Iranian Journal of Catalysis 7(1), 2017, 53-59

IRANIAN JOURNAL OF CATALYSIS

Promoting effects of calcium on the performance of Cu-MgO catalyst in hydrogenation of furfuraldehyde

Vahid Farzaneh[a,b], Samira Shirvani[a,b], Samahe Sadjadi[a,c], Mohammad Ghashghaee[a,b,]*

[a]*Biomass Conversion Science and Technology (BCST) Division, Iran Polymer and Petrochemical Institute, P.O. Box 14975-115, Tehran, Iran.*

[b]*Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, P.O. Box 14975-112, Tehran, Iran.*

[c]*Gas Conversion Department, Faculty of Petrochemicals, Iran Polymer and Petrochemical Institute, P.O. Box 14975-112, Tehran, Iran.*

Received 6 September 2016; received in revised form 13 November 2016; accepted 16 November 2016

ABSTRACT

In the present study, the effects of calcium doping on the performance of the co-precipitated Cu-MgO catalysts prepared with different calcium loadings in the selective hydrogenation of furfuraldehyde were investigated. The results proved that the addition of this promoter had a remarkable impact on the catalytic performance. The conversion of furfuraldehyde enhanced up to 83% and the furfuryl alcohol selectivity remained above 96% over the run length on the promoted Cu-Ca-MgO catalyst. However, the conversion level decreased to 60% after 240 min of operation period which was still superior with respect to the negligible conversion with the non-promoted Cu-MgO catalyst.

Keywords: *Hydrogenation, Furfuraldehyde, Furfuryl alcohol, Cu-MgO, Calcium promoter, Biomonomer, Heterogeneous catalyst.*

1. Introduction

Today, by enhancing demands of biofuels and chemicals, climate concerns and strict environmental regulations on using fossil fuels and the reduction of petroleum reservoirs, efforts have been taken to find new environmental, energy-efficient, and accessible sources to reduce dependence on petroleum resources. Biomass as a source of power and chemicals is a good replacement for providing green energy.

Furfuraldehyde is produced by acid catalyzed digestion of pentosan sugar in biomass. It is one of the most important and promising intermediates that attracted a lot of interests due to its simple production process directly from biomass and its potential to convert to a wide range of furan chemicals which are applicable in different industries [1-6]. Furfuryl alcohol is produced by catalytic hydrogenation of furfuraldehyde and it is a key material in polymer industries. It is mainly used for the production of foundry sand binders, corrosion-resistant mortar, various synthetic fibers and farm chemicals [7,8].

Hydrogenation of furfuraldehyde is carried out both in liquid and vapor phases but the latter has become more attractive and industrialized because of its mild reaction conditions. Depending on the nature of the catalyst, method of preparation, and operating conditions, a wide variety of products such as furfuryl alcohol, 2-methyl furan, tetrahydrofurfuryl alcohol, furan and even ring opening products can be produced in this process [7]. Copper-chromite catalyst is mostly used for the selective production of furfuryl alcohol in the furan industries. The greatest disadvantage of this catalyst is related to the toxicity of Cr_2O_3, which limits its application. Several attempts were made in the last decades to find an environmentally friendly catalyst [3,7-12]. Some of the reported catalysts include Cu/C catalyst [9], Raney Ni [13], Ni amorphous alloys [14,15], mixed copper zinc oxides with Al, Mn, and Fe [14,16,17] and homogenous mixture of Rh, Ru, and Pt [18]. Cu-MgO is the proposed catalyst which has a low cost, high activity, significant yield and selectivity towards furfuryl alcohol. These features lead to attract a lot of attentions during the last decades [8,10,19-20].

Several promoters such as Cr, Ni, Pd, Fe, Zn, and Co were previously reported in the litrature [20] for the

---

*Corresponding author email: m.ghashghaee@ippi.ac.ir
Tel.: +98 21 4866 2481; Fax: +98 21 4478 7032

Cu-MgO catalysts prepared through the impregnation of the promoter. In the present contribution, the potential role of calcium as a promoter was inspected with the hope of improving the performance of the co-precipitated Cu-MgO catalysts in the gas-phase furfuraldehyde hydrogenation process.

