

Concept and progress in coupling of dehydrogenation and hydrogenation reactions through catalysts

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Abstract. This review focuses on the importance of coupling of catalytic reactions which involves dehydrogenation and hydrogenation simultaneously and the study of catalytic materials that are designed, adopted and/or modified for these reactions. The special features of these reactions are minimization of H₂ utilization and reduction in production cost. Structural and textural properties also play a decisive role in this kind of coupled reactions. This particular review although not comprehensive discusses the significant progress made in the area of coupled reactions and also helps future researchers or engineers to find out the improvements required in areas such as advancements in catalytic material preparation, design of the new reactors and the application of new technologies.

Keywords. Coupling; hydrogenation; dehydrogenation; catalyst.

1. Introduction

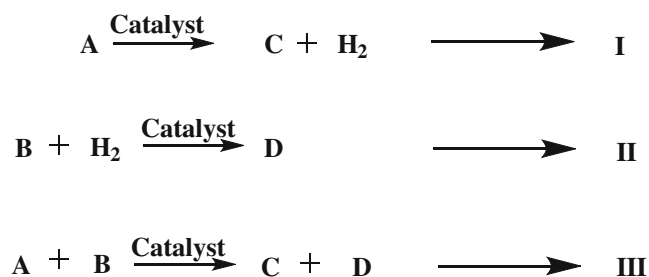
Catalysis is an important field in chemistry where most of the chemical processes employ catalysts at least in one of their steps.¹ Similarly, most biochemically significant processes are catalysed. A survey in the US showed that more than 60% of the 63 major products and 90% of the 34 process innovations from 1930 to 1980 have involved catalysis, which illustrates the vital role of this field in the fuel and chemical industries.² Catalytic reactions are preferred in environment-friendly green chemistry due to the reduced amount of waste generated;³ as opposed to stoichiometric reactions in which all reactants are consumed and more side products are formed. In the beginning, only pure components were used as catalysts, but after 1900, multicomponent catalysts were studied and these are now commonly used catalysts in the industry today.^{4,5} Continuous research and development (R & D) programmes are in progress in order to find new catalyst formulations to fulfill economic and environmental demands for various industrial reactions. In recent years, environmentally benign catalysts have gained more significance. Substantial importance has been given to developing a good active catalyst with a

special emphasize on eco-friendly catalytic materials. In addition to this, economical use of a catalyst/catalyst material is important. Consequently, people are trying to reduce production cost in all possible ways. This can be vital for the chemical industry. In addition to this, importance of hydrogen is one more point to be considered while performing a hydrogenation reaction. Hence, all these constraints led the researchers to combine two individual reactions namely dehydrogenation and hydrogenation in which the former reaction acts as a hydrogen source. This combination can reduce the capital, time and hydrogen usage. As a result, R & D is concentrating on developing different catalyst systems which can serve as both hydrogenation and dehydrogenation catalysts.

Recently, a review has highlighted the coupling of exothermic and endothermic reaction, types of reactors that are used and various types of couplings.⁶

Research on coupling of reactions, mainly endothermic and exothermic has emerged as work of high significance. Coupling of two contradictory chemical transformations over a single catalyst bed has several advantages such as operational simplicity, mitigation of thermodynamic limitations,⁷ eco-friendly operations and enhanced product selectivity. As shown in scheme 1, reaction I involves dehydrogenation which is generally an endothermic equilibrium process and

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Scheme 1. General scheme of individual and coupling reactions.

is governed by Le chatelier's principle and reaction II is a hydrogenation reaction which in most cases is an exothermic process. When the reactions I and II are performed simultaneously, the hydrogen released in reaction I will be used up in reaction II, enhancing conversions in reaction I (by Le chatelier's principle). Hence, this process provides an advantage of avoiding the usage of external H_2 . An additional benefit of this coupling process is maintainance of good thermal balance, and hydrogen in adsorbed form produced during dehydrogenation process is more reactive compared than molecular hydrogen in gaseous phase. Thus, the study of coupling processes have gained importance in recent times. It is necessary to study the coupling reactions intrinsic factors, screen the catalysts and optimize the operating conditions before such a process is carried out. Hence, various research groups started working on the coupling processes and obtained encouraging results.

