Selective Hydrogenation of Unsaturated Aldehydes and Ketones

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Abstract

Selective hydrogenation of α, β unsaturated aldehydes, ketones and esters, in general, is useful in perfumery, hardening of fats, drugs and in synthesis of organic chemical intermediates. This is an important and interesting area of research especially if there are two or more C=C bonds. The reaction becomes challenging in olefinic compounds having functional groups, since the hydrogenation of C=C is thermodynamically more favourable than C=O or CHO. The product selectivity depends on stereo-chemistry as well as the preferential hydrogenation of either the C=C or the functional group. The selectivity for α, β unsaturated alcohol is not easy and requires specific reaction conditions and catalyst system.

Chemeoselective hydrogenation catalysts are mostly based on supported metals involving Pt, Ru, Rh and Pd. The physico-chemical properties of a support, its acid-base character, metal reducibility and the extent of metal-support interaction play an important role in the complex chemistry of supported metal catalysts. It is therefore important to understand the supported catalysts and its preparation from the point of view of support. Mixed basic layered hydroxides for example, Hydrotalcite (HT) types of materials are being tried as novel supports in place of conventional oxides. The advantage in using HT type material is the layered structure with specific Mg^{2+}/Al^{3+} ratios and basic characteristics. Metals can be incorporated during synthesis (*in situ* synthesis) of the layered oxides or following post synthesis procedures. Synthesis of basic support itself is an interesting and challenging job. It will be useful to study the nature of metal species present on the support from the point of view of reduction characteristics, dispersion and metal support interaction.

A few simple and complex hydrogenation reactions are discussed to highlight the usefulness of hydrotalcite and metal - hydrotalcite systems. Conversion and selectivity of products are compared with the conventional catalyst systems.

1. Introduction

Hydrogenation is one of the common organic reactions used in the synthesis of chemicals. Catalytic hydrogenation is used in the hardening of fats and production of alcohols from aldehydes, and ketones. The direct catalytic hydrogenation of unsaturated aldehydes and ketones, fatty acids and their esters is however a challenging propostion. The reduction of C=C bond is thermodynamically more favored in comparison with that of the C=O bond. Suitable chemoselective hydrogenation catalysts for the reactions are all based on Pt, Pd, Ru, Pd and Ni. The performance of these catalysts is usually enhanced by using promoters of reducible oxides such as TiO_2, WO_3, and MoO_3 or by a combination of two metals. Very often supported metal catalysts are used in such hydrogenation reactions. The type of support, metal dispersion and the metal-support interactions are the factors that would determine the availability of metal for the reaction. The crystallite size of metal may decide the conversion and selectivity of the products. Therefore it is important to understand the support material we use for loading a hydrogenating metal. Conventionally, inorganic oxides such as SiO_2, Al_2O_3 are used as supports. However in recent times anionic clay materials with basic properties are tried for supporting metals, and are used for hydrogenation reactions.

Mixed basic layered hydroxides for example, Hydrotalcite (HT) types of materials are novel supports which are yet to be tried in place of conventional oxides. The advantage in using HT type material is the layered structure with specific Mg^{2+}/Al^{3+} ratios and basic characteristics. Metals can be incorporated during synthesis (*in situ* synthesis) of the layered oxides or after the synthesis; Post synthesis of basic support itself is an interesting and challenging job. It will be useful to study the nature of metal species present on the support from the point of view of reduction characteristics, dispersion and metal-support interaction. Therefore, the layered materials as well as metal supported material are well characterized using surface and bulk analytical techniques.

The preliminary catalyst screening studies are done for hydrogenation of acetone, benzene, phenol and acrolein. The studies are to be extended to the olefinic aldehydes and ketones. The corresponding allylic alcohols are useful as intermediates, pharmaceuticals, and as flavour chemicals. Conventional supported metal catalysts are not selective in the hydrogenation of molecules having both C=C and C=O groups. To selectively hydrogenate C=O, supported metal catalysts using layered double hydroxides are being tried. The layered structure will have to be judiciously used in the preparation of the supported metal catalysts.

2. Hydrotalcite type Clays

Research efforts are being made to develop catalysts based on simple inorganic oxides, mixed oxides, supported oxides, zeolites and clay minerals for environmentally safe processes. Because of their benign nature and special structural features a lot of renewed interests have emerged in using clays as catalysts and support. Generally, clays can be classified into two broad groups. Cationic clays, which nature prefers and anionic clays which are in nature (1). Cationic clay has infinite sheets of tetrahedra or octahedra of silica and alumina and also contains hydrates of magnesium, iron and other metals. The excess negative charge of the silicate sheets are compensated by alkali or alkaline cations (2). On the other hand anionic clays are composed of positively charged sheets of di– and trivalent metal hydroxides. The sheets share octahedral edges and contain interstitial anions to compensate the positively charged sheets (3). Hydrotalcite (HT) belongs to the large class of anionic clays. Hydrotalcite has Mg,$^{2+}$ Al^{3+} and CO_3^{2-} ions as its constituents.