2. Experimental

2.1. Material

$Cu(NO_3)_2.3H_2O$ (99.5%), $Mg(NO_3)_2.6H_2O$ (ACS reagent, 99%), K_2CO_3 (ACS reagent, 99.5%) and $Ca(NO_3)_2.4H_2O$ were used as starting materials. All chemicals employed for the synthesis of catalysts were used in analytical grade and supplied from Merck Company. The materials used for the catalytic reactions were furfuraldehyde (98.90%, Merck) and high purity hydrogen (99.99%) and nitrogen (99.99%).

2.2. Catalyst preparation

The parrent Cu-MgO catalyst, which is called CM herein, was prepared with the percentage weight ratio of 16:84 for Cu:MgO through a facile co-precipitation method. In a typical procedure, a mixture of 1 M solution of copper precursor and $Mg(NO_3)_2.6H_2O$ was precipitated at a pH of 9.0 by slow addition of 1 M aqueous solution of K_2CO_3 at room temperature and stirred vigorously for 3 h. The obtained precipitate was filtered and washed several times with distilled water and subsequently dried at 423 K for 12 h. The dried sample was then calcined in air at 723 K for 5 h with a heating rate of 1 K/min. The Ca-Cu-MgO catalysts were synthesized according to a similar procedure as mentioned above except that the elements weight ratio was 8:16:76 and 1:16:83 for Ca(8%)CM and Ca(1%)CM, respectivly. The samples were finally calcined in air at 823 K for 5 h.

2.3. Catalyst characterization

The synthesized catalysts were characterized by using SEM/EDX and XRD techniques. The SEM images were obtained on a Tescan instrument, using Au-coated sample with an acceleration voltage of 20 kV. Powder X-ray diffraction (XRD) studies were carried out with Siemens, D5000 diffractometer using Cu Kα radiation in the range of 25–70° with a step size of 0.02° and an exposure time of 2 s per step. The component distribution and analysis on the surface of the samples were studied by energy dispersive spectrometry (EDS) using scanning electron microscopy (SEM).

2.4. Hydrogenation Tests

Catalytic hydrogenation of furfuraldehyde (FF) was carried out in a tubular reactor of 10 mm internal diameter. First, the catalyst was reduced in hydrogen flow diluted by nitrogen with the total flow rate of ~6 L/(g.h) at 523 K for 3 h. The catalyst was cooled down to the reaction temperature of 453 K in pure hydrogen flow and feedstock was then injected into the reactor with a space velocity (WHSV) of 1.7 1/h. The reactions were performed under atmospheric conditions with an H_2/FF volumetric ratio of 10 for 4h. The products were characterized with an Agilent 6890 GC-MS analyzer equipped with a network mass selective detector (MSD) and an HP-5ms column.

3. Results and Discussion

The BET surface areas of all samples were measured and presented in Table 1. As shown in this table, CM possessed the highest surface area (47.5 (m^2/g)). The surface area of the Ca(1%)CM sample was slightly lower than CM indicating the fact that the presence of Ca as the promotor could reduce the catalyst surface area. A higher loading of the promoter in Ca(8%)CM led to a significant decrease of the surface area to 24.5 (m^2/g). The low catalytic activity of Ca(8%)CM sample can be attributed to the low surface area of this catalyst.

The morphologies of the samples were studied by means of the SEM technique (Fig. 1, (a) CM, (b) Ca(1%)CM, and (c) Ca(8%)CM). The SEM images of CM exhibited a rod-like morphology together with aggregates. As shown in the SEM images of Ca(1%)CM, the addition of a very low amount of Ca changed the morphology of the obtained catalyst significantly and the rod-like morphology would be more pronounced in Ca(1%)CM. Interestingly, the increase in the amount of Ca promoter to 8%, sample Ca(8%)CM, also altered the morphology of the catalyst. In this case, the rod-like morphology disappeared and only the aggregated particulates were detectable. It can be concluded that not only the presence of Ca promoter can result in the morphological changes, but also the amount of promoter has a remarkable impact on the catalyst morphology.