2. Scope of the review

The major purpose of this survey is to excavate literature on coupling of dehydrogenation–hydrogenation reactions. It presents us the present status of coupled reactions in the area of catalysis. It reveals various catalytic materials used for various combinations of reactions and their operating conditions. It also presents the disadvantages, improvements/modifications to be made and suggestions to improve the yields and gaps to be filled to take these reactions to commercial scale.

2.1 Advantage in usage of CO_2

Several researchers coupled the dehydrogenation reaction with CO_2 flow. In 1988, Sato *et al.* conducted dehydrogenation of ethyl benzene (EB) to styrene in presence of CO_2 over sodium oxide/ Al_2O_3 catalyst.⁸ Thereafter, more studies on development of this reaction were reported which could achieve gradual improvement in the reaction output.^{9–17} Some of them revealed that the presence of CO_2 oxidizes the oxygen defects of the metal oxides present in the catalyst. Various other reports that dealt with the nature of acidic/basic sites and other parameters were published using modified and unmodified ZrO_2 , TiO_2 , MnO_2 and CeO_2 materials.^{18–22} All the reports emphasized the benefit of using CO/CO_2 as co-feed. The advantages of this coupling are that CO_2 could suppress the catalyst deactivation; formation of syn gas (mixture of carbon monoxide and hydrogen) and utilization of global warming culprit, CO_2 . However, the second process which is a reverse water–gas shift reaction (RWGS) is also an endothermic reaction which requires high temperatures. Mimura *et al.*¹² used steam in the dehydrogenation process to supply heat, to dilute EB for increasing conversion and to avoid coke deposition on the catalyst. It was reported that equilibrium conversion of EB to styrene is greater in presence of CO_2 than in presence of steam. Also, though the RWGS is endothermic in nature, shifting of equilibrium from EB to styrene is more dominant in steam.

Integrated membrane reactors were used to synthesize styrene and cyclohexane simultaneously.^{23,24} Wang *et al.* have reported the coupling of EB in presence of nitrobenzene using supported Pt catalysts.²⁵ Studies on coupling of EB and nitrobenzene (NB) with focus on EB dehydrogenation at low temperatures were reported.^{26–28} Zhu *et al.* (2002) reported the coupling of hydrogenation of maleic anhydride (MA) and dehydrogenation of 1,4-butanediol (BDO) over Cu–Zn catalysts.²⁹ They have reported that by coupling two reactions, reaction temperatures decreased by 30–50°C, which is because of the rich active hydrogen species generated on the catalyst surface. Further, Yang *et al.*

Table 1. Physico-chemical characteristics of the catalysts.

| Sl. No | Catalyst | BET surface area (m^2/g) | N_2O pulse chemisorption results | | |
|--------|----------|--|--|--|--------------------------|
| | | | Cu dispersion (%) | MSA (m^2/g) $\times 10^{19}$ | Cu crystallite size (nm) |
| 1 | CM | 25 | 12.1 | 11.57 | 45 |
| 2 | CA | 68 | 13.4 | 14.53 | 30 |
| 3 | CS | 150 | 20.6 | 23.2 | 20 |
| 4 | CHT | 60 | 10.3 | 13.3 | 33 |

Table 2. NH₃ TPD results of the catalysts.

| Sl. No | Catalyst | Temperature (K) | Acidic strength | Volume of NH ₃ desorbed (μml/g) |
|--------|----------|-----------------|-----------------|--|
| 1 | CM | 336 | Weak | 15 |
| | | 592 | Moderate | 33 |
| | | 970 | Strong | 74 |
| 2 | CA | 359 | Very weak | 223 |
| | | 494 | Moderate | 893 |
| 3 | CS | 346 | Very weak | 108 |
| | | 522 | Moderate | 65 |
| | | 933 | Strong | 30 |
| 4 | CHT | 643 | Moderate | 97 |

modified the Cu–Zn catalysts with Al, and used it in the synthesis of butyrolactone (BL) and 2-methylfuran (MF) by the coupling of 1,4-butanediol and furfural.³⁰

