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Original Research Article

Use of Magnesium Ferrite as Catalyst in Cannizaro Reaction

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ABSTRACT

Magnesium ferrite was used to catalyse the cannizaro reaction of benzaldehyde in the presence of potassium hydroxide. Magnesium ferrite was prepared by hydrothermal process. Similarly Copper, nickel, cobalt, zinc etc. were prepared by same method. It was characterized by Field Emission Scanning Electron Microscopy (FESEM), X-Ray Diffraction Spectroscopy (XRD), and Energy Dispersive X-Ray Spectroscopy (EDX). The crystalline size of magnesium ferrite was found to have 82.47 nm. These magnesium ferrites are nano-flowers in shape. It was found that the yield of the product (benzoic acid) in the presence of Mg ferrite was 49% which is almost 3.4 times the yield obtained in the absence of catalyst. Other metal ferrites were also used as a catalyst but we get higher yield with magnesium ferrite. A comparitive study was made with different metal ferrites as catalyst and found that the activity of metal ferrites followed the order-

 $MgFe_{2}O_{4}\left(49\%\right) > CuFe_{2}O_{4}\left(46\%\right) > Ni \ Fe_{2}O_{4}\left(17.05\%\right) > ZnFe_{2}O_{4}\left(5.8\%\right) > CoFe_{2}O_{4}\left(1.1\%\right)$



Keywords: Cannizaro reaction Magnesium ferrite, Catalyst, Synthesis, Hydrothermal method

Introduction

Wang et al. [1] carried out asymmetric intramolecular Cannizzaro reaction of alkyl and aryl glyoxals with alcohols using congested trisoxazolinic ligand. This reaction has high level of enantioselectivity and also a gradual liberation protocol of active glyoxals from glyoxal monohydrates. The enantioselective addition of alcohols to glyoxals was considered responsible for stereoselectivity. Subbiah et al. [2] developed an efficient, simple, atom efficient and scalable method for the synthesis of 2,5-dihydroxymethylfuran (DHMF) and 5-

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hydroxymethylfuranoic sodium salt (HMFA). They could obtain 80% yield from 5hydroxymethylfurfural (HMF) by Cannizzaro reaction in water, when 0.9 eq. NaOH was used. It was noted that building blocks DHMF and HMFA; both could be easily isolated using selective crystallisation. Marvi and Talakorbi [3] used montmorillonite K-10 and KSF clays as catalyst for Cannizzaro reaction by 1,4-diazabicyclo [2.2.2]octane (DABCO) in presence of microwave irradiation and solvent-free conditions within seconds and that too with excellent yields. It was also revealed that solid montmorillonite K-10 and KSF can be recovered and reused in the few more subsequent cycles in this reaction. Galli et al. [4] reported that facile Cannizzaro disproportionation is there in case of 1,3-distal *cone*-calix[4] arenedialdehyde in presence of a strong base. On the contrary, 1,2-vicinal regioisomer and the analogous monoaldehyde were found to be unreactive under similar conditions. They evaluated intramolecular reactivity of the 1,3-distal regioisomer. Lolli et al. [5] investigated oxidation of 5-hydroxymethylfurfural (HMF) to 2,5-furandicarboxylic acid (FDCA) in water. They used supported Pd-Au nanoparticles as catalyst. It was also reported that Au and Pd monometallic nanoparticles both formed 5-hydroxymethyl-2-furancarboxylic acid (HMFCA) under these conditions; but HMFCA was not further transformed in presence of Pd nanoparticles whereas Au and bimetallic Pd-Au systems both catalysed oxidation of HMF to FDCA. The thermal treatment of Pd-Au catalysts considerably modified their catalytic activity, because Pd atoms migrated and concentrated onto the outer part of bimetallic nanoparticles. They also synthesized PVP-protected Pd-Au nanoparticles with different structures (alloy or core-shell morphology) and their reactivity was evaluated in Cannizaro reaction. Albuquerque et al. [6] investigated Cannizzaro reaction of pyruvaldehyde to lactic acid using ZrO₂ catalysts in a flow reactor. It was reported that crystalline structures of two ZrO₂ polymorphs affected the conversion of pyruvaldehyde and monoclinic phase of zirconia was found to be most active in this reaction. It was also revealed that there was a good correlation between the reaction rate and the concentration of Lewis acid sites. Santos et al. [7] investigated Cannizzaro reaction in a flow reactor with various catalysts having different acidity. It was revealed that Lewis acid sites on their heterogeneous catalysts were important for the reaction but Brønsted sites played no role at all. The results revealed that catalytic activity is indeed directly related to acidity of catalyst. It was found that ZrO₂, TiO₂, and Nb₂O₅ were potential catalysts and their activity was dependent on their water-tolerant Lewis acid sites. Out of there, the Nb₂O₅ was stable catalyst and it exhibited highest most activity. Marczewski et al. [8] studied Cannizzaro transformation of benzaldehyde to benzyl alcohol at 323 K and it can be used as a test reactions for evaluating