3. Structure of anionic clays

The structure of the sheet containing Mg^{2+} and Al^{3+} is similar to that of magnesium hydroxide and they are often referred to as “brucite like layers’. The unit cell of the hydrotalcite may contain either three layers of metal hydroxide and interlayer anions with rhombohedral symmetry or two layers of metal hydroxide and interlayer anions with hexagonal symmetry. The overall composition of the HTLcs can be expressed with a general formula (4)

$[M^{2+}_{1-x}\ M^{3+}\ x\ (OH)\ ]\ [A^{n-}]_{x/n}.\ zH_2O$

where M^{2+} and M^{3+} represent divalent and trivalent metal cations, A^{n-} is the interlayer anion and z represents the varied state of hydration of the layered double hydroxide (LDH).

4. Variables in the synthesis of hydrotalcite – type materials

There are wide range of variables possible during the process of synthesis which affect the physico-chemical properties of HT - type compounds. Tailor made materials can be used as catalysts and supports. Generally co-precipitation and sol-gel methods are used for the preparation of HTs in the laboratory. Precipitation can be done at high pH (>13) or at low pH (in the range 7-10) conditions (5,6). The variation in preparation conditions such as crystallization time, temperature and pH will determine the crystallite size of HT support which in turn can affect the dispersion of a metal (3). Prinetto *et al* (7) have recently reported a comparative investigation on the synthesis and characterization of Mg/Al and Ni/Al layered double hydroxides prepared by sol gel and coprecipitation methods. Table 1 gives the crystallographic parameters of HTs prepared by coprecipitation method having different Mg/Al ratios.

Sels *et al*. (8) have narrated a variety of catalytic organic reactions that have been attempted over HT like anionic clays. Very little information is available on the use of HT as support for metal. Most of the studies are devoted to the electronic effect of the HT support on metal. The textural properties of LDH materials is altered by the introduction of a metal in the lattice layers. Hydrotalcite supported metals have not been generally well characterized. Only a few attempts have been made to correlate hydrogenation reactions with adsorption properties such as CO or H_2 uptake, metal surface area, dispersion and crystallite size. The objective of the present study is to understand how HT supported metals work as catalysts for selective hydrogenation reactions involving simple molecules such as acetone, phenol, acrolein as well as complex molecules of olefinic aldehydes and ketones.

Table 1
Cell parameters and phases of HTx identified by XRD

Code	Sample	Al/Al+Mg	Cell Constants		Phase identified
			a	c	XRD
A	HT0.15	0.15	3.088	24.243	HT, boehmite*
B	HT0.20	0.20	3.078	23.781	HT
C	HT0.25	0.25	3.058	23.265	HT
D	HT0.30	0.30	3.050	22.291	HT
E	HT0.35	0.35	3.042	22.743	HT

Boehmite (ASTM File No.21-1307)

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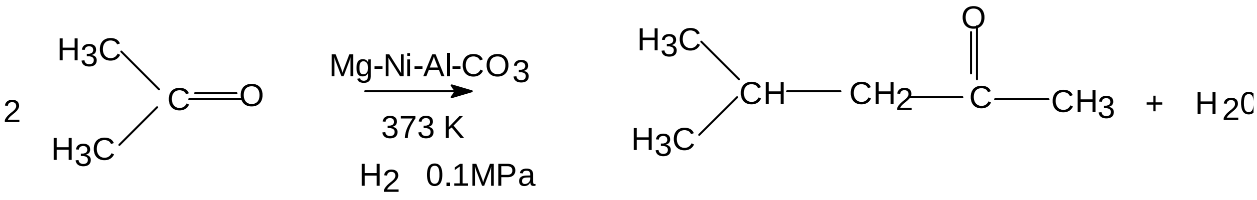
5. Selective Hydrogenation of Acetone

Methyl isobutyl ketone (MIBK) is an important industrial solvent for paints and protective coatings. It is usually manufactured by a three-step synthesis from acetone, and the process is rather cumbersome involving corrosive acid catalysts in liquid medium. The operating costs are also high. In recent years, attention has been shown in one step synthesis of MIBK from acetone and hydrogen using a catalyst with condensation, dehydration and hydrogenation functions. Patent literature claims several catalytic systems based on Pd supported on KOH-Alumina, $MgO\text{-}SiO_2$, $CaOMgOSrO\text{-}Al_2O_3$, Nb_2O_5, $ZrPO_4$ and cation exchanged resins for one-step synthesis of MIBK. The development of catalyst operable at gas phase conditions has been attempted in recent times. Lin and Ko (9) used Na promoted Pd/MgO for the low pressure one step synthesis of MIBK from acetone (473 K and 1 atms) and reported 64-47% conversion and 50-65% selectivity. Narayanan and Unni Krishnan.(10-12) used Fe, CO, and Ni supported on conventional alumina as well as on layered double hydroxides prepared by coprecipitation method for the synthesis of MIBK from acetone. Hydrotalcite based catalysts have been found to be efficient for this reaction at 373 K with 78% selectivity for MIBK at 48% conversion with a very little of hydrogenation product namely isopropanol. One step synthesis of MIBK from acetone can be performed with Ni-Mg-Al hydrotalcites with Ni substituted in lattice position. The reaction is also feasible with Pd and Ni impregnated on Mg-Al-Hydrotalcite



Acetone
(48% conv)

MIBK
(>78% selectivity)

A mechanism of product formation based on the bifunctional nature of the catalysts involving both metallic and acid-base nature has been proposed (11,12). Chen *et al*. (13) have reported using Pd and Ni on calcined Mg-Al hydrotalcite (CHT) with various ratios of Mg/Al for the one step synthesis of MIBK from acetone. They have evoked strong metal-support interaction and assessed that the reaction depends on metal loading and the temperature. Table 2 gives the conversion and selectivity on Pd and Ni supported CHT catalysts. The selectivity for MIBK varies between 61-68% at the conversion level of 37-44%.