Research has continued on various catalytic materials for a number of coupled reactions by our group producing different varieties of industrially important compounds. Initially, Cu–MgO catalysts were used to produce furfuryl alcohol and cyclohexanone (CHN) by the coupling of cyclohexanol (CHA) dehydrogenation and furfural (FA) hydrogenation.³¹ Producing encouraging results. Later, Cu–MgO–Cr₂O₃ catalysts were employed in the same reaction.³² It is observed that the addition of Cr₂O₃ as a promoter enhanced the activity and decreased the particle size of Cu when compared to that of unpromoted catalyst. A US patent has been granted for the same study.³³ Another coupling reaction of 1,4-butanediol and nitrobenzene was

reported over Cu–MgO catalyst.³⁴ The same catalyst system was also tried in the coupling of acetophenone and 1,4-butanediol.³⁵ Effect of metal loading and the method of preparation involving Cu–MgO–Al₂O₃ (precursor such as hydrotalcite) catalyst were studied in the coupling of cyclohexanol and nitrobenzene.^{36,37} Preparation method of the catalyst also plays a vital role in metal dispersion.³⁸ The synergy mechanism was well-established between the reactant molecules in all those reported coupled reactions. Moreover, the conversions increased significantly in the coupled reactions when compared to that of individual reactions which serves as an additional advantage of these coupled reactions.

In addition to the above mentioned coupled reactions, continuous research on new catalysts suitable for various coupled reactions was carried out. Keeping 10 wt% of Cu (active metal) in each catalyst, various supports such as MgO, Al₂O₃, SiO₂, and Mg–Al HT have been chosen keeping the strength of acidities in mind for the coupling of 1,4-butanediol (1,4-BDO) dehydrogenation and NB hydrogenation reaction. Physico-chemical characteristics of catalysts (CM, CA, CS and CHT represents Cu/MgO, Cu/Al₂O₃, Cu/SiO₂ and Cu/HT catalysts, respectively) are displayed in table 1. Table 2 shows the acidic strengths of the catalysts at different temperatures. Experimental procedure for catalyst characterization was followed according to procedure given in literature.³⁹ It is observed that the BET surface areas of catalysts are on the lower side when compared to bare supports (MgO = 42 m²/g, Al₂O₃ = 180 m²/g, HT = 80 m²/g, SiO₂ = 380 m²/g). From the N₂O pulse chemisorption studies, it is evident that the support influences surface Cu species and active metal area and thereby metal particles. Figure 1 shows the activity profile of the coupling of 1,4-butanediol dehydrogenation and nitrobenzene hydrogenation at 523 K. Figure 1 and table 2 show that although metal dispersion is higher for CS catalyst, the material with non-acidic sites/moderate basic sites play an

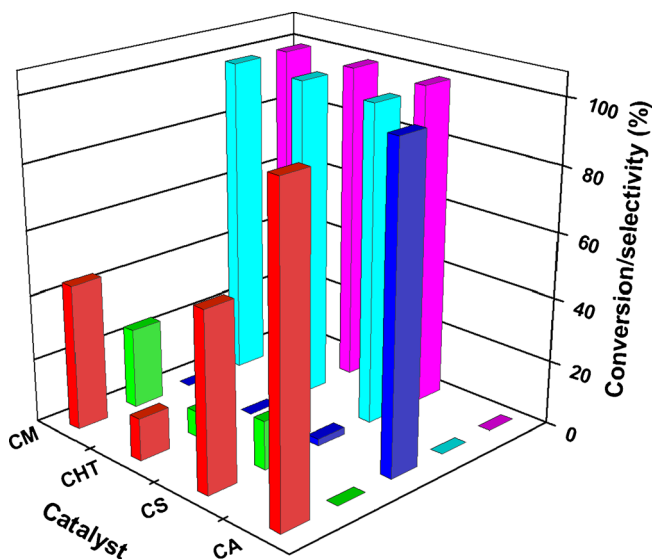


Figure 1. Activity profile of various Cu catalysts. Reaction conditions: 1 atm, temperature = 523 K, 0.5 g catalyst, 1, 4BDO/NB = 3/2, N₂ flow = 18 ml/min. ■ Conversion of 1, 4 BDO. ■ Conversion of NB. ■ Selectivity to THF. ■ Selectivity to GBL. ■ Selectivity to ANL.

