Formic acid assisted hydrogenation of levulinic acid to γ -valerolactone over ordered mesoporous Cu/Fe₂O₃ catalyst prepared by hard template method

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Abstract. Vapor phase hydrogenation of levulinic acid using formic acid as a hydrogen source has been conducted over ordered mesoporous Cu/Fe₂O₃ catalysts prepared by hard template method using mesoporous silica, SBA-15. X-ray diffraction result reveals the absence of copper peaks because of either highly dispersed state, or formation of a solid solution with iron oxides. The N₂ sorption analysis and TEM results indicate the retainment of mesoporous nature in the samples. Among the catalysts tested, 10 (wt%) Cu/Fe₂O₃ seems to be an efficient catalyst to yield higher amounts of γ -valerolactone under hydrogen-free conditions. The results reveal the formation of spinel species, which gets reduced easily at a lower temperature (as evidenced from TPR studies), and as a consequence of this synergism, significant improvement in the catalytic performance for the synthesis of γ -valerolactone from levulinic acid and formic acid in presence of water has been achieved. The presence of water plays a crucial role in obtaining a higher yield of γ -valerolactone. This makes the catalytic system a viable methodology for hydrogenation of levulinic acid to get γ -valerolactone.

Keywords. Levulinic acid; formic acid; hydrogenation; γ -valerolactone; Cu/Fe₂O₃ mesoporous catalyst.

1. Introduction

Effective utilization of biomass to produce fuels and chemicals has emerged as an important area of research.¹ During the past few decades, people all over the world are increasingly being dependent on fossil fuels like coal, crude oil and natural gas as energy resources, though it is well-known that these resources last only for 46, 58 and 116 years, respectively.² Moreover, utilization of these resources discharge large amount of CO₂ into the atmosphere³ which can sustain in the atmosphere for longer times ($\sim$ 120 years) resulting in global warming. In this context, global scientific community actively engages in search of alternative fuels. Among the alternatives, biomass seems to be a promising feedstock because of its ready availability through forestation. Nature produces around 200 billion tons of biomass by means of photosynthesis, which comprises about 3000 GJ of energy per annum,⁴ wherein, only 14%

of the biomass is being utilized for energy purposes. Compared to the direct use of biomass as fuel, its conversion into a fuel or fuel additive chemicals improves the calorific value. Utilization of the biomass-derived fuels also contributes CO₂ towards atmosphere but it can be recycled for the growth of biomass through photosynthesis.

Due to energy scarcity and global warming problems, the catalytic transformation of inexhaustible renewable sources like biomass and/or biomass-derived platform molecules to fuels, fuel additives and value-added chemicals is presently one of the choices for consideration. To accomplish the need for sustainable progress, it is indispensable to discover the efficient catalyst for the transformation of biomass and/or biomass-derived platform molecules. Conversion of biomass/biomass-derived platform molecules to fuels, fuel additives and chemicals can be achieved through catalysis. Even though an outstanding progress has been made, there is still room for the design and development of an efficient

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catalytic system for the transformation of biomass and/or biomass-derived platform molecules such as levulinic acid.

Levulinic acid is generally obtained through acid hydrolysis of cellulose.^{5,6} Due to the presence of two functional groups like keto and acid in levulinic acid, it can be transferred into various promising fuels, fuel additives and chemicals by means of different processes like hydrogenation, esterification, oxidation, reductive amination and so on.^{7–14} Hydrogenation of levulinic acid is a promising route among these. Hydrogenation of levulinic acid can be carried out in both the ways as shown in Scheme 1.

Literature studies reveal the usage of formic acid as hydrogen source for levulinic acid hydrogenation in batch processes.^{15–19} For practical applications, fixed bed continuous processes and development of an efficient catalyst for the hydrogen generation and its *in situ* utilization for the hydrogenation of levulinic acid is of great importance. A number of catalysts have been reported for either the decomposition of formic acid, or levulinic acid hydrogenation.^{15–22} The combination of these two reactions is a good strategy for multiple advantages no necessity of separation of levulinic acid and formic acid, and that it can be further processed to obtain biofuels like γ -valerolactone and methyl tetrahydrofuran.

