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Calcined Layered Double Hydroxides as Basic Heterogeneous Catalysts for the Oppenauer Oxidation of Alcohols

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The oxidation of various alcohols with a ketone was carried out over a series of calcined layered double hydroxides, producing corresponding ketones in a batch reaction system. From the observed results it was found that the layered double hydroxide, Mg^{II}–Al^{III} (4:1) ratio), calcined in air at 723 K efficiently oxidize alcohols compared with other LDHs.

The oxidation of alcohols with carbonyl compounds to the corresponding aldehydes or ketones by catalysis is known as Oppenauer-type oxidation. Generally, oxidation has been carried out by the use of alkoxide catalyst, and aluminium isopropoxide has been found to be the most suitable reagent for this reaction.[1] However, it has several disadvantages, such as the need for tedious purification and the reusability of the catalyst. In recent years, increasing interest has been paid to the use of eco-benign heterogeneous catalysts[2] to promote organic reactions. Some of the heterogeneous catalysts, like silica, magnesia,[3] and bis(cyclopentadienyl)-dihydrido zirconium(IV),[4] have been used for oxidation reactions. Also, H. Kuno et al. has explored the oxidation of various primary and secondary alcohols over hydrous zirconium(IV) oxide.[5]

Layered double hydroxides (LDHs) of the hydrotalcite (HT) type, which are also referred to as anionic clays, are interesting class of materials, which can be utilised as precursors for mixed metal oxides with pronounced basic properties. The most common case of di- and trivalent cations leads to the general chemical formula $[M^{II}_{1-x}\text{-}M^{III}_{x}(OH)_2]\text{-}[A^{n-}]_{x/n}\cdot m\ H_2O$, where '$x$' refers to the $n[M(III)]/n[M(II)+M(III)]$ ratio, ranging between ca. 0.25 to 0.4. The synthesis, characterization and catalytic properties of LDHs have been reported elsewhere.[6,7] Calcined LDHs give highly dispersed mixed metal oxides of the $M^{II}(M^{III})O$ periclase type with a larger surface area and uniform size, and are stable to thermal treatments.[8] It has basic[9] and redox properties depending on a wide variety of parameters, such as the metal cations, their ratio in the layered matrices, the presence of alkali dopes, the nature of interlayer anions and thermal treatments.[10] In the present investigation the possibility of employing calcined LDHs as basic catalyst for the Oppenauer oxidation of different alcohols with toluene as a solvent and benzophenone as a proton acceptor was attempted and reported. The influences of various interlayer anions, the atomic ratios of Mg^{II}/Al^{III}, and different LDHs have also been briefly discussed.

Experimental

Analar-grade samples of metal nitrates were used to prepare aqueous solutions. A sequential precipitation method was adopted to prepare different LDHs.[6] To an aqueous solution containing $Mg(NO_3)_2\cdot6H_2O$ and $Al(NO_3)_3\cdot9H_2O$ mixed at the desired ratio, an aqueous solution of NaOH and Na_2CO_3 was added dropwise with stirring until the pH reached 10. The resulting slurry was stirred at 313 K for 18 h, then filtered and washed with deionised water until the pH of the water became neutral and dried at 373 K for 12 h. The calcined (698 K in air for 12 h) samples were stored in a desiccator before use.

The characterization of LDHs and calcined-layered double hydroxides (CLDHs) were carried out using XRD, thermogravimetry and BET surface-area measurements. The ICPES method was adopted to estimate the ratios of the M^{II} and M^{III} ions in LDHs. All of the reactions were carried out batch wise in a 100 ml R. B flask fitted with a reflux condenser with constant stirring. In a typical run, 100 mg of the catalyst was dispersed in a solution containing cyclohexanol (0.25 mmol), benzophenone (10 mmol), and toluene (15 ml). The resulting mixture was stirred at 383 K for 1 h. After separating the catalyst by filtration, the products were analyzed in a gas chromatograph (Shimadzu GC 15A) using a carbowax column and FID detector. The identity of the products was further confirmed by GC-MS (Shimadzu, QP 2000A).

Results and Discussion

Typical XRD, IR, TGA, and DTA patterns have substantiated the formation of LDHs.[11—13] The Oppenauer oxidation of cyclohexanol to cyclohexanone employing different catalysts is depicted in Fig. 1. It can be seen that Mg^{II}–Al^{III} HT is the best catalyst, which has given a maximum conversion of 98% under the present reaction conditions. All other catalysts displayed poor activity. The higher activity