Table 3. Physical characteristics of the catalysts.

| Sl. No | Catalyst | BET surface area (m ² /g) | XRD phases | | Crystallite size of reduced catalysts (nm) | Crystallite size of spent catalysts (nm) |
|--------|----------|--------------------------------------|------------|--|--|--|
| | | | Calcined | reduced | | |
| 1 | 5CM | 30 | CuO, MgO | Cu ⁰ , Cu ₂ O, MgO | 30 | 40 |
| 2 | 10CM | 25 | CuO, MgO | Cu ⁰ , Cu ₂ O, MgO | 45 | 60 |
| 3 | 15CM | 18 | CuO, MgO | Cu ⁰ , Cu ₂ O, MgO | 75 | 93 |
| 4 | 20CM | 15 | CuO, MgO | Cu ⁰ , Cu ₂ O, MgO | 108 | 145 |

important role in determining the activity. No NB conversion was observed over CA catalyst as dehydration pathway is followed towards the formation of THF. Hence, the nature of the support will play a crucial role in governing the reaction pathway.

Later, using MgO as a suitable support, a catalyst series was made with 5, 10, 15 and 20 wt% of Cu prepared by incipient wet impregnation method. The catalysts were denoted as 5CM, 10CM, 15CM and 20CM, respectively. Physical characteristics of these catalysts are displayed in table 3. Based on the surface area data, it is concluded that the blockage of MgO pores is by CuO or formation of solid solution.

Effect of metal loading on individual reactions (conversion of 1,4-butanediol to GBL and conversion of NB to ANL) for all the catalysts has been tested and it was found that the activity of catalysts is in the order:

20CM>15CM>10CM>5CM. Although metal dispersion is higher at lower Cu loadings, 20CM exhibited higher activity because of the presence of higher Cu species that are active during coupling reaction. Therefore, effect of temperature on the coupling reaction has been conducted for 20CM catalysts. Figure 2 shows the effect of temperature on the activity of 20CM catalyst for the coupling reaction. It is found that 523 K is the optimum temperature for the coupling reaction, beyond this temperature, a decline in the conversion of NB is observed which may be due to competitive adsorption of both the reactants and due to the exothermic nature of NB hydrogenation. Liberated water vapour may be another factor responsible for decline in the conversion of NB during time on stream study.^{44,45}

Recently, we have tried the coupling of 1,2-butanediol and NB over Cu/SiO₂ catalyst (20 wt% Cu loading) to synthesize 1-hydroxy 2-butanone (1, 2 BDN) and aniline (ANL), respectively and the results are shown in figure 3. It is found that optimum temperature for the coupling reaction is 523 K and hence a