Table 2

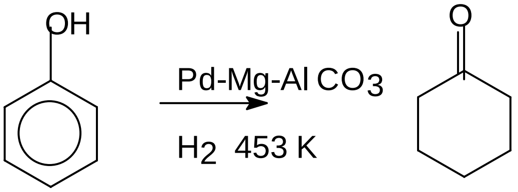
A comparison of Ni/CHT and Pd/CHT catalysts for acetone hydrogenation at 372 K (13)

Catalyst	Activity mol/h g cat	Selectivity, %			
		MIBK	IPA	C+9	MIBK+DIBK
0.2%Pd/CHT	3.2	67.8	6.9	6.8	85.2
5%Ni/CHT	4.0	57.2	17.3	3.9	75.0
3%Ni/CHT	3.8	61.5	11.3	8.7	77.8
1%Ni/CHT	2.2	66.0	3.4	12.8	81.4

1 atms, WHSV =500/ h, H_2/acetone=1/5

6. Selective hydrogenation of phenol

Catalytic hydrogenation of phenol is an important industrial route of preparing cyclohexanone which is an intermediate for the production of nylon-6. Industrially the reaction is carried out over Pd/Al_2O_3 catalysts modified with alkali or alkali-earth metals (14). The reaction is also tried industrially as an alternative to the more common auto-oxidation of cyclohexane. Narayanan and Krishna (15-20) have synthesized Hydrotalcite materials extensively and studied the preparation variables. They used both uncalcined and calcined forms of the material for the preparation of Pd/HT catalysts



Phenol
(> 98% Conv)

Cyclohexanone
(>95% Selectivity)

Dispersion studies were carried out using CO chemisorption. They found some interesting observations with respect to structure and dispersion relationship. It was found that Pd is highly dispersed over HT having a layered structure with carbonate interlayer anions and also on a mixture of crystalline MgO and $MgAl_2O_4$ spinel. Pd containing HT prepared by $PdCl_2$ impregnation have been tested for the selective reduction of phenol to cyclohexanone under vapor phase reaction conditions at 453 K. Pd/HT with high dispersion gave nearly 100% conversion with > 95% selectivity for cyclohexanone. Pd/HT catalysts are better than the conventional supported metal catalysts with respect to metal dispersion and catalytic activity as well as selectivity for cyclohexanone. Specific adsorption modes of phenol on HTs can give rise to unique selectivity that can not be achieved with other catalysts.

In Table 3, CO chemisorption and the corresponding Pd dispersion data are given for both the catalysts prepared by impregnation and ion-exchange methods using uncalcined HT. Phenol conversion varies with the Mg/Al ratio and not due to the differences in the metal loading. Cyclohexanone selectivity is above 90%. Calcined HT shows higher surface area due to the removal of water from interstitial spacings and possibly due to some decomposition of carbonate anions as well. Otherwise there is not much of a difference with respect to phenol conversion and cyclohexanone selectivity. (Table 4)

A comparison of Pd/HT catalyst is made with LiAlHT and ZnAlHT catalysts for CO chemisorption and phenol hydrogenation. ZnAlHT with relatively low surface area and low dispersion show very low catalytic activity than the other two (Table5). Chen etal (21) studied phenol hydrogenation over 0.3 %Pd on calcined Mg/Al hydrotalcite catalyst between 433 – 453 K. They observed >95% selectivity for cylclohexanone at phenol conversion of 40%.

Table 3
CO adsorption and phenol hydrogenation on 1 wt% Pd/HTx (HTx dried at 373 K).

Catalyst	Surface area	Pd disp. %		Phenol Conv. %		Cyclohexanone Select.%	
	HTx ,m^2g^{-1}	Imp.	I.E	Imp.	I.E	Imp.	I.E
1wt%Pd/HT0.15	107	43	40	36	32	98	95
1wt%Pd/HT0.20	61	44	38	43	28	97	95
1wt%Pd/HT0.25	47	53	47	58	39	96	98
1wt%Pd/HT0.30	53	58	52	59	50	96	95
1wt%Pd/HT0.35	72	61	59	66	61	95	90

Table 4
CO adsorption and phenol hydrogenation on 1wt%Pd/CHTx (HTx calcined at 973 K)

Catalyst	Surface area CHTx, m^2g^{-1}	CO uptake cm^3g^{-1} cat	Pd dispersion %	Conversion % (Phenol)	Selectivity % (Cyclohexanone)
1wt%Pd/CHT0.15	160	0.90	43	59	95
1wt%Pd/CHT0.20	173	0.70	33	38	99
1wt%Pd/CHT0.25	165	0.85	40	45	97
1wt%Pd/CHT0.30	182	0.83	39	45	97
1wt%Pd/CHT0.35	190	0.92	44	56	95

Table 5
CO adsorption and phenol hydrogenation properties of 1wt% Pd catalysts.