Table 1. Textural properties of the synthesized catalysts.

Sample	CuO crystallite size (nm)	BET surface area (m^2/g)
CM	17.0	47.5
Ca(1%)CM	9.3	43.8
Ca(8%)CM	14.8	24.5

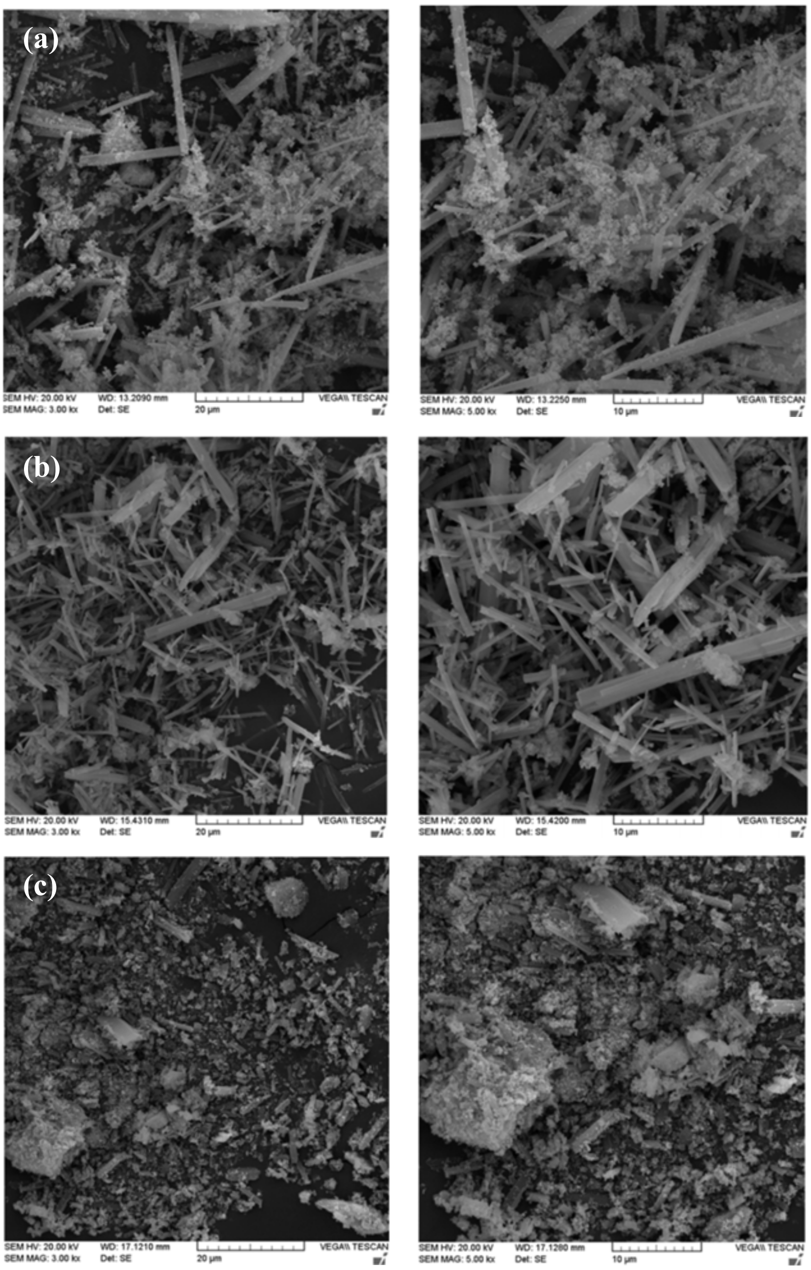

Fig. 1. SEM image of (a) CM, (b) Ca(1%)CM, and (c) Ca(8%)CM catalysts.

