CR) from aqueous solution in a batch mode. NiAl LDH synthesized under ultrasound irradiation for 1h, NiAl-S_1 LDH exhibits the highest dye removal efficiency. Various parameters such as, contact time, adsorbent amount, initial dye concentration, and solution pH have been studied for optimizing the adsorption process. Adsorption isotherm study demonstrates that isotherm data fitted well to the Langmuir model, signifying

monolayer adsorption of CR over sonochemically synthesized NiAl-LDH. Pseudo-second order kinetics best determine the adsorption kinetics for CR removal. The temperature effect on adsorption process has been studied thoroughly over a range of temperatures. The standard Gibbs free energy change (ΔG°), entropy change (ΔS°) and enthalpy change (ΔH°) for adsorption process has also been evaluated. The result demonstrates the spontaneous and endothermic nature for adsorption process. The adsorbent shows multicyclic efficiency upto three successful cycles without any significant loss of the adsorption efficiency. The interaction of the dye molecules to the LDH surface has been further confirmed through the XRD, SEM and FTIR study.

Chapter 4: Photocatalytic degradation of organic pollutants by using ZnFe layered double hydroxide (LDH)

This chapter describes the complete characterization of ZnFe LDH synthesized via a simple co-precipitation method and its catalytic activity towards the photodegradation of various organic pollutants from aqueous solution. The chapter has been further divided into two sections: section 4A and section 4B.

Section 4A: Photocatalytic degradation of phenol and its compounds from aqueous solution by ZnFe LDH

This section focuses on the photocatalytic degradation of various phenolic compounds such as phenol, 2-chlorophenol (2CP), 3-chlorophenol (3CP) and 4-chlorophenol (4CP) using ZnFe LDH under both visible and UV light irradiations. The effect of various reaction parameters such as catalyst amount, initial concentration of phenolic compounds and solution pH on photodegradation process has been studied thoroughly in order to achieve an optimized reaction condition. The catalyst displays efficient photocatalytic activity towards the degradation of various phenolic compounds under visible light compared to the UV light irradiation. The degradation kinetics has been analyzed through Langmuir-Hinshelwood first order kinetic model. The possible degradation mechanism and degradation pathway are also discussed herein. The recyclability test shows that the photocatalyst is stable upto four successive cycles.

Section 4B: Photocatalytic activity of ZnFe LDH for removal of methylene blue and rhodamine B from aqueous solution

This section describes the photocatalytic activity of ZnFe LDH synthesized via a simple co-precipitation method towards the oxidative degradation of organic dye pollutants such as methylene blue (MB) and rhodamine B (RhB) from aqueous solution. The degradation study has been employed under both UV and visible light irradiations. The photocatalytic study shows that efficient degradation of MB and RhB is achieved under UV light irradiation compared to visible light. The effect of various reaction parameters such as contact time, catalyst amount, solution pH and initial concentration of dyes on photocatalytic process has also been studied. The kinetics and possible mechanism of photocatalytic degradation of MB and RhB are discussed herein. The degradation pathways of the dyes are also included. Moreover, the catalyst has been subjected to multicyclic photodegradation and become active upto four successive cycles indicating excellent stability of the catalyst.

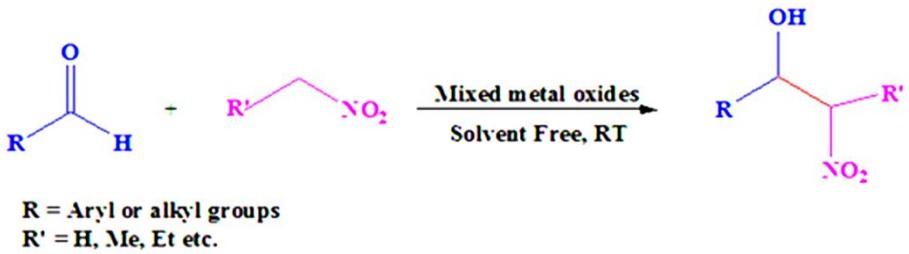
Chapter 5: Layered double hydroxide (LDHs) derived mixed oxides for solvent free nitro-aldol condensation reaction

This chapter describes the synthesis of various ternary LDH-derived mixed oxides and their catalytic activity for nitro-aldol condensation (Henry) reaction under mild and microwave irradiation condition. The chapter has been divided into two sections: section 5A and section 5B.