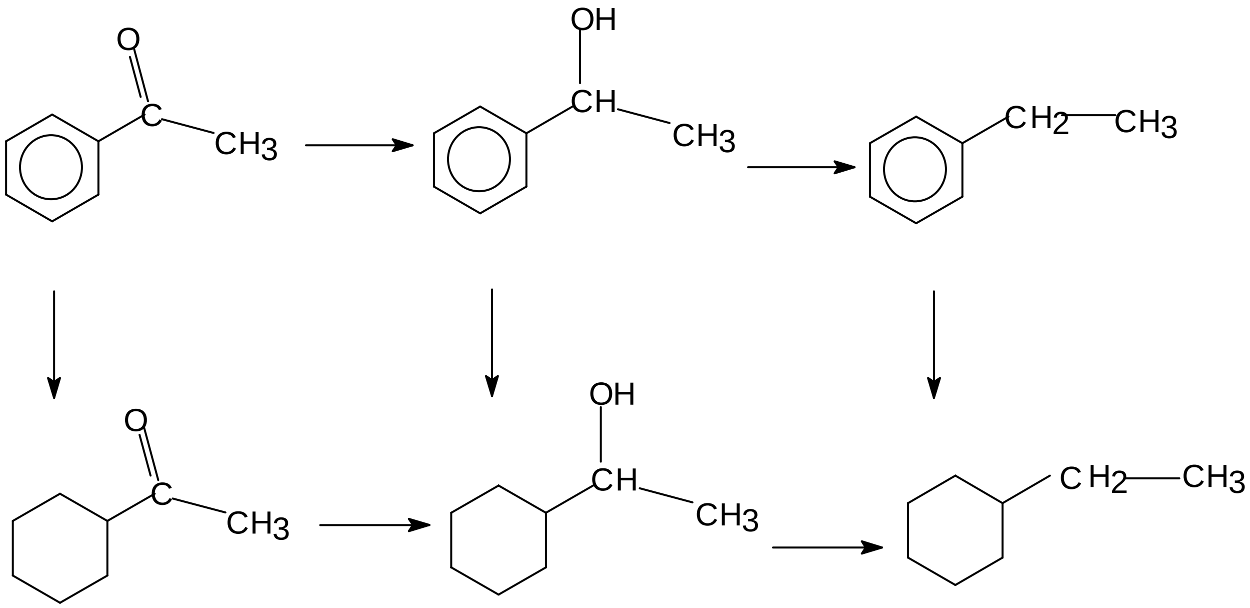
Support	BET surface area, m^2g^{-1}	Pd dispersion, %	Conversion, %	Cyclohexanone selectivity %
HT0.33	51	58	55	95
LiAlHT	60	52	53	60
ZnAlHT	37	27	2	100

7.Selective hydrogenation of acetophenone

The control of hydrogenation selectivity of a complex molecule containing both C=C and C=O bonds have been studied rather intensively by several workers. However, the competitive hydrogenation between phenyl and carbonyl group in one molecule has not been significantly addressed to . Chen *et al.* (22) have recently studied the selective hydrogenation of acetophenone on Pt/SiO_2 catalyst under gas-phase conditions. The reduced Pt/SiO_2 containing 4.7 wt% of Pt prepared by impregnation gave 3.4–3.9% conversion and 40-80% selectivity for 1-phenyl ethanol (PE) and 11-39% for cyclohexyl ethanol (CE) at room temperature. Oxidized Pt catalyst provides a lower catalytic activity than the reduced Pt, but selectivity shifts to 1-phenylethanol and ethylbenzene (EB). The hydrogenation of aromatic ring is almost suppressed by oxygen. The oxidized Pt induces activation of C=O and hence favoring C=O hydrogenation than C=C hydrogenation. The adsorption geometry of acetophenone on Pt surface is assumed to be an important factor in controlling molecular decomposition and hydrogenation selectivity. The product formation is proposed to follow the route AP to 1-phenyl ethanol to cyclohexyl ethanol. There is not much information available on the use of HT based metal catalysts for this reaction and this offers a new opportunity to exploit.

8. Selective hydrogenation of α,β-unsaturated aldehydes

Selective hydrogenation of α,β-unsaturated aldehydes such as crotonaldehyde, cinnamaldehyde, citral, acrolein and maleic anhydride to their corresponding α,β-unsaturated alcohols is highly desirable. The bond energy of C=C bond is smaller (615 kcal/mol) than that of C=O bond (715 kcal/mol), which makes the hydrogenation of C=O bond difficult. Selective hydrogenation of α,β-unsaturated aldehydes is by far more complex than the hydrogenation of olefins or saturated aldehydes. Two primary products are formed on hydrogenation of olefinic bond and the carbonyl bond, viz., the saturated aldehyde and unsaturated alcohol, respectively. Further reduction of the partially reduced products to the saturated alcohol can also occur adding to the side reactions that have to be considered.