basic properties of solid catalysts. The minimum basic strength (H_min) for benzaldehyde transformation is 15.4. Daemi et al. [9] used polyurethane dispersion as a green catalyst (ionic solvent), which facilitates the Cannizzaro reaction under very mild alkaline conditions. The anionic polyurethane nanomicelle is considerd as green polymer ionic solvent for the progress of Cannizzaro reaction. The main advantages are eco-friendly polymer solvent, excellent yields of the products, shorter reaction times, low temperatures and reusability.

Experimental

Synthesis of metal ferrite nanoparticles

Hydrothermal method was used to prepare magnesium ferrite using a similar method as Naidu and Madhuri¹⁰.Megnesium nitrate [Mg (NO₃)₂] and ferric nitrate [Fe (NO₃)₃.9H₂O] was used as precursor of Megnesium and iron, respectively. A Teflon coated autoclave was used for this purpose. Megnesium and iron nitrates were dissolved in distilled water keeping the ratio of nitrates and water as 1:3. The resultant solution was stirred and NaOH was added drop wise into the solution in 1:4 ratios till the pH was maintain. The mixture was vigorously stirred for 2 h and transferred into Teflon coated stainless steel autoclave and sealed. Then autoclave was heated at 150°C around 48 h. After heating, the autoclave was allowed to cool at room temperature. The product in the autoclave was filtered and washed several times from water and then acetone, till its pH reaches 7.

Cannizaro reaction catalysed by magnesium ferrite

Potassium hydroxide (10.0 g) was dissolved in water (10.0 mL) and the solution was cooled to about 25°C. Benzaldehyde (10.0 mL) was taken in another flask and potassium hydroxide solution and 0.08 g magnesium ferrite was added to it. The flask was corked firmly and mixture was shaken thoroughly until an emulsion is formed. Then the mixture was allowed to stand for twenty four hours or even longer when the odour of benzaldehyde is no longer detectable. The precipitates were dissolved in sufficient amount of water, shaken and Conc. hydrochloric acid was added to get crystals. The solution was filtered and recrystallized with boiling water.

The Cannizzaro reaction is-



RESULTS AND DISCUSSION

Field Emission Scanning Electron Microscopy

The as-prepared magnesium ferrite particles were characterized by scanning electron microscope (SEM) on JSM-6100 (JEOL) with a digital image processor. The SEM images have been given in Figure 1. The morphology of magnesium ferrite was found to be Nano flower like structures.



Figure 1. FESEM Images of magnesium ferrite

X-Ray diffraction (XRD)

The crystalline nature of the synthesized magnesium ferrite sample was observed by X-Ray diffraction pattern. A X' Pert Pro XRD is equipped with X' Celerator solid – state detector was used and result are reported in Figure 2. The average particle size of particles was measured by Debye-Scherer equation and it was found to be in nano-range (82.47 nm).



Figure 2. XRD Images of magnesium ferrite

X-Ray photoelectron spectroscopy (XPS)

X-Ray photoelectron spectral analysis was also carried out using a Thermo K-alpha + Xray spectrometer. Contact angle measurement was carried out using a KRUSS drop shape analyzer. XPS of magnesium ferrite indicated that Mg, Fe, and O are present in 1s, 2p, and 1s states, respectively in this sample.