Since the discovery of mesoporous materials, researchers paid much attention to the synthesis of various types of mesoporous materials such as MCM-41, SBA-15, KIT-6 and COK-12, *etc.*, because of their uniform pore size, high surface area and high thermal stability. These materials were used as catalysts as well as catalyst supports. But, lately people pay more attention to synthesize mesoporous catalysts and nanostructured materials rather than supports. Nanocasting method for the preparation of nanostructured Zn-Fe

mixed oxides and α -Fe₂O₃/SnO₂ catalysts photocatalytic applications were reported.^{23,24} In this regard, an attempt has been made to fabricate ordered mesoporous catalyst i.e., Cu/Fe₂O₃ by nanocasting method using SBA-15 as hard template. In addition to the huge abundance of iron on earth (6th most abundant in the world), it has been effectively utilized in various hydrogenation reactions. To the best of our knowledge, this is the first report of the application of ordered mesoporous Cu/Fe₂O₃ catalysts in the vapour phase at atmospheric pressure for hydrogenation of levulinic acid with formic acid as a hydrogen source.

2. Experimental

2.1 Preparation of SBA-15

Ordered mesoporous silica, SBA-15 was prepared as reported elsewhere.^{25–28} In a typical experiment, 20 g of the triblock copolymer (P123, M/s. Aldrich Chemicals, USA) was dispersed in a mixture of 560 g of distilled water and 137.5 g of 35% hydrochloric acid (M/s. Loba Chemie, India). Then, 44 g of Tetraethylorthosilicate (TEOS, M/s. Aldrich Chemicals, USA) was added under constant stirring conditions at 313 K for 12 h and the mixture was subjected to the hydrothermal treatment at 373 K for 24 h. The resultant slurry was filtered, dried in air at 373 K for 12 h and then calcined in air at 823 K for 8 h at a ramping rate of 1 K min^{−1}.

2.2 Preparation of supported Cu Catalysts

The prepared SBA-15 was utilized as a hard template for the synthesis of Cu/Fe₂O₃ catalyst according to a similar method adopted for various mesoporous metal oxides.^{29,30} In a typical synthesis procedure, requisite amounts of nitrate precursors of Cu (M/s. Loba Chemie, India) and Fe (M/s. Loba Chemie, India) were thoroughly mixed and grounded along with SBA-15 to get a homogeneous mixture. The resultant mass was then dispersed in n-hexane, stirred and refluxed overnight at 343 K. Later, the mass was filtered, dried followed by calcination in air at 873 K for 5 h. Finally, the silica framework was removed by dissolution in NaOH solution at room temperature. Bare Fe₂O₃ was also prepared by a similar procedure and denoted as F and Cu/Fe₂O₃ catalysts were designated as xCF where 'x' stands for Cu content in weight%.

2.3 Structural characterization

X-ray diffraction studies were applied to know the phases of the prepared samples using Ultima-IV X-ray diffractometer (M/s. Rigaku Corporation, Japan) with Cu K α radiation. The morphological features were assessed by JEM field emission scanning electron microscope (M/s. JEOL) and with JEM-1010 transmission electron microscope (M/s. JEOL), N₂ adsorption/ desorption isotherms of the prepared samples

Scheme 1. Levulinic acid hydrogenation with H₂ and formic acid.

were obtained using Quadsorb SI (M/s. Quantachrome Instruments, USA) at 77 K. Before the analysis, the samples were outgassed at 423 K for 3 h using turbojet vacuum pump. Temperature programmed reduction (TPR) of the fresh catalysts were performed on a homemade reactor setup. About 50 mg of catalyst was placed in a quartz reactor and pre-treated in Ar flow at 373 K for 2 h. The flow of 5% H₂-Ar mixture gas (60 cm³ min⁻¹) with a temperature ramping of 10 K min⁻¹ was maintained during the TPR run. The hydrogen consumption was monitored by using a thermal conductivity detector (TCD) equipped gas chromatograph (M/s. CIC Instruments, India) coupled with standard GC software.