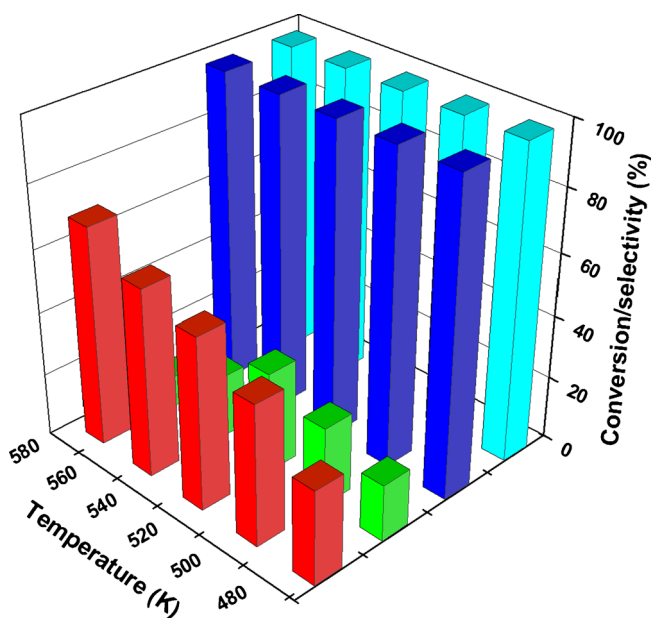


Figure 2. Effect of temperature on 20CM catalyst. Reaction conditions: 1 atm, 0.5 g catalyst, temperature range = 473–573 K, 1, 4 BDO/NB = 3/2, N₂ flow = 18 ml/min. Conversion of 1, 4 BDO. Conversion of NB. Selectivity to 1, 4 GBL. Selectivity to ANL.

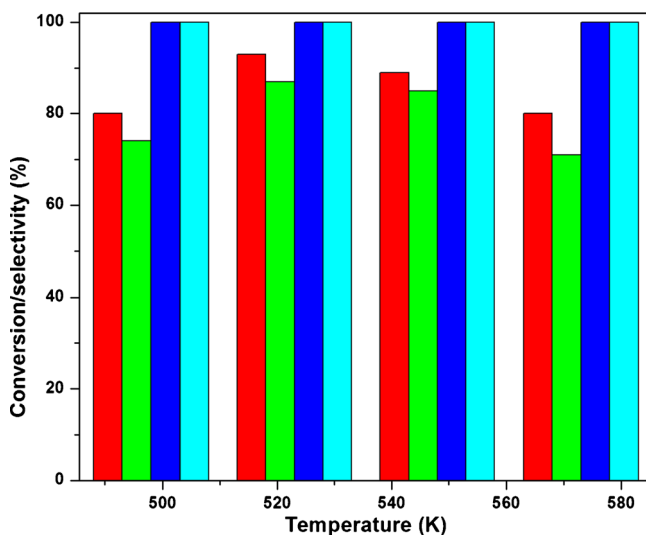


Figure 3. Effect of temperature over Cu/SiO₂ catalyst. Reaction conditions: 1 atm, 1 g catalyst, temperature range = 498–573 K, 1, 2 BDO/NB = 3/1, N₂ flow = 20 ml/min. Conversion of 1, 2 BDO. Conversion of NB. Selectivity to 1, 2 BDN. Selectivity to ANL.

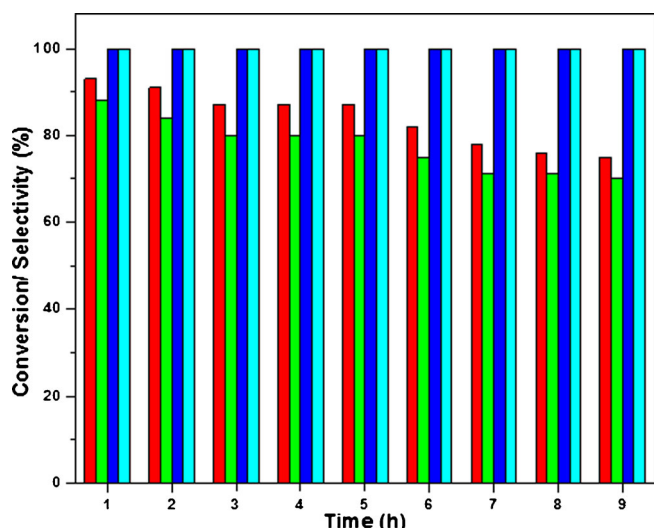


Figure 4. Time on stream studies over Cu/SiO₂ catalyst. Reaction conditions: 1 atm, 1 g catalyst, temperature = 573 K, 1, 2 BDO/NB = 3/1, N₂ flow = 20 ml/min. ■ Conversion of 1, 2 BDO. ■ Conversion of NB. ■ Selectivity to 1, 2 BDN. ■ Selectivity to ANL.

time on stream study has been conducted to evaluate the catalyst stability, depicted in figure 4. A gradual decrease in the activity of the catalyst is observed after 5 h. The reason for deactivation is yet to be analysed.