Figure 3. XPS Images of magnesium ferrite

Energy-dispersive X-Ray spectroscopy (EDX)

Energy-dispersive X-ray spectroscopy (EDS) with JSM 7600 F (Jeol) showed only peaks for Fe, Mg , and O, which indicates that megnesium ferrite is in pure state and it does not contain any impurity.



Figure 3. EDX Images of magnesium ferrite

Fourier transforms infrared Spectrum (FTIR)

FTIR Spectrum RX-I was used to record IR spectrum of the product. The spectrum is gives in Figure 5.



Figure 5. FTIR spectrum of product

Some bands are observed in the region $3500 - 2819 \text{ cm}^{-1}$ (a broad band) for single bond –OH stretching vibration and C-H vibration in aromatic system. Band at 1547 cm⁻¹ may be attributed C=C stretching vibration, In-plane bending vibrations of – OH at 1072 cm⁻¹ was observed. The C=O and C-O in-plane bending vibrations were observed at 972 and 833 cm⁻¹ while out-of-plane bending vibrations was observed at 706 cm⁻¹. All these bands supported that the product is benzoic acid.

Nuclear magnetic resonance spectrum (NMR)

FT-NMR spectrometer model Advance-II (Bruker) (400 MHz) was used to record NMR spectrum of the product. The spectrum is given in Figure 6.



Figure 6. FTNMR spectrum of product

NMR spectrum of the product indicated the presence of multiplets between 7.21- 7.23 and a doublet at 7.31-7.32 δ which may be assigned to m- and o- aromatic protons. There was another multiplets at 7.82- 7.84 δ and it was attributed to aromatic protons at p- positions. There was a singlet around 10.0 δ indicating the presence of a carboxylic proton. On the basis of FT-FTIR and NMR results, it was concluded that the product was benzoic acid. It was also confirm by m.p. and m.m.p.

Comparitive Study of Cannizaro Reaction

Different factors were varied to achieve optimum conditions such as amount of benzaldehyde, catalyst, potassium hydroxide, etc. The effect of benzaldehyde was observed in the range of 5.0- 20.0 mL. The pH was maintained around 12. The result are presented in Table 1.

| Benzaldehyde | КОН | Magnesium ferrite | Yield |
|--------------|--------------|-------------------|-------|
| (mL) | (g) | (g) | (%) |
| 5.0 | 10.0 | 0.08 | 20.2 |
| 7.5 | 10.0 | 0.08 | 38.1 |
| 10.0 | 10.0 | 0.08 | 49.0 |
| 12.5 | 10.0 | 0.08 | 34.7 |
| 15.0 | 10.0 | 0.08 | 22.8 |
| 17.5 | 10.0 | 0.08 | 16.4 |
| 20.0 | 10.0 | 0.08 | 12.5 |

 Table 1. Effect of benzaldehyde

It was found that when the amount of benzaldehyde was increased, the yield of product increases up to 10.0 mL of benzaldehyde and then it declined on further increasing its amount. It may due to the fact that the 10.0 mL is the required amount of benzaldehyde, above which it remain unreacted. The effect of amount of potassium hydroxide was observed by keeping it in the range of 5.0 - 20.0 g and the result are reported in Table 2.

It was observed that as the amount of potassium hydroxide was increased keeping all other parameters constant, then the yield increases up to 0.10 g of potassium hydroxide and then it showed a declining behavior above 10.0 g. It may be due to the fact that 10.0 g is the required amount of potassium hydroxide in this reaction above which it remains unreacted. The effect

of magnesium ferrite was observed by keeping it in the range of 0.05 - 0.15 g and the result are reported in Table 3.

| Benzaldehyde | КОН | Magnesium ferrite | Yield | |
|--------------|------|-------------------|-------|--|
| (mL) | (g) | (g) | (%) | |
| 10.0 | 5.0 | 0.08 | 20.4 | |
| 10.0 | 7.5 | 0.08 | 33.5 | |
| 10.0 | 10.0 | 0.08 | 49.0 | |
| 10.0 | 12.5 | 0.08 | 31.6 | |
| 10.0 | 15.0 | 0.08 | 25.1 | |
| 10.0 | 17.5 | 0.08 | 22.0 | |
| 10.0 | 20.0 | 0.08 | 19.96 | |
| | | | | |