2.4 Catalysis procedure

The catalytic tests were carried out at atmospheric pressure in a downflow fixed bed glass reactor (14 mm inner diameter, 200 mm long) loaded with 1 g of catalyst mixed with 1 g of quartz beads. Prior to the catalytic performance, the catalyst was reduced at 553 K online for 3 h in H₂ flow (30 cm³ min⁻¹). The feed solution comprising of the required molar ratio of levulinic acid and formic acid, was continuously fed at a flow rate of 1 cm³ h⁻¹ through a liquid feed pump (M/s. B. Braun co., Germany) in a stream of N₂ flow (30 cm³ min⁻¹). The product samples were collected at regular intervals at the outlet of the reactor in an ice-cold trap and the quantification of product components were evaluated by a gas chromatograph equipped with a flame-ionization detector. Particularly, the breakdown of formic acid to gases like H₂ and CO₂ were analyzed by a gas chromatograph equipped with a thermal conductivity detector.

3. Results and Discussion

In order to know the silica content in the catalyst samples, the ICP analysis was performed and it was noticed that no silica content was present in the samples. Figure 1 illustrates the XRD patterns of calcined ordered mesoporous Fe₂O₃ and Cu loaded Fe₂O₃ nanoparticles prepared by nanocasting method. The diffraction pattern of parent Fe₂O₃ show the reflections at 2θ values of 24.26 (012), 33.21 (104), 35.70 (110), 40.94 (113), 49.52 (024), 54.06 (116), 57.52 (018), 62.61 (214), 64.07 (300), 72.02 (1010), 75.66 (220) which can be attributed to the existence of α-Fe₂O₃ (i.e., hematite form, JCPDS No. 87-1166).^{30,31} Upon increasing the loading of Cu on α-Fe₂O₃, an increase in the intensity of a reflection at a 2θ value of 35.70° is noticed, which may be ascribed to a disturbance in lattice parameter due to the formation of solid solution/spinal in the samples. The absence of reflections due to Cu-oxides at all Cu loadings indicates either the formation of spinel or solid solution or the presence of Cu-oxides in amorphous form.

Figure 1. XRD patterns of calcined catalysts.

Figure 2. XRD patterns of reduced catalysts.

Figure 2 illustrates the XRD patterns of reduced Cu/Fe₂O₃ catalysts. Significant changes were noticed in the reduced catalysts (553 K for 3 h in H₂ flow). Reflections at 2θ values of 35.54, 62.74, 30.17, 57.13, 43.20° can be attributed to the CuFe₂O₄ spinel structure (JCPDS No. 77-0010). Presence of Fe₃O₄ species cannot be ruled as the 2θ values of this phase overlaps with those of CuFe₂O₄ spinel structure. It is interesting to note the absence of reflections due to Cu metal, an indication for its amorphous nature.

To verify the redox behavior, the samples were subjected to TPR studies. The results were shown in Figure 3.

The TPR profile of Fe₂O₃ generally demonstrated two peaks centred at around 707 and 913 K respectively,

Figure 3. TPR patterns of calcined catalysts.

which are due to the reduction of Fe_2O_3 to Fe_3O_4 and Fe_3O_4 to Fe respectively.³⁰ Shifting of T_{max} related to the reduction of Fe oxides to lower temperatures in presence of CuO is an indication of strong interaction. As compared to the TPR profile of Fe_2O_3 , another peak with shoulder was noticed in the TPR patterns of Cu incorporated samples at lower temperature, i.e., at around 473 K which can be attributed to the reduction of CuO and spinel species (i.e., CuFe_2O_4).^{31–33} It appears that CuO readily reduces to Cu metal compared to the reduction of CuFe_2O_4 . That is the reason why the XRD patterns of

reduced catalysts show the reflections due to CuFe_2O_4 . The textural properties such as surface area pore volume and pore size were compiled in Table 1.