The results of EDS analysis for the surface of the catalysts are illustrated in Fig. 2. The presence of the Cu, Mg, Ca, N, and C elements in the EDS analysis of the samples can confirm the formation of Cu-Ca-MgO and Cu-MgO catalysts. Although other analyses such as XRD could not detect the presence of Ca for the Ca(1%)CM sample, the co-existence of calcium could be proved by the EDS technique. Based on the EDS data, it is suggested that all of the components especially the active phases were homogeneously dispersed on the surface.

The XRD patterns of the samples synthesized in the presence of calcium salt proved without contamination of impure phases (Fig. 3). The reflections at 35.5°, 39°, 49°, 53.5°, 58°, 66°, and 68° were ascribed to CuO (JCPDS No. 89-5898) and reflections at 37°, 43° and 62° were ascribed to MgO (JCPDS No. 45-0946) in the diffractogram. However, in XRD pattern which is a technique to determine the formed phases, no diffraction peaks related to the crystalline CaO were found in the XRD patterns of Ca(1%)CM and Ca(8%)CM due to the high dispersion of the metals and the low fraction of the promoter [21].

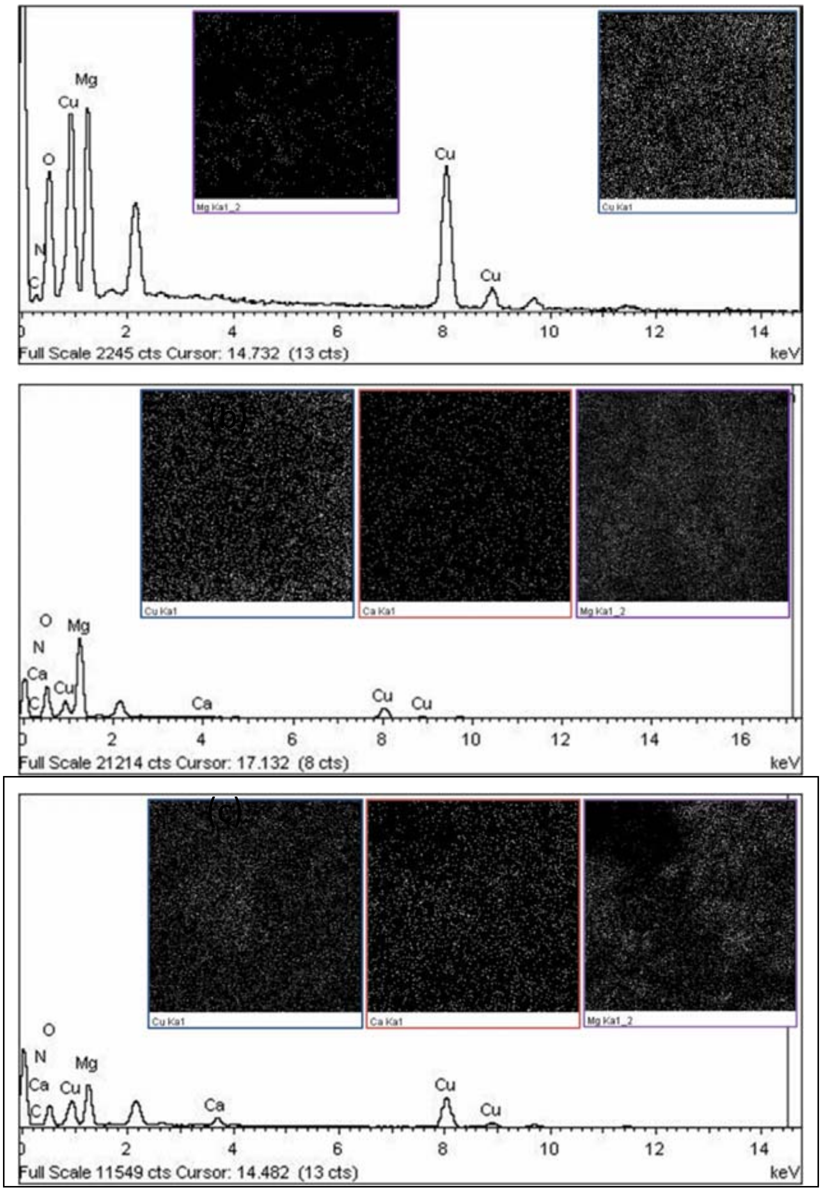

Fig. 2. EDS analysis of (a) CM, (b) Ca(1%)CM, and (c) Ca(8%)CM catalysts.