Table 2. Effect of potassium hydroxide

 Table 3. Effect of magnesium ferrite

| Benzaldehyde | КОН | Magnesium ferrite | Yield |
|--------------|------|-------------------|-------|
| (mL) | (g) | (g) | (%) |
| 10.0 | 10.0 | 0.05 | 18.2 |
| 10.0 | 10.0 | 0.07 | 26.4 |
| 10.0 | 10.0 | 0.08 | 49.0 |
| 10.0 | 10.0 | 0.09 | 40.0 |
| 10.0 | 10.0 | 0.10 | 20.8 |
| 10.0 | 10.0 | 0.12 | 11.8 |
| 10.0 | 10.0 | 0.15 | 8.9 |

It was found that when the amount of magnesium ferrite was increased, the yield of product increases up to 0.08 g of magnesium ferrite and then it declined on further increasing its amount. It may be attributed to the fact that all active sites are occupied (saturated state) and

as a result, yield decreases. The highest yield of benzoic acid could be obtained under the following optimum conditions:

Benzaldehyde = 10.0 mL, Potassium hydroxide = 10.0 g, Magnesium ferrite = 0.08 g.

A comparative study was also carried out to compare the efficacy of different metal ferrites for Cannizaro reaction, which followed the order;

 $\label{eq:mgFe2O4} \begin{array}{ll} MgFe_2O_4 \ (49.0 \ \%) > CuFe_2O_4 \ (46.0 \ \%) \\ >Ni \ Fe_2O_4 \ (30.2 \ \%) > ZnFe_2O_4 \ (28.5 \ \%) \\ > CoFe_2O_4(17.5 \ \%) \end{array}$

DISCLAIMER

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

CONCLUSION

The MgFe2O4 nanoparticles were prepared an average size of 82.47nm via hydrothermal process in a Teflon coated autoclave. These nanoparticles were used as catalyst in presence of Potassium hydroxide for Cannizaro reaction of benzaldehyde under mild conditions. Some of the important advantages of this method are high yield, less time, and mild reaction conditions. This process is easy. The catalyst can be reused 5-6 times without any significant loss of catalytic activity. This catalyst is environment friendly in nature.

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References

[1] P. Wang, W. J. Tao, X. L. Sun, S. Liao, Y. Tang, J. Amer. Chem. Soc., 135(45), 16849-16852 (2013).

[2] S. Subbiah, S. P. Simeonov, J. M., Esperança, L. P. N. Rebelo, C. A. Afonso, *Green Chem.*, **15**(10), 2849-2853 (2013).

[3] O. Marvi, M. Talakoubi, Orient. J. Chem., 32(1), (2016).

[4] M. Galli, J. A. Berrocal, S. Di Stefano, R. Cacciapaglia, Mandolini, L, L. Baldini, et al, *Org. Biomol. Chemi.*, **10**(26), 5109-5112 (2012).

[5] A. Lolli, S. Albonetti, L. Utili, R. Amadori, F. Ospitali, C. Lucarelli, et al, *App. Catal. A: Gen.*, **504**, 408-419. (2015).

[6] E. M. Albuquerque, L. E. Borges, M. A. Fraga, C. Sievers, *Chem. Cat. Chem.*, 9(14), 2675-2683 (2017).

[7] K. M. Santos, E. M. Albuquerque, L. E. Borges, M. A. Mol. Catal., 458, 198-205 (2018).

[8] M. Marczewski, Y. Kavalchuk, U. Ulkowska, M. Gliński, O. Osawaru, *React. Kinet. Mech. Catal.*, **126**(1), 199-217 (2019).

[9] H. Daemi, M. Barikani, M. Jahani, New J. Chem., 40(3), 2121-2125(2016).

[10] K. C. Babu Naidu, W. Madhuri, Bull. Mater. Sci., 40 417-425 (2017).

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