Chemoselective Transfer Hydrogenation Reactions over Calcined-Layered Double Hydroxides

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The transfer hydrogenation of aromatics containing various reducible groups has been carried out employing isopropanol as a hydrogen donor in the presence of different calcined LDHs. It was found that the Ni^{II}–Al^{III} (mol ratio 3) catalyst is highly active in bringing about chemoselective reduction compared to other calcined LDHs.

A wide variety of homogenous as well as heterogeneous catalyst systems in combination with different hydrogen donors have been employed for selective functional-group reductions.[1,2] Transfer hydrogenation has shown distinct advantages over the molecular hydrogen method, because it requires only milder conditions and offers enhanced selectivity; moreover, closed pressure systems involving hazardous hydrogen gas can be avoided. Heterogeneous catalysts have several advantages over homogenous catalysts, such as ease of recovery, recycling and enhanced stability. Most common of the heterogeneous catalysts is Raney Nickel, which is used extensively with hydrazine hydrate or isopropyl alcohol.[3] However, it does not show any chemoselectivity towards the functional groups, and also leads to hydrogenolysis during the reduction of ketones. Upadhya et al. reported that Nickel-stabilized zirconia shows chemoselectivity in transfer hydrogenation reactions with isopropanol as a hydrogen donor.[4] Kumbar et al. have found that the Fe_2O_3–MgO catalyst prepared from a Mg–Fe hydrotalcite precursor can be used for the reduction of nitrocompounds using hydrazine hydrate as the hydrogen donor.[5] Recently, properly activated Mg–Al hydrotalcite (Mg/Al = 3) has been found to be a highly active, selective and regenerable catalyst for Meerwein–Ponndorff–Verley reduction in the liquid phase.[6]

Layered double hydroxides (LDHs) of the hydrotalcite type, also referred to as anionic clays, are an interesting class of materials which can be utilized as precursors of mixed metal oxides with pronounced basic properties.[7–9] Hydrotalcites consists of positively charged brucite (Mg-$(OH)_2$)-like layers interspersed with hydrated anions in the layer. They are represented by the general formula $[M^{II}_{1-x}M^{III}_x(OH)_2][A^{n-}]_{x/n} \cdot mH_2O$, where '$x$' refers to the n[M-(III)]/n[M(II)+M(III)] ratio, ranging between ca. 0.25 and 0.4; M(II) and M(III) are divalent and trivalent cations such as Mg^{2+}, Mn^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+}, Zn^{2+}, and Al^{3+}, Fe^{3+}, Cr^{3+}, respectively. A^{n-} represents the interlayer anions, such as

Cl^-, NO_3^-, and CO_3^{2-}. Upon calcination in air at around 723 K, these materials give rise to solid solutions between M^{2+} and M^{3+} ions. We have recently used these materials in the Oppeneaur-type oxidation of different alcohols.[10] In this paper, we report on the use of these materials in the transfer hydrogen reduction of aromatics containing various reducible groups.

Experimental

Analar-grade samples of the metal nitrates were used to prepare aqueous solutions. A typical method to prepare different hydrotalcites via a sequential precipitation method is given below. To an aqueous solution containing $Mg(NO_3)_2 \cdot 6H_2O$ and $Al(NO_3)_3 \cdot 9H_2O$ mixed at the required ratio, an aqueous solution of NaOH and Na_2CO_3 was added dropwise with stirring until the pH reached 10—10.5. The slurry was stirred at 313 K for 13 h, filtered and washed with deionised water to neutral pH and then dried at 373 K for 24 h. All of the catalysts were finally calcined at 723 K in air for 12 h.

The physico-chemical characterization of the catalysts has been done by X-ray diffraction, thermogravimetry and surface-area measurements. The ICPES (inductively coupled plasma emission spectroscopy) method was adopted to estimate the ratio of M^{II} and M^{III} ions in LDHs.

All of the reactions were carried out batch wise in a 100 ml round-bottom flask fitted with a reflux condenser with constant stirring. In a typical run, 50 mg of the catalyst was dispersed in a solution containing 500 mg (4.06 mmoles) of nitrobenzene, 250 mg of KOH (4.46 mmoles) pellets and 10 ml of isopropyl alcohol. The mixture was vigorously stirred and heated under reflux for one hour. After completion of the reaction, the catalyst was filtered off and washed with isopropyl alcohol; excess distilled water was added to obtain an emulsion. It was then extracted with dichloromethane, and any excess solvent removed by rotary evaporation. The products were analyzed in a gas chromatograph (Shimadzu GC 15A) fitted with a SE30 column and a flame-ionization detector. In most cases, the products were isolated by column chromatography and their identities were established by ^1H NMR, GC-MS, and FT-IR.