The morphology of Fe_2O_3 looks like spherical in its shape but after incorporation of copper, a thread-like morphology is noticed in Figure 4.

Additionally, the retention of mesoporous arrays even after incorporation of copper is evidenced from the TEM images (Figure 5).

Furthermore, 10% $\text{Cu}/\text{Fe}_2\text{O}_3$ was investigated by HR-TEM and found that the copper particles are well-dispersed throughout the Fe_2O_3 surface with particle size ranging between 8 to 15 nm. As can be seen from Scheme 1, hydrogenation of levulinic acid using formic acid as hydrogen source seems to be expeditious. Since formic acid is co-produced along with levulinic acid, it is worth to hydrogenate levulinic acid with formic acid rather than hydrogen. Comparison of levulinic acid hydrogenation with molecular hydrogen with that of formic acid (Table 2) clearly indicates that formic acid-assisted levulinic acid hydrogenation is a better choice.

Hydrogen independent hydrogenation of levulinic acid in vapour phase conditions at atmospheric pressure was conducted and the data was corroborated in Figure 6.

As can be seen from Figure 6, bare Fe_2O_3 can also catalyse both formic acid decomposition and levulinic acid hydrogenation.³⁴ About 81% selectivity towards the γ -valerolactone (GVL) was noticed at a 70%

Table 1. Surface area, pore size and pore volume of catalyst samples prepared by nanocasting method.

Catalyst code	Cu content wt %	BET SA (m^2/g)	Pore volume (cc/g)	Pore size (nm)
F	Fe_2O_3	63	0.24	15.9
2.5 CF	2.5 $\text{Cu}/\text{Fe}_2\text{O}_3$	56	0.18	13.7
5 CF	5 $\text{Cu}/\text{Fe}_2\text{O}_3$	49	0.24	19.5
7.5 CF	7.5 $\text{Cu}/\text{Fe}_2\text{O}_3$	48	0.25	19.4
10 CF	10 $\text{Cu}/\text{Fe}_2\text{O}_3$	45	0.19	15.4
15 CF	15 $\text{Cu}/\text{Fe}_2\text{O}_3$	40	0.22	19.9

Figure 4. SEM images of (a) Fe_2O_3 and (b) $10\text{Cu}/\text{Fe}_2\text{O}_3$ catalysts.

Figure 5. TEM images of (a) Fe₂O₃ and (b) 10Cu/Fe₂O₃ (c) HR-TEM image of 10Cu/Fe₂O₃ catalyst.

Table 2. Comparison of activity studies with different H₂ source.

Sl.No.	Catalyst	Hydrogen source	Reaction Temp	Conversion of LA	Selectivity to GVL
1	10Cu/Fe ₂ O ₃	Formic acid	523 K	100%	100%
2	10Cu/Fe ₂ O ₃	H ₂	523 K	70%	85%

Figure 6. Catalytic performance of various Cu/Fe₂O₃ catalysts. Reaction Conditions: catalyst weight = 1 g, Temperature = 523 K, Formic acid/Levulinic acid = 5.

conversion of levulinic acid over bare Fe₂O₃. On increasing the Cu loading from 2.5 wt% to 10 wt%, an increase in the conversion of levulinic acid from 75% to 100% and the GVL selectivity from 97% to 100% is noticed. Full conversion is observed in the catalysts containing a Cu content of ≥ 10 wt%. As evidenced by the literature, the presence of both copper and iron oxide particles are responsible for the transformation of levulinic acid.^{35–38} Additionally, iron oxide particles are also able to decompose formic acid.³⁴ In the present study, we noticed the high catalytic performance of 10 Cu/Fe₂O₃ in the levulinic acid hydrogenation and formic acid decomposition in a single step continuous process.