Scheme: Reaction pathway for acetophenone hydrogenation

Table 6
Hydrogenation of various α,β-unsaturated aldehydes over Co-alumina (23)

Reactant molecule	Conversion %	Selectivity %			
		UOL	SAl	SOL	Acetal
2-Propenal (Acrolein)	38.7	7.4	61.9	0	30.7
3-Phenyl 2-Propenal (Cinnamaldehyde)	55.0	99.3	0	0	0.7
3-Butynal (Crotanaldehyde)	78.8	78.2	8.7	5.0	8.1
2-Methyl butynal	31.7	75.9	8.9	4.3	10.9
3-Methyl 2-butenal	39.7	61.0	3.2	0	35.8
2-Ethyl- 2-butynal	35.7	60.2	11.1	10.8	17.9
2-Hexenal (leafaldehyde)	97.6	77.0	1.2	11.2	7.7
2-Ethyl 2-hexenal	43.2	73.6	8.9	9.1	8.4

T= 323 K, Reaction Time = 2h, Catalyst wt = 1 g, H_2 Pr.= 0.98 M.Pa, Solvent = 50 ml Reactant = 3 ml
Co (Wt%) = 37 (by XRF)

Table 6 gives conversion of several unsaturated aldehydes and ketones over Co/Al_2O_3 catalyst and the selectivity of different saturated products. Co/Al_2O_3 prepared by precipitation method is a useful catalyst for the selective hydrogenation of various unsaturated aldehydes to the corresponding unsaturated alcohols. The selectivity of a product depends on the steric hindrance around C=C bond. A substituent at α or β position especially a bulky substituent at β position was found to be very effective for the formation of unsaturated alcohols (23).

The industrial interest in the selective hydrogenation of olefinic aldehydes is due to the use of unsaturated alcohols as important intermediates in the production of fine chemicals and pharmaceuticals. For example in vitamin A synthesis, retinal has to be hydrogenated to retinol; citral and furfural have to be selectively hydrogenated to the desired alcohols viz., citrenollol and furfuryl alcohol. It would be interesting and profitable to replace the expensive and environmentally delicate reduction of such aldehydes with $LiAlH_4$, $NaBH_4$ by benign catalytic process. Unsaturated alcohols with more than one C=C can be found in etheric oils like geraniol, linalool, farmesol and plytol. Pheromones like bibykol, a secretion of the silk moth, is of great interest for industrial manufacturing.

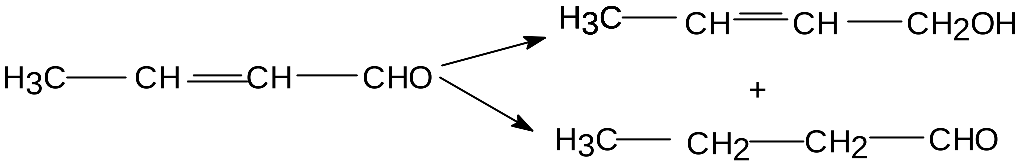
Catalysis in the perfumery industry is one of the new research fields using hydrogenation catalysts. There are numerous hydrogenation processes both in gas and liquid phases, for which catalytic properties and, the selectivity to the target compound are improved by adding bases, or more generally electron donor promoters, to the reaction medium. Modification of the catalyst surface by adding bases could be beneficially replaced by the design of new catalyst formulations. Hydrotalcites, a new class of basic mixed hydroxides having layered structure proved to be good precursors for loading noble metals and non noble metals. Metals supported on hydrotalcites have not been so far well evaluated for the hydrogenation reactions. Choudary etal.(24) have recently reported the reduction of several aromatic and heterocyclic aldehydes at atmospheric pressure over calcined Ni/Al hydrotalcite requiring no pre-reduction.

The structure of adsorbed α,β-unsaturated aldehydes subtly depends on the exposed metal surface planes and the substituents at the C=C bond. The relative accessibility and binding strength of the C=C and C=O groups in various α,β-unsaturated aldehydes to the catalyst is important for selectivity. The adsorption through C=O group becomes more easy with increasing steric hindrance of the olefinic group.

Catalyst plays an important role in decreasing the bond energy of C=O by selective adsorption and further by selective hydrogenation. The effect of metal-support interaction is significant in determining the selectivity of the products. Promoters play an important role in creating such polar sites and are indispensable as they are needed to activate the carboxylic group for hydrogenation. Promoters of metals play an essential role in the hydrogenation of unsaturated bonds such as in carbonylic compounds (25,26). This promotion is key to a high selectivity of unsaturated alcohols in the hydrogenation of α,β-unsaturated aldehydes. The cabonylic group is activated by a chemical bond between the O of C=O and the cation of the promoter. Many supported catalyst systems and modified supported metal systems have been studied for selective hydrogenation of αβ-unsaturated aldehydes and ketones. Nevertheless, the task of achieving the absolute selectivity towards the desired product, using heterogeneous catalytic system, especially in gas phase remains a difficult and a challenging task. There is a constantly growing interest to use heterogeneous catalysts in chemical processes.