This high dispersion can arise from the interactions between CuO and the supports or the promoter [22]. On the contrary, only weak $CaCO_3$ signals were detected at the $2\theta = 28°$ (JCPDS No. 47-1743) in the case of Ca(8%)CM sample.

Generally, an average crystallite size could be estimated for Ca(1%)CM, Ca(8%)CM and CM using the Scherrer equation based on the peak at $2\theta = 39°$, which were found to be 9.3, 14.8, and 17 nm, respectively (Table 1). The lowest crystallite size belongs to the Ca(1%)CM sample which showed the best catalytic activity. According to the obtained results, it was found that there was an interaction between magnesium, calcium and copper oxides, which is promoting the dispersion of the three species.

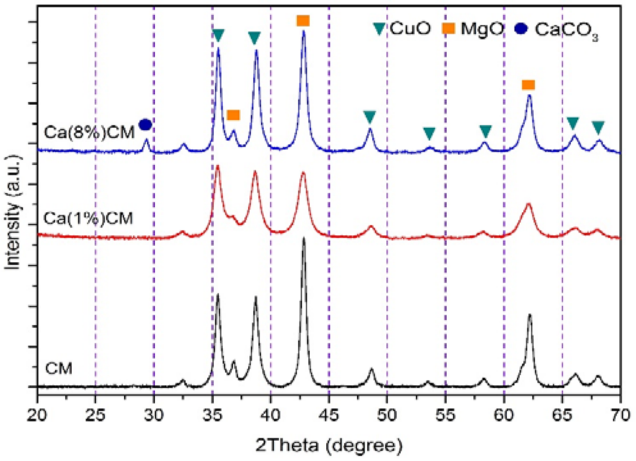

Fig. 3. XRD patterns of the synthesized catalysts.

Considering the analyses, it can be concluded that the incorporation of a small amount of Ca as the promoter could modify the structural properties of the catalyst in a manner that improved the catalytic performance.

In order to investigate the effect of calcium on the catalytic performance of the co-precipitated Cu-MgO catalysts, the catalytic hydrogenation results of CM, Ca(1%)CM, and Ca(8%)CM after 60 min and 240 min of operation were compared in Fig. 4. As it is seen in this figure, upon the incorporation of calcium as a promoter in the CM catalyst, the performance of the catalyst has improved dramatically particularly in terms of furfuraldehyde conversion and yield of furfuryl alcohol, which improved to more than 70% after 60 min and 54% after 240 min TOS being much more than the corresponding negligible amounts on CM. In addition, due to the synergic effect between Cu-MgO catalysts and Ca species, the furfuryl alcohol selectivity was enhanced and maintained above 96% during the 4 h TOS, which is a considerable selectivity compared to that on the non-promoted catalyst (being nearly 55% after this period).

To obtain insight into the calcium loading effect, the results of Ca(1%)CM and Ca(8%)CM were also compared in Fig. 4. Obviously, increasing the amount of calcium which was loaded on CM catalysts up to 8%, initially improved the two performance parameters shown in this figure, but the durability of the catalyst in terms of conversion of furfuraldehyde and selectivity of furfuryl alcohol decreased in comparison to Ca(1%)CM. As it is evident in this figure, the selectivity did not experience any considerable changes after 240 min of operation on Ca(8%)CM.

