**HYDROTALCITE AS CATALYSTS**

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The search for alternate materials to be used as catalysts has been always continuing. The exploitation of natural resource materials for possible catalytic applications has been in practice for decades. Many synthetic catalytic systems have been modelled based on clay material and these fall under the category of hydrotalcites. There are many reviews in recent times and selected few are given in references 1-8. Clay mineral are lamellar structured solids characterized by charged layers. Clay minerals fall under two broad categories namely cationic and anionic clays [9-11]. The cationic clays are formed by negatively charged alumino-silicate layers with cations as counter ions in the interlayer region of the structure. Anionic clays are formed by metal hydroxide layers with compensation anions like CO32->>SO42->>OH->F>Cl->Br->NO3->I- and water molecules present in the interlayer region [12]. For industrial use cationic clays are prepared from natural resources while most of the anionic clays are synthetically prepared. The purpose of this presentation is to view why and how hydrotalcite materials are exploited as catalytic materials. Hydrotalcites belong to the class of clay materials. These materials can be classified as cationic or anionic clays. Among these two class of materials, anionic clays have been used as catalytic materials. Hydrotalcite (HT) type anionic clays are also known as layered double hydroxides. They have positively charged brucite-type metal hydroxide layers with balancing anions and water molecules located interstitially.

Typical structure of hydrotalcites is pictorially shown in Fig.1. The red shaped ones in this figure are the interlayer anions and green shaped ones are water molecules. The possible anions that are employed in hydrotalcites in the order CO32->>SO42->>OH->F>Cl->Br->NO3->I-.

 

Fig.1. Typical structure of Hydrotalcite. Red and green shaped species are anions and water molecules respectively.

The important properties of hydrotalcites for use as catalysts are:

(1) High surface area

(2) Homogenous inter-dispersion

(3) Basic properties, this is important property for a set of organic transformations

(4) Memory effect as it can regain its layered structure from changes due to calcination and other treatments.

Anionic clays find many applications like catalysts, catalyst supports, adsorbents, medicinal use. Generally, the hydrotalcite can be prepared employing a general procedure shown in Fig.2.

 +

 Stirring 3-4 Hour; pH = 11-13

 334 K 18 h

 Washed, filtered & dried at 373 K, 12h

Hydrotalcites can promote various reactions and their catalytic property can be generally classified as follows:

1. Redox catalyst - Various hydrotalcites, generally including copper or a heavy metal, are known to be function as oxidation or reduction catalysts.
2. Acid/Base catalyst – Typical Mg/Al hydrotalcites have a unique and highly tunable structure with both acidic and basic properties. Hydrotalcites with their bi-functionality allow for the use of these materials as catalysts for various organic conversions.
3. Catalyst support - Hydrotalcites are known to be used as support for numerous catalytic species, such as transition metals, alkali metals and even various anions.

Hydrotalcites (HT), belong to a set of solids whose structure is closely related to that of the mineral hydrotalcite, that is, rhombohedral Mg6Al2(OH)16CO3⋅4 H2O. Hydrotalcites have three important characteristics that make them useful for various applications.

1. HTs have a good anion-exchange capacity [13,14] and are therefore used as ion-exchangers, adsorbants [15,16] or sensors [17].
2. Hydrotalcites in most of the cases behave as solid bases; and hence used as basic catalysts for several reactions like self-condensation, cross-aldol condensation of aldehydes and ketones, Knoevenagel condensation, Claisen–Schmidt condensation, Michael addition, transesterification, and alkylation.[13] In particular, Mg–Al hydrotalcite and their calcination products are considered as models for basic catalysis,[18-20]. Zn–Al hydrotalcites, although less investigated, could also be useful for this purpose [21].
3. Hydrotalcite can be prepared with several reducible bi-valent (Ni, Cu, Co) and trivalent (Fe, Cr) cations in the structure together with the classical ones (Mg, Zn, Al) serving as precursors for the preparation of different mixed oxides active for oxidation and hydrogenation/dehydrogenation reactions.

Hydrotalcites may be employed as catalytic acid-basic materials:

1) They can be used, as such, in their lamellar structure. In this case, their reactivity is mainly governed by the nature of the intercalated anion and by the amount of remaining water.

2) Highly homogeneous mixed oxides obtained from their decomposition can catalyze a wide range of reactions. In this case, the creation of M2+![[BOND]]()O2− acid–base pairs are the key parameter.

3) Reconstructed lamellar materials can be obtained from rehydration of calcined hydrotalcites, which allows introducing almost any kind of compensating anions that can be of use in the catalytic process.

Determination of basicity of hydrotalcites

|  |  |  |  |
| --- | --- | --- | --- |
| Probe molecule/reaction | Essential results | Technique employed characteristic values | Ref |
| Carbon dioxide | Several forms of carbonate species |  | 2223 |
|  | Mono, bi dentate and bicarbonate  | IR absorption in the range 1700-1300 cm-1 Thermal desorption usually around 320-550K | 22,23,24,25, |
|  | Monodentate on oxide ions | Strong basic sites; 1510-1560 cm-1 and or1360-1400 cm-1; thermal desorption around 550K; Heat of adsorption above 80 kJ/mol | 26,27 |
|  | Bidentate species on acid–base pairs, such as Mg2+[BOND]O2− or Al3+[BOND]O2- | Intermediate basic sites1610-1630 cm-1 1320-1340 cm-1; thermal desorption around 460K; Heat of adsorption above 80 kJ/mol | 27 |
|  | Bicarbonate require surface hydroxyl groups | Weak basic sites 1270,1650,1480 cm-1 thermal desorption around 320-400 K | 23 |
|  | 13CO2/CO2 isotope exchange studies | A non-linear variation of rate with time shows the sites are heterogeneous | 22 |
| adsorption deuterated chloroform | The vibration modes of the C[BOND]D bond followed | weak acidic probe suitable to get insights both on the amount and on the strength of basic sites | 28 |
| Sulfur dioxide | Adsorption calorimetry | 190 kJ mol−1 strong basic sites | 28 |
| Trimethyl borate | IR spectra of adsorbed species | 1360 and 1063 cm−1 assigned to B[BOND]O and C[BOND]O stretching modes . These bands are modified (they split) upon interaction with surface basic sites | 29 |
| CH3CN is an amphoteric probe | IR spectroscopy two regions need to be scanned | The 2360-2230 cm−1 range is characteristic of species formed on Lewis acidic sites. Vibration modes of the probe chemisorbed on basic O2− sites fall in the 2230–2050 cm−1 region | 30 |
| benzoic acid | styrene epoxidation | reduction in the catalytic activity | 31 |
| phenol and acrylic acid |  |  | 32 |
| trichloroacetic acid in benzene |  |  | 27,33 |
| β-isophorone to α-isophorone |  |  | 34,3536 |
| diacetone alcohol (DAA) retroaldolisation |  |  | 37 |
| Isomerisation of glucose into fructose |  |  | 38,39 |
| condensation of benzaldehyde with activated methylenic groups (ethyl cyanoacetate, ethyl malonate, ethyl bromoacetate) |  |  | 40 |
| base-catalysed disproportionation of 2-methyl-3-butyn-2-ol to acethylene and acetone |  |  | 41,42 |
| binding energy of O 1s electrons | Lower the binding energy, the more basic the surface  |  | 35 |

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