9. Hydrogenation of crotonaldehyde

Crotonaldehyde is a typical α,β-unsaturated aldehyde. Hydrogenation of only the carbonyl group yield crotyl alcohol leaving the C=C bond unaffected. Therefore, this reaction is taken for this study. Crotyl alcohol is commercially produced by the reduction of crotonaldehyde with $LiBH_4$ or $NaBH_4$ or $LiAlH_4$ at room temperature



10. Hydrogenation of acrolein

Large quantities of allyl alcohol is required in the manufacture of glycerol. It is also an intermediate in the production of polymerizable allyl ethers and esters, especially diallyl phthalate. Polymeric allyl alcohol reacts with unsaturated fatty acids to give drying oils. Sulfurdioxide and allyl alcohol yield polymeric allyl sulphonic acids which have been proposed as intermediates for plasticizers and textile auxiliaries. Allyl alcohol can be co-polymerized with other monomers and then used as an intermediate in the production of flame resistant materials or as nematicide, fungicide and preservatives. Allyl alcohol is commercially prepared by hydrolysis of allyl chloride using a 5-10% sodium hydroxide solution at 423 K and 1.3-1.4 MPa with an yield of 85-95%. It is also prepared by the hydrolysis of allyl acetate over an ion-exchanger at 373 K (yield 90%). Another preparation method is by hydrogenation of acrolein in the vapor phase over a Cd-Zn catalyst or alumina/silica supported Ag-Cd alloys (yield 70%)

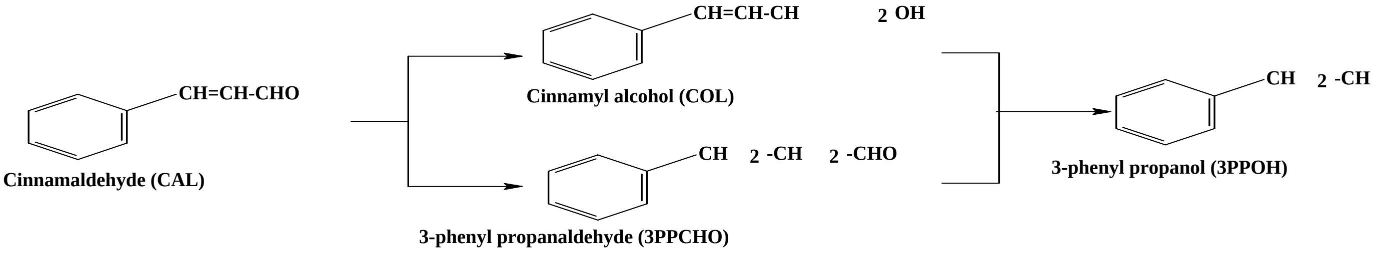
$$\underset{\text{Acrolein}}{CH_2{=}CH{-}CHO} \longrightarrow \underset{\text{Allyl alcohol}}{CH_2{=}CH{-}CH_2OH}$$

11. Hydrogenation of Cinnamaldehyde

Cinnamyl alcohol is a valuable chemical in the perfumery industry for its odor and fixative properties. It is a component of many flower compositions like lilac, hyacinth and lily of the valley and is a starting material for cinnamyl esters, several of which are valuable fragrance compounds. The alcohol is used for cinnamon notes and for rounding off fruit aromas. It is used as an intermediate in the synthesis of antibiotic chloromycetin. Cinnamyl alcohol is industrially produced by (i) reduction of cinnamaldehyde with isopropyl or benzyl alcohol in the presence of the corresponding aluminium alcoholate (yield Ca. 85%) or (ii) by the reduction of cinnamaldehyde using a Osmium-Carbon catalyst (yield 95%) or (iii) reduction of cinnamaldehyde with alkali borohydrides.