1426 *Bull. Chem. Soc. Jpn., 73, No. 6 (2000)*

Catalysts for the Chemoselective Transfer Hydrogenation

Results and Discussion

The XRD of synthesized samples show sharp and symmetric peaks for the (003), (006), (110), and (113) planes and broad and unsymmetric peaks for the (102), (105), and (108) planes, which are characteristic of clay minerals possessing a layered structure. Typical IR, TGA, and DTA patterns also substantiate the formation of LDHs.[11—13] The reduction of nitrobenzene to aniline employing isopropanol as a hydrogen donor using different calcined LDHs is depicted in Table 1. We have compared the activity of these materials with Raney nickel, and single metal oxides (NiO, Al₂O₃, MgO) and a physical mixture of NiO and Al₂O₃. It can be seen that out of the different catalysts investigated, the mixed-oxide catalyst prepared from a Ni–Al hydrotalcite-like precursor exhibited significantly higher activity compared to Raney nickel and the other catalysts. Simple oxides showed poor activity.

The hydrogen-transfer reduction of various organic substrates over Ni–Al catalyst is depicted in Table 2. The present catalyst system reduces carbonyl compounds also efficiently to corresponding alcohols. Remarkably, *p*-nitrobenzophenone and cinnamaldehyde are chemoselectively reduced to *p*-aminobenzophenone and cinnamyl alcohol. Moreover, the C–Cl, C–CH₃, and C–OCH₃ bonds are not affected by reduction. Interestingly, *m*-dinitrobenzene is regioselectively reduced to *m*-nitroaniline. The catalyst, after filtration, was washed several times with dichloromethane, followed by through washing with distilled water to remove any alkali; it was then dried at 383 K and finally calcined in air; the regenerated catalyst showed the same activity. However, recycling of the catalyst after each reaction resulted in a decrease of nitrobenzene conversion. An attempt to carry out this reaction while taking a smaller amount of potassium hydroxide resulted in a diminution in nitrobenzene conversion. Moreover, under these conditions an appreciable amount of azoxybenzene was formed as the result of a partial reduction of the nitro group. It is worth noting that the reaction was

Table 1. Hydrogen Transfer Reduction of Nitrobenzene over Different Catalysts Using Isopropanol

Catalysts	Surface area/m² g⁻¹	Aniline yield/%
Mg–Al (3 : 1)	193	42
Co–Al (3 : 1)	138	49
Mn–Al (3 : 1)	145	39
Zn–Al (3 : 1)	160	29
Ni–Al (3 : 1)	148	97
Mg–Fe (3 : 1)	178	63
NiO–Al₂O₃ [a]	96	61
MgO	111	18
NiO	93	20
Al₂O₃	212	25
Raney Ni	—	23

Reaction conditions: Substrate 10 mmol, KOH 10 mmol, Catalyst 10 wt% of substrate, propan-2-ol 10 ml, reflux for one hour. a) Physical mixture of NiO and Al₂O₃ (Ni/Al = 3).

Table 2. Transfer Hydrogenation of Various Aromatic Substrates Using Ni(II)–Al(III) Catalyst

| Substrate	Time/h	Product	Yield/%[a]
Nitrobenzene	1	Aniline	95
p-Chloronitrobenzene	1	*p*-Chloroaniline	92
p-Nitroanisole	1	*p*-Anisidine	93
o-Nitrotoluene	1.5	*o*-Toluidine	89
m-Dinitrobenzene	2	*m*-Nitroaniline	65
		m-Phenylenediamine	22
Acetophenone	1	1-Phenethyl alcohol	93
Benzophenone	2	Benzhydrol	90
p-Nitroacetophenone	1	*p*-Aminoacetophenone	86
p-Nitrobenzophenone	1	*p*-Aminobenzophenone	89
Cinnamaldehyde	1	Cinnamyl alcohol	75

Reaction conditions: Substrate 10 mmol, KOH 10 mmol, Catalyst 10 wt% of substrate, propan-2-ol 10 ml, reflux. a) Isolated by column chromatography.

not proceeded either in the absence of a catalyst or potassium hydroxide.