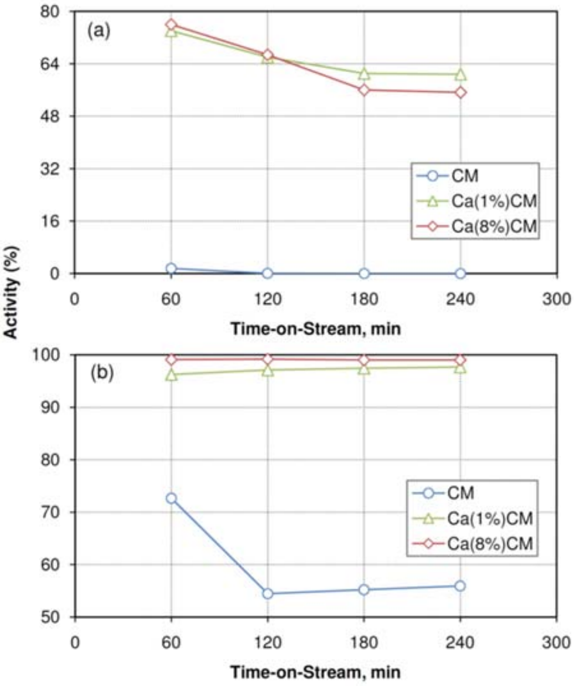

Fig. 4. Comparison of the performance data for the CM, Ca(1%)CM, and Ca(8%)CM catalysts: (a) furfural conversion, and (b) furfuryl alcohol selectivity.

Evidently, the prevailing product of furfuraldehyde hydrogenation over the three copper catalysts was furfuryl alcohol but various byproducts could be formed during the hydrogenation process depending on the nature of the catalyst and the reaction conditions. Fig. 5 depicts the major byproduct of furfuraldehyde hydrogenation over the prepared catalysts. As it is shown in this figure, 5-methyl furfural (MFF) and 2-acetylfuran (AF) were formed in remarkable amounts (on average, 31 and 3 mol%, respectively) during the hydrogenation process over the non-promoted CM catalyst.

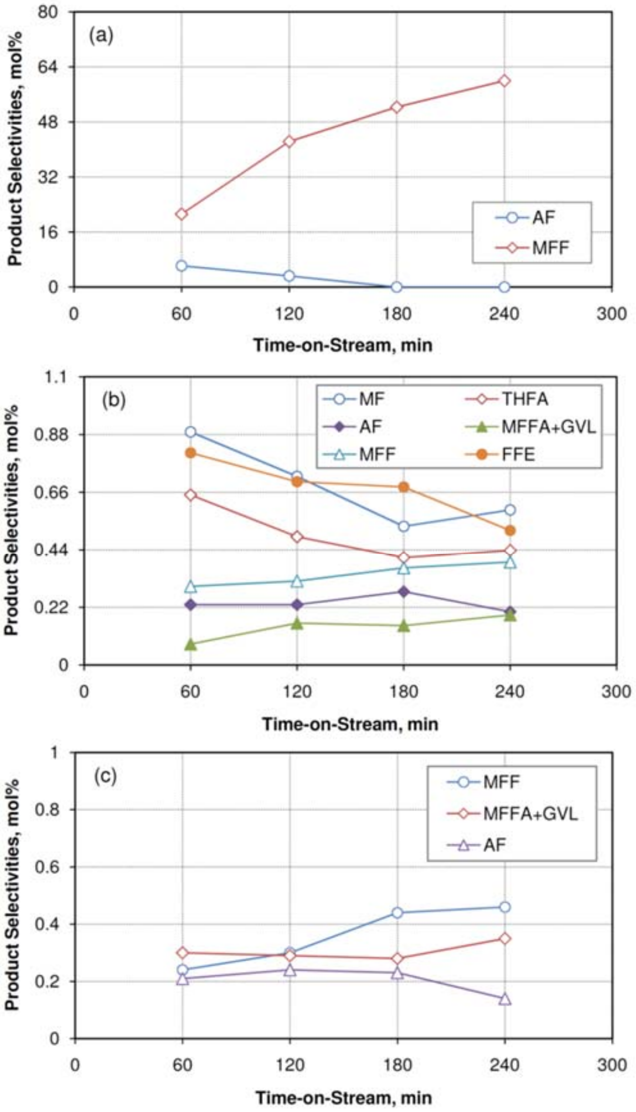

Fig. 5. Byproduct selectivities on (a) CM, (b) Ca(1%)CM, and (c) Ca(8%)CM.