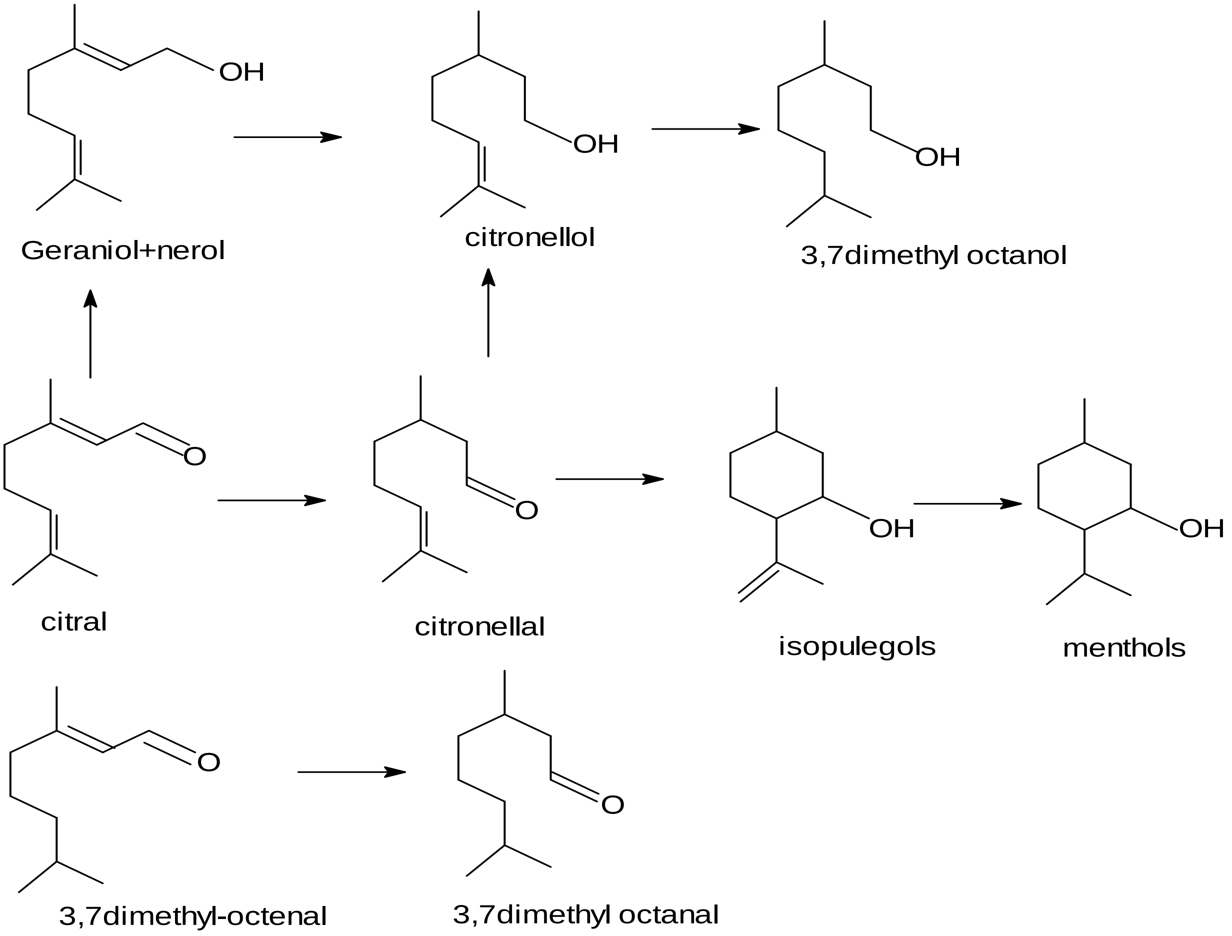
Chen *et al.*(26) described the promoting effect of La dopant to Co-B-SiO_2 amorphous catalyst in enhancing the cinnamaldehyde activity and selectivity of cinnamyl alcohol to around 80% under liquid phase conditions. La species in the form of La $^{2+}$ or La $^{3+}$ might activate the C=O bond via side-bond interaction of C=O bond. Da Silva etal. (27) using bimetal catalysts such as Pt-Sn and Pt-Fe supported on reducible TiO_2 were able to hydrogenate rapidly CAL to COL with almost stoichiometric yields. They attributed the high selectivity to SMSI behavior.

Scheme: Cinnamaldehyde hydrogenation



12.Hydrogenation of citral

Geraniol is obtained by the selective hydrogenation of only the carbonyl group of citral. It is one of the most frequently used terpenoid fragrance materials used in all flowery rose-like compositions and does not discolor soaps. In flavor compositions, geraniol is used in small quantities to accentuate citrus notes. It is an important intermediate in the manufacture of geranyl esters and citronellol. Geranyl acetate is used in perfumery to increase flowery, fruity nuances (rose) and for citrus and lavender notes. Geraniol is produced commercially by the following methods (i) isolation from essential oils (ii) synthesis from β-pinene which involves a pyrolysis step of β-pinene to myrcene which is then converted into geranyl chloride in the presence of Cu_2Cl_2/HCl. This geranyl chloride is converted to geranyl acetate over triethyl amine/sodium acetate and is saponified to geraniol. (iii) it is also produced from linalol by isomerization over *ortho* vanadate catalyst to give 90% yield.



Scheme: Citral hydrogenation

Citronellol is widely used as a fragrant material particularly for rose notes and for floral compositions in general. As flavor material, it is added for boquetting purposes to citrus compositions. It is the starting material for numerous citronellyl esters and for hydroxydihydrocitronellol, an intermediate in the production of dioxydihydrocitronellal.

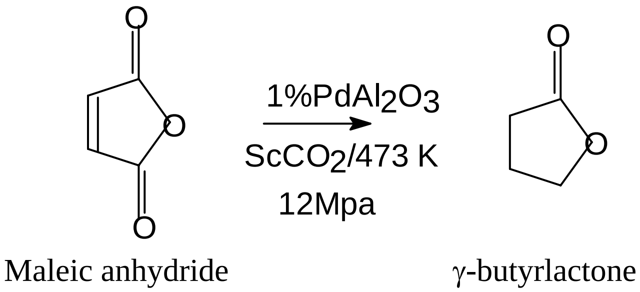
Selective hydrogenation of citral to citronellol has been studied over Ni catalysts and a selectivity upto 85% was reported on 8.8 Wt% Ni/Al_2O_3 (28). The selectivity is dependent on conversion. Ni supported zeolite Y on the other hand was not selective towards the formation of citrenellol. Silva *et al* (29) studied the kinetic behavior of the hydrogenation of citral over high temperature (HTR) and low temperature (LTR) reduced Ru/Sn/TiO_2 catalyst in liquid phase. The nature of support and the addition of tin have a profound effect on the production of isopulegols in the hydrogenation of citral over Ru-Sn catalyst. Aramendia *et al.(*30) prepared several basic MgO/M_2O_3 catalysts with M= Al, Ga and In by coprecipitation, sol-gel and precipitation methods and obtained pure hydrotalcite phase except in the case of indium. These catalysts were tested for Meerwein-Ponndorf-Verley (MPV) reactions between *trans* crotonaldehyde and isopropyl alcohol. The catalyst was also tested on the MPV reduction of various α,β unsaturated aldehydes with isopropyl alcohol. The mechanism for the process is assumed to involve a hydrogen transfer between the two substrates adsorbed on the acid-base sites of the catalysts. The yield and selectivity were greater than 90%. The reduction rates were found to be dependent on the nature of the hydrocarbon chain.