Recently Cu-Fe catalysts with good conversion in a batch process for the hydrogenation of levulinic acid were reported.^{35,38} In contrast, we have noticed excellent catalytic performance in the transformation of hydrogen-free hydrogenation of levulinic acid using formic acid as a hydrogen source in vapour phase conditions. Whenever, iron is one of the constituents, better catalytic performance was achieved.^{34–39} Similarly, we

also noticed moderate conversion of levulinic acid over the mesoporous Fe₂O₃ catalyst. By incorporation of copper to Fe₂O₃, we noticed an increase in both conversion and selectivity. This clearly explains the excellence of catalytic power of the system.

The time on stream studies was performed to know the stability of the catalyst for hydrogenation of levulinic acid without external hydrogen source and data is shown in Figure 7a.

A slight decrease in levulinic acid conversion after 8 h is noticed during the time on stream which can be attributed to the coking of the catalyst (i.e., through the formic acid promoting the condensation of reaction intermediates). In general, declining of activity during the time on stream is either due to coking of the catalyst or due to the agglomeration of Cu particles. In this particular scenario, coking of the catalyst is predominant over the agglomeration of Cu particles. We performed the CHNS analysis of spent catalysts and noticed 3% carbon in the catalyst. Additionally, we performed the time on stream study of the spent catalyst by calcining it in air followed by reduction and noticed similar catalytic performance. This is a clear indication that declining of activity during the time on stream is due to coke formation, rather than the agglomeration of Cu particles.

Generally, the crude composition (Levulinic acid and formic acid) as it is obtained through the hydrolysis of biomass that contains water. In this context, we have performed the hydrogenation of levulinic acid with formic acid in presence of water (LA: FA: H₂O 1:5:1) and the results are displayed in Figure 7b.

The results indicate better performance of the catalyst toward GVL formation than without water.³⁸ Thus the presence of water is advantageous in yielding more amount of GVL (beneficial role of water) in the

Figure 7. (a) Time on stream study over 10Cu/Fe₂O₃ catalyst without water co-feeding. Reaction Conditions: catalyst weight = 1 g, Temperature = 523 K, Formic acid/Levulinic acid = 5. (b) Time on stream study over 10Cu/Fe₂O₃ catalyst with water co-feeding. Reaction Conditions: catalyst weight = 1 g, Temperature = 523 K, Formic acid/Levulinic acid = 5.

conversion of LA. Similar scenario was noticed in aqueous phase hydrogenation of biomass-derived carbonyl compounds *viz.*, levulinic acid.^{40,41} This clearly indicates the robustness of the present catalytic system for the transformation of levulinic acid with formic acid as a hydrogen source in the presence of water. Further results

are underway to find out the role of water in the transformation of levulinic acid with formic acid. Activity comparison (Table 3) reveals that the activity of present catalyst is either on par or better than those reported in the literature.^{14,19}

4. Conclusions

In summary, the successfully synthesized ordered mesoporous Cu/Fe₂O₃ catalyst with the mesoporous silica as hard template has been applied for the vapor phase hydrogenation of levulinic acid using formic acid as a hydrogen source. The bare mesoporous Fe₂O₃ also acts as a catalyst for levulinic acid hydrogenation with formic acid. Further, upon doping of Cu to Fe₂O₃, we have noticed better catalytic performance and reaches a perfect conversion over 10 wt% of Cu. This high catalytic performance was attributed to the interaction between copper and iron oxide particles because of which a large number of easily reducible CuO species was present.

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Table 3. Comparison of activity studies.

Sl. No.	Catalyst	Levulinic acid/formic acid ratio	Reaction temp	Conversion of LA	Reference
1	Ni/Al ₂ O ₃	1:5	523 K	100%	13
2	Ni-Cu/SiO ₂	1:3	538 K	98%	18
3	10Cu/Fe ₂ O ₃	1:5	523 K	100%	Present work

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