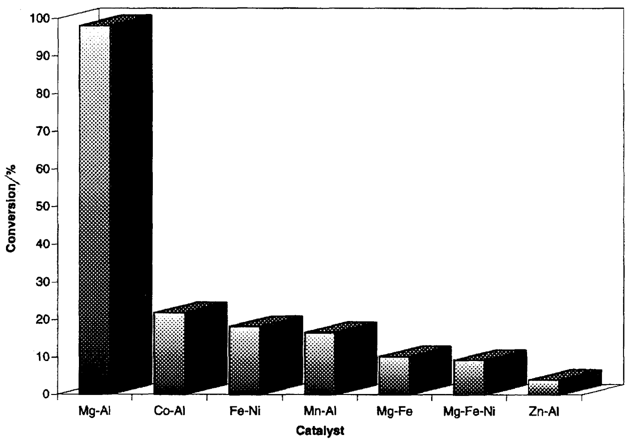

Fig. 1. Effect of catalysts on Oppenauer oxidation.

of $\mathrm{Mg^{II}}$–$\mathrm{Al^{III}}$ HT calcined at 723 K is attributed to the activated surfacial MgO and MgO–$\mathrm{Al_2O_3}$ mixed oxides.[14,15] The Oppenauer oxidation is believed to proceed via the adsorption of alcohol on the basic sites and ketone on the acidic sites followed by the transfer of hydrogen from the alcohol to the ketone. The present results substantiate the need for strong basic sites, as in the case of calcined $\mathrm{Mg^{II}}$–$\mathrm{Al^{III}}$ hydrotalcite. It is suggested that the incorporation of different transition metal ions decreases the basicity of LDHs, which leads to a decrease in alcohol conversion.

The oxidation of different alcohols using Mg–Al hydrotalcite is presented in Table 1. No side products were detected in any of the cases. The catalytic activity of hydrotalcite is influenced by the nature of the interlayer anion present before calcination of the precursor material. From Table 2, due to the volatility, the catalytic activity follows the order $\mathrm{CO_3{}^{2-}} > \mathrm{NO_3{}^{-}} > \mathrm{SO_4{}^{2-}} > \mathrm{Cl^{-}}$.[16,17] This is in accordance with an observation by Gusi et al.[18] It is proposed that the surface bidentate carbonate anion at high temperature moves over the surface in such a way that the free oxygen in the anion approaches the adjacent atom leading to give the $\mathrm{O^{2-}}$ ion, which has a synergetic effect, which in turn enhances the catalytic activity.[19] For a specific base catalysed reaction, the strength and number of active sites are of paramount importance to control the activity and selectivity.[20] If the calcination temperature exceeds 723 K the hydrotalcites go to the spinel form, which are not active for this reaction. At a calcination temperature at and above 723 K the various transition metals containing LDHs easily transform to spinel,[21] and causing less basicity, this has been substantiated by the poor conversion of substrates.[22] From Table 3 it is worth noting that the calcination temperature has a considerable influence on the nature of the precipitates and their catalytic activity.[23]

Table 1. Effect of Alcohols Using HT $(\mathrm{Mg^{II}}$–$\mathrm{Al^{III}})\mathrm{CO_3{}^{2-}}$ as a Heterogeneous Catalyst

Substrate	Time/h	Conversion/%
Cyclohexanol	1	98.00
2-Methylcyclohexanol	4	91.00
2-Hexanol	1	100.00
1-Heptanol	1	73.00
1-Octanol	2	10.09
Borneol	4	62.00
Borneol	8	86.00

Interlayer anion: $\mathrm{CO_3{}^{2-}}$ Calcination temperature: 723 K; Catalyst amount: 100 mg, Cyclohexanol: 0.30 mmol. Ketone: 10 mmol: Sovent; Toluene (15 ml). Reaction time: 1 h. Reaction temperature 383 K.

Table 2. Effect of Interlayer Anions

Interlayer anion	Conversion/%
$(\mathrm{Mg{-}Al})\mathrm{CO_3{}^{2-}}$	98.00
$\mathrm{Cl^{-}}$	65.90
$\mathrm{SO_4{}^{2-}}$	46.19
$\mathrm{NO_3{}^{-}}$	37.64

Table 3. Effect of Calcination Temperature

Temperature	Conversion/%	
K	$(\mathrm{Mg{-}Al})\mathrm{CO_3{}^{2-}}$	$(\mathrm{Co{-}Al})\mathrm{CO_3{}^{2-}}$
383	4.50	Nil
573	16.03	3.20
723	98.00	21.13
823	2.96	1.51

Catalyst = 100 mg; Cyclohexanol (0.30 mmol); Ketone (100 mmol); Toluene (15 ml); Reaction time (1 h).

The results have shown that various alcohols can be efficiently oxidized by employing $\mathrm{Mg^{II}}$–$\mathrm{Al^{III}}$ HT as a heterogeneous catalyst. Catalysts other than HT showed poor performance. Calcination of these LDHs lead to a redistribution of the cations, and in turn, will influence the conversion and thermal stability of this reaction. We thus conclude that a $\mathrm{Mg^{II}}$–$\mathrm{Al^{III}}$ HT catalyst possessing good intrinsic thermo stability, concomitant "acidic–basic" active pairs and a synergetic effect on a facile pathway accounts for the significance of these types of reactions. The calcination temperature and active sites are two critical factors that influence the activities of the investigated catalysts.

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