13. Hydrogenation of maleic anhydride

This is another important selective hydrogenation reaction to yield a very important and valuable product. viz., γ-butyrolactone. The main use of butyrolactone is as an intermediate in the synthesis of N-methyl pyrrollidone and the rubber additive thio digutyric acid, as a herbicide and growth regulator. It is used as a solvent for polymers and a polymerization catalyst; in hairwave compositions, sun lotions and in pharmaceuticals. It is also used in printing inks (e.g. ink-jet printing), an extractant in the petroleum industry, as a stabilizer for chlorohydroccarbons and phosphorous-based pesticides and as a nematicide. Most important process for the production of γ-butyrolactone is the endothermic dehydrogenation of butane-1,4-diol in the gas phase.

14. Selective hydrogenation using non-conventional techniques

Synthetic organic reactions performed under non-traditional conditions are gaining popularity because of the environmental considerations. The emerging area of green chemistry envisages the use of minimum hazardous chemicals as far as possible and the use of efficient and catalytic processes with less waste. One of the approaches for achieving this target is to look for alternative reaction conditions and reaction media to accomplish the desired chemical transformations with minimal by-product and waste. A solvent free approach includes the use of microwave (MW) assisted catalytic reaction as well as the use of ultra sound (US) method to accelerate the reaction rate with fewer disturbances to the catalyst surfaces. MW and US have been successfully applied as alternate energy sources for the selective epoxidation of α,β-unsaturated ketones over hydrotalcites.



The use of Sc.CO_2 as an attractive medium for the selective hydrogenation of maleic anhydride and α,β-unsaturated aldehydes such as cinnamaldehyde (CAL) over supported Pt and Pd catalysts has been described (31-33). Pillai *et al.* (31,32) have recently demonstrated a selective hydrogenation of maleic anhydride to either γ-butyrolactone or succinic anhdyride over Pd/Al_2O_3 under supercritcal CO_2 medium. It is possible to fine tune the reaction conditions to achieve the desired selectivity with out the use of expensive solvents such as PEG or EGDME or acetone for these reactions.

Table 7 describes the reaction conditions and the product selectivity using Sc.CO_2 .The advantage of using Sc.CO_2 as a medium in hydrogenation is further exemplified by the transformation of cinnamaldehyde over Pd/Al_2O_3. In the absence of methanol as solvent and in presence of Sc.CO_2 , only C=C hydrogenation takes place yielding 3-phenylpropionaldehyde whereas, cinnamaldehye dimethyl acetal is the major product in methanol medium.

Table 7.Comparison of maleic anhydride hydrogenation over 1% Pd/Al_2O_3 under Sc.CO_2 and in organic solvents at 473 K (31)

CO_2 Pr, bar	Organic Solvent	Conversion (%)	Yield (%)	
			GBL	SAH+SA
117	No solvent	100	~80	ND
-	PEG 10 ml	100	2	78
-	EGDME 10 ml	100	7	80
-	Acetone 10ml	100	2	96

Reaction conditions: 25 mmol MA, 0.5g catalyst, 21 bar H_2

Zhao *et al*. (33) have investigated the selective hydrogenation of CAL using silica supported platinum catalysts in supercritical carbondioxide . The study describes the influence of electronic state and dispersion of platinum particles on the conversion and selectivity. Selectivity to cinnamyl alcohol (COL) is enhanced as Pt^o/Pt^{2+} ratio increases. Metallic platinum in zero valent state is beneficial to the formation of COL compared with the less reduced surface. Pt^o/Pt^{2+} ratio affects the selectivity more than conversion. The selectivity for COL is high when Pt dispersion is also high. However, the CO_2 pr did not affect the conversion and selectivity very much (Table 8).

Table 8.CAL hydrogenation in Sc.CO_2 with Pt/SiO_2 catalyst (33)

Catalyst	Pressure of CO_2 (Mpa)	Conversion (%)	Selectivity (%)		
			CAL	3PPCHO	3PPOH
	6	16.8	79.7	16.1	4.2
	8	19.8	84.5	11.4	4.1
	10	23.0	85.4	10.3	4.2
	12	26.9	86.3	9.9	3.8
	14	25.9	88.1	8.6	3.3

15. Conclusions

The study brings out the relationship between catalytic properties of hydrotalcite supported as well as oxide supported metals for the selective hydrogenation of simple molecules such as acetone, phenol, acetophenone and also more complicated molecules such as α,β-unsaturated aldehydes and ketones to valuable products. Selectivity to the desired products is possible by fine tuning of the catalyst properties as well as the reaction conditions. Non-conventional techniques such as microwave assisted reaction and the use of Sc.CO_2 in solvent free systems have come a long way in achieving the objective of selective hydrogenation in an environmentally friendlier way than the conventional processes.

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