Table 4 provides a brief history of coupled reactions using different catalyst systems. Keen observation reveals that most of these reactions used Cu-based catalyst as it can dehydrogenate as well as hydrogenate the substrate. Moreover, these coupling processes proved

that they are energetically favoured since the necessary heat required to drive the dehydrogenation reaction has been provided by the exothermic hydrogenation process when both of them are combined.

3. Suggestions

From the literature available so far on the coupled reactions, it is possible to formulate some of the suggestions.

- (i) Reactions were performed so far on metal oxide supports, however, these reactions can be tried over mesoporous supports such as SBA-15, SBA-16, KIT-6, COK-12, etc. as they possess regular porous structure and high surface which may help in enhancement of activity.
- (ii) New methods of catalyst preparation which increase metallic dispersion may be followed.
- (iii) Reactions can be extended to asymmetric/chemoselective hydrogenations. These can be tried in the hydrogenation step so as to obtain a unique product.
- (iv) Most coupling processes have never been tried at industrial scale; hence, a proper and sincere effort should be made to evaluate the aspects such as mass transfer limitations and thermodynamic limitations.

Table 4. Brief history of coupling reactions over different catalyst systems.

| Reaction | Catalyst system | Year | Reference |
|-----------------------------------|--|------|-----------|
| Ethyl benzene + CO ₂ | Sodium oxide/Al ₂ O ₃ | 1988 | 8 |
| Ethyl benzene + CO ₂ | Activated carbon-supported iron catalyst | 1995 | 10 |
| Ethyl benzene + CO ₂ | Iron oxide catalysts | 1998 | 12 |
| Ethyl benzene + nitrobenzene | - | 2002 | 27 |
| Ethyl benzene + nitrobenzene | Activated carbon | 2011 | 28 |
| 1,4-Butanediol + maleic anhydride | Cu-Zn-Al | 2005 | 40 |
| 1,4-Butanediol + maleic anhydride | Cu-Zn | 2002 | 29 |
| n-butanol + maleic anhydride | Cu-Zn-Ce | 2008 | 43 |
| Ethanol + maleic anhydride | Cu-ZrO ₂ , Cu-Al ₂ O ₃ , Cu-ZnO | 2013 | 46 |
| Ethanol + maleic anhydride | Cu-Zn-Zr | 2009 | 47 |
| n-Butanol + maleic anhydride | Cu-ZnO-TiO ₂ | 2008 | 48 |
| Cyclohexanol + furfural | Cu-Zn-Al | 2006 | 41 |
| Cyclohexanol + furfural | Cu-Mn-Si | 2008 | 42 |
| Cyclohexanol + furfural | Cu-MgO-Cr ₂ O ₃ | 2007 | 32 |
| Cyclohexanol + furfural | Cu-MgO | 2011 | 31 |
| Cyclohexanol + nitrobenzene | Cu-MgO-Al ₂ O ₃ | 2012 | 36 |
| Cyclohexanol + nitrobenzene | Cu-MgO-Al ₂ O ₃ | 2013 | 37 |
| 2-Propanol + acetone | Ru-Pt composite | 1994 | 49 |

4. Conclusion

In this review, effort has been made to provide information regarding past and present status of coupled reactions. Earlier reports suggested that the presence of CO₂ during H₂ utilization enhanced the activity in dehydrogenation reaction in all the cases. Later, various industrially important products were synthesized simultaneously by changing the reactants. Studies that have been reported till now reveal the significance of the coupling of dehydrogenation and hydrogenation reactions, especially in terms of H₂ economy and energy preservice, reduction in size and number of equipments. It is expected that molecular hydrogen is less reactive than the nascent hydrogen which is obtained in the dehydrogenation step. Also, preparation method of catalyst and selection of catalyst support plays a decisive role in its activity. Hence, every parameter pertaining to the support, active metal and preparation method has to be taken care of. The synergy between the two reactants has been well-exploited. Various suggestions were made in order to modify and increase the yield of the reaction. However, these coupled reactions need further research in order to be used in the industry. They can be considered as a useful source, keeping the world economy in view, to synthesize various products.

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