Section 5A: Synthesis of high surface area mixed metal oxide from the NiMgAl LDH precursor for nitro-aldol condensation reaction

The complete characterization of various ternary M^{2+}MgAl LDHs (M^{2+} is Ni^{2+} or Co^{2+}) synthesized via the simple co-precipitation route with M^{2+}/Mg molar ratio of 3, followed by calcination of the samples at 450 °C for 6h have been discussed herein. The effect of M^{2+} cations on the structural as well on the catalytic activity of precursor LDHs and their derived mixed oxides have been explored. The catalytic activity of the mixed oxides has tested as base catalyst for nitro-aldol condensation (Henry) reaction under mild

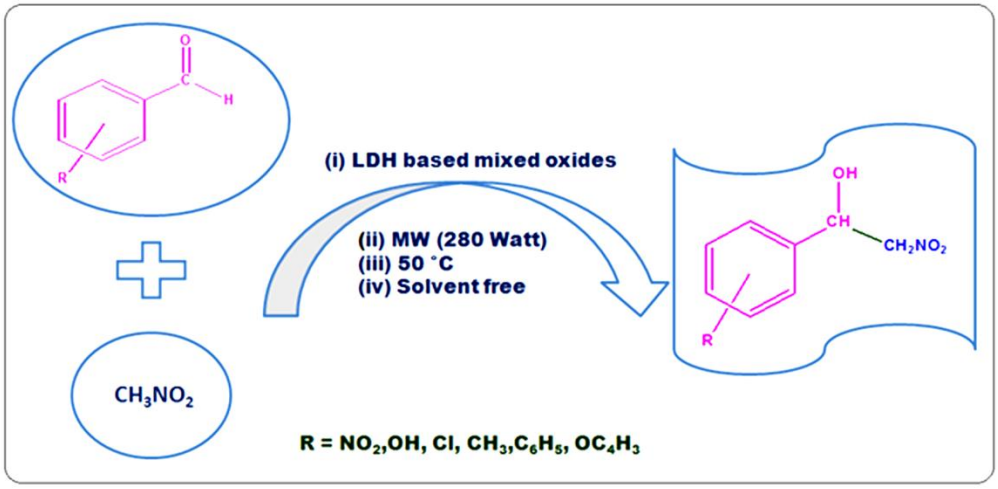
conditions. The mixed oxides interestingly shows high catalytic performance compared to their precursors. Effects of various reaction parameters such as temperature, amount of catalysts and substituents on nitro-aldol reaction have also been studied and explained in details. The NiMgAl LDH derived mixed oxide possessing the high surface area and pore volume is found to be more efficient catalyst for nitroaldol condensation under solvent free conditions at room temperature.



Scheme 1: Henry reaction catalyzed by LDH-derived mixed oxides

Section 5B: Effect of Ni on structural properties of NiMgAl-LDH derived mixed oxides and their catalytic activity for nitro-aldol condensation reaction

This section describes the complete characterization of mixed oxides derived from various NiMgAl LDHs of variable Ni composition. A co-precipitation method has been employed to synthesize the precursors with varying molar ratios of Ni^{2+}/Mg^{2+} by keeping the molar ratio of $(Ni^{2+} + Mg^{2+})/Al^{3+} = 3$, at constant pH. Thermal treatment of the precursor LDHs at 450 °C for 6h result in the formation of high surface area mixed oxides. The catalytic activity of the derived mixed oxides has been evaluated for base catalysed nitro-aldol condensation (Henry) reaction under solvent free microwave (MW) condition. The presence of Ni greatly affects the structural as well as the catalytic properties of the LDH precursors and their derived mixed oxides for nitro-aldol reaction. The mixed oxide derived from NiMgAl LDH with Ni^{2+}/Mg^{2+} ratio of 1:1 possesses the efficient activity, selectivity and stability towards the selective synthesis of 2-nitro-alkanol. The enhanced catalytic activity is ascribed due to high surface area than the other catalysts. Various reaction parameters such as catalyst amount, reaction temperature, microwave power and substituents have great impact on the catalytic reaction process. Moreover, the catalyst shows recyclability upto four successive cycles.



Scheme 2: Henry reaction catalyzed by LDH-derived mixed oxides under microwave conditions.

Chapter 6: Conclusions and future scope

This chapter describes the overall conclusions of the work. The future scopes of the studied area are also included in this chapter.