According to Upadhya et al., the active Ni(0) species formed instantaneously during the reaction are the active species responsible for reduction, as is evident from cyclic voltammetry (CV) measurements.[4] This reaction is similar to the classical Meerwein–Ponndorff–Verley (M–P–V) reduction, which takes place in the presence of aluminium isopropoxide. Posner et al. have used dehydrated alumina in the selective reduction of aldehydes using isopropyl alcohol.[14] It is proposed that propan-2-ol is adsorbed on the basic site and ketone on the adjacent acidic site, and finally hydrogen is transferred as hydride ion to the substrate. As pointed out earlier, the reaction does not proceed in the absence of basic conditions or in the absence of a catalyst. It can thus be concluded that a catalyst promotes the transfer of hydrogen from isopropyl alcohol by potassium hydroxide. The nitro group attached to the benzene ring can pull an electron more strongly from the benzene ring compared to the keto group, and hence can be relatively easily adsorbed on the catalyst surface. This may be the reason for the chemoselective reduction of the nitro group in the case of *p*-nitrobenzophenone. Moreover, it seems that the C–T character of the formed *p*-aminobenzoyl structure prevents any further hydrogenation of the keto group. The reduction of nitrobenzene to aniline proceeds via. different intermediates, as proposed by Haber from his work on the electrochemical reduction of nitrobenzene (Scheme 1).[15] We believe that the nitro group attached to the acid site of the catalyst is reduced to nitrosobenzene by hydrogen transfer from isopropyl alcohol adsorbed on an adjacent basic site, as in the case of the M–P–V reduction of ketones (Scheme 2). Nitrobenzene can undergo complete reduction to form aniline. The acidity (Lewis type) in hydrotalcites is attributed to the dissolution of Al³⁺ in the oxide lattice during calcination at around 723 K and co-ordinatively unsaturated O²⁻ ions acting as strong Lewis basic sites.[16] The higher activity of the Ni–Al HT catalyst may be due to activated surfacial NiO and NiO–Al₂O₃ double oxides. In other words, a synergistic interaction exists between the
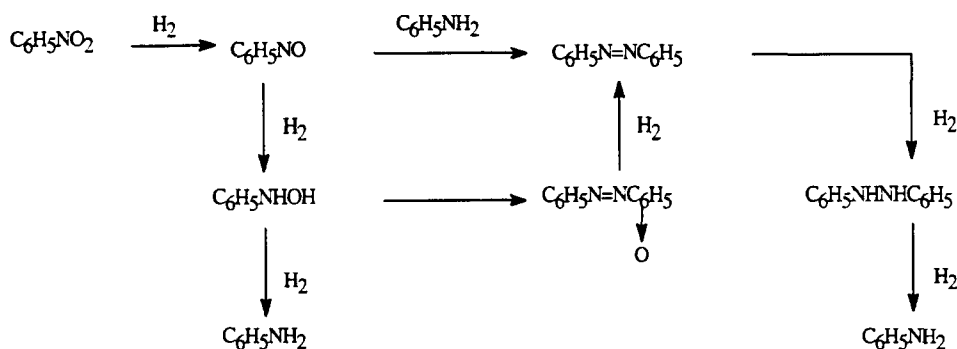
Scheme 1. Intermediates in the formation of aniline from nitrobenzene.
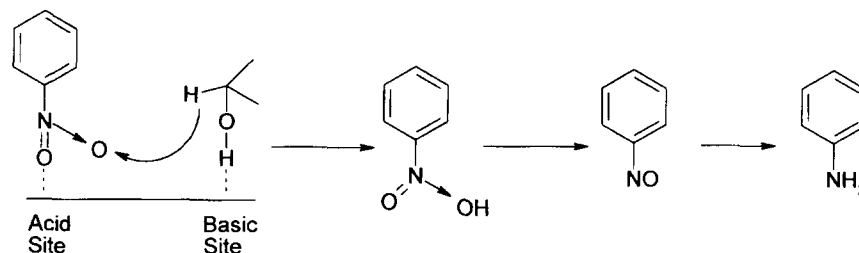
Scheme 2.

components of mixed oxides prepared by thermal calcination of a precursor with a high surface area and porosity, leading to the formation of active sites which control the reaction, which is absent in the case of physically mixed oxides.

It has been found that mixed metal oxides prepared from a hydrotalcite-like precursor are active catalysts for transfer hydrogenation reactions using isopropyl alcohol. The Ni–Al catalyst is more efficient compared to other systems, and its activity is attributed to highly active surfacial NiO and the redox nature of Ni^{2+} species present. Both the basicity of the catalyst and its redox nature must be the deciding factors which affect the transfer hydrogen reduction of aromatic substrates.

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