This is absolutely the cause of the low amount of furfuryl alcohol selectivity for the CM catalyst as it was discussed above (see Fig. 4). As a consequence of high furfuryl alcohol selectivity for the calcium-promoted catalysts, the byproducts were produced in trace amounts (see Fig. 5). The major byproducts for Ca(1%)CM included furfuryl ether (FFE), 2-methfuran (MF), tetrahydrofurfuryl alcohol (THFA), and 5-methylfurfural (MFF). However, the catalysts produced also AF, methylfurfuryl alcohol (MFFA) and γ-valerolactone (GVL) in low amounts (see Fig. 5). The diversity of byproducts for Ca(8%)CM catalyst was less than Ca(1%)CM, so that the main byproducts of this catalyst were MFF, MFFA, GVL and AF with average selectivities lower than 0.4%.

The results demonstrate that the introduction of Ca as a promoter can improve the stability and performance of the catalyst. This observation is in accordance with the previous reports in which Ca was known as a basic metal usually applied for improving the stability of the obtained catalyst [22]. It is also known that the catalyst with multi-metal ion interaction exhibits synergistic effects by enhancing the basicity on the active site of the catalyst [23]. However, the amount of this promoter has a crucial role in the catalyst stability and the use of a high amount of promoter has a detrimental effect on the catalyst stability. Considering the structural properties of the catalysts, it is suggested that the addition of 1% of the Ca promoter can improve the dispersion of the active phase and, consequently, enhance the catalytic activity. However, the addition of more Ca (8%) resulted in a poorer dispersion of the catalytic species which emerged from the more aggregated morphology of the catalyst.

As a final note, the catalystic results of the Cu-Ca-MgO catalyst were compared against those of copper chromite as the well-known commercial catalyst for the vapor-phase hydrogenation of furfuraldehyde (Table 2). As it is obvious, the synthesized catalyst has shown a clearly higher performance at a much lower H_2/FF ratio. Contrary to the copper chromite catalyst, the Cu-Ca-MgO catalyst suggested in this work is free from Cr and, hence, it is eco-friendly. Moreover, the catalyst prepared in this work possessed a better durability in comparison with the commercial copper chromite catalyst which lost more than half of its activity after ~4 h of operation.

4. Conclusion

The results discussed here showed that incorporating calcium as a promoter into the Cu-MgO catalysts prepared via co-precipitation could enhance all three performance parameters of the catalyst in the hydrogenation of furfuraldehyde (i.e., furfuraldehyde conversion, selectivity, and yield of furfuryl alcohol). In addition, it was found that increasing the molar ratio of calcium in the synthesis gel from 1% to 8% improved the performance characteristics of the catalyst only slightly while also reducing the durability of the catalyst in the hydrogenation of furfuraldehyde.

References

[1] H.E. Hoydonckx, W.M. Van Rhijn, W. Van Rhijn, D.E. De Vos, P.A. Jacobs, Furfural and Derivatives, In: Ullmann's Encyclopedia of Industrial Chemistry, Wiley Online Library, 2007.

[2] S. Sitthisa, T. Sooknoi, Y. Ma, P.B. Balbuena, D.E. Resasco, J. Catal. 277 (2011) 1–13.

Table 2. Comparison of the activities of selected copper catalysts for the selective hydrogenation of furfuraldehyde to furfuryl alcohol.

Catalyst	Temp. (°C)	H_2/FF	Conversion (%)	Selectivity (%)	Yield (%)	Stability	Ref.
Commercial Copper Chromite (Cu-1800P)	200	25	22	91.2	20	Poor	[24]
Commercial Copper Chromite	200	25	98.2	18	17.7	Poor	[6]
Commercial Copper Chromite (Cu-1800P)	140	72	Specific activity: 0.26 μmol/(m^2.s)	70	—	—	[17]
Commercial Copper Chromite (Cu-1800P)	180	—	46	65	30	—	[12]
Ca (1%)CM	180	10	60.8	97.7	59.8	Very Good	This work

[3] D. Vargas-Hernández, J.M. Rubio-Caballero, J. Santamaría-González, R. Moreno-Tost, J.M. Mérida-Robles, M.A. Pérez-Cruz, A. Jiménez-López, R. Hernández-Huesca, P. Maireles-Torres, J. Mol. Catal. A: Chem. 383–384 (2014) 106–113.

[4] K. Yan, J. Liao, X. Wu, X. Xie, RSC Adv. 3 (2013) 3853–3856.

[5] R. Mariscal, P. Maireles-Torres, M. Ojeda, I. Sadaba, M. Lopez Granados, Energ. Environ. Sci. 9 (2016) 1144–1189.

[6] H. Zhang, C. Canlas, A.J. Kropf, J.W. Elam, J.A. Dumesic, C.L. Marshall, J. Catal. 326 (2015) 172–181.

[7] B.M. Reddy, G.K. Reddy, K.N. Rao, A. Khan, I. Ganesh, J. Mol. Catal. A: Chem. 265 (2007) 276–282.

[8] B.M. Nagaraja, A.H. Padmasri, B. David Raju, K.S. Rama Rao, J. Mol. Catal. A: Chem. 265 (2007) 90–97.

[9] R.S. Rao, R.T.K. Baker, M.A. Vannice, Catal. Lett. 60 (1999) 51–57.

[10] B.M. Nagaraja, V.S. Kumar, V. Shasikala, A.H. Padmasri, B. Sreedhar, B.D. Raju, K.S. Rao, Catal. Commun. 4 (2003) 287–293.

[11] M. Li, Y. Hao, F. Cárdenas-Lizana, M.A. Keane, Catal. Commun. 69 (2015) 119–122.

[12] B.M. Nagaraja, H.P. Aytam, S. Podila, K.H.P. Reddy, B.D. Raju, S.R.R. Kamaraju, J. Mol. Catal. A: Chem. 278 (2007) 29–37.

[13] L. Baijun, L. Lianhai, W. Bingchun, C. Tianxi, K. Iwatani, Appl. Catal. A 171 (1998) 117–122.

[14] S.-P. Lee, Y.-W. Chen, Ind. Eng. Chem. Res. 38 (1999) 2548–2556.

[15] H. Luo, H. Li, L. Zhuang, Chem. Lett. 5 (2001) 404–405.

[16] J. Kijeński, P. Winiarek, T. Paryjczak, A. Lewicki, A. Mikołajska, Appl. Catal. A 233 (2002) 171–182.

[17] R. Rao, A. Dandekar, R.T.K. Baker, M.A. Vannice, J. Catal. 171 (1997) 406–419.

[18] M.J. Burk, T.G.P. Harper, J.R. Lee, C. Kalberg, Tetrahedron Lett. 35 (1994) 4963–4966.

[19] B.M. Nagaraja, V. Siva Kumar, V. Shashikala, A.H. Padmasri, S. Sreevardhan Reddy, B. David Raju, K.S. Rama Rao, J. Mol. Catal. A: Chem. 223 (2004) 339–345.

[20] B.M. Nagaraja, A.H. Padmasri, B.D. Raju, K.S. Rama Rao, Int. J. Hydrogen Energ. 36 (2011) 3417–3425.

[21] S. Mallik, S.S. Dash, K.M. Parida, B.K. Mohapatra, J. Colloid Interf. Sci. 300 (2006) 237–243.

[22] J. Wu, Y. Shena, C. Liu, H. Wang, C. Geng, Z. Zhang, Catal. Commun. 6 (2005) 633–637.

[23] H.V. Lee, J.C. Juan, N.F. Binti Abdullah, R. Nizah MF, Y.H. Taufiq-Yap, Chem. Cent. J. 8 (2014) 30.

[24] D. Liu, D. Zemlyanov, T. Wu, R.J. Lobo-Lapidus, J.A. Dumesic, J.T. Miller, C.L. Marshall, J. Catal. 299 (2013) 336–345.