Liquid phase hydrogenation of furfural using 2-propanol over ZrO_2

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Abstract. Hydrogenation of furfural is carried out efficiently by ZrO_2 using 2-propanol as a hydrogen source in liquid phase. Various characterizations like XRD, Pyridine-FTIR, NH_3 -TPD (acidity), CO_2 -TPD (basic property), and N_2 physisorption study for surface area analysis were used to understand the properties and to correlate with the activity results. These results revealed that zirconia calcined at low temperature (573 K) possesses amorphous phase, high surface area and large number of acid-base sites which are helpful in achieving higher activity.

Keywords. Furfural; ZrO_2 ; furfuryl alcohol; 2-propanol.

1. Introduction

Biomass conversion strategies are advancing in the present catalytic research as they are presently the main substitute to fossil resources for chemicals and fuels. In the transformation of biomass, a significant role is played by furan derivatives.^{1–3} For example, furfural (FF) obtained from hemicellulose is an essential platform molecule as it can be easily upgraded to a number of products such as furfuryl alcohol (FFA), furan derivatives, THF, etc.^{4–6} FFA is widely used in the chemical industry, mainly for the production of foundry resins, synthetic fibers, farm chemicals, adhesives, and fine chemicals.^{7,8} Furfural hydrogenation in the industry is mainly carried out by Cu-Cr catalyst modified by various promoters.⁹ But Cr is highly toxic and thus calls for eco-friendly catalysts. At present, noble, non-noble and bimetallic metals supported catalysts^{7,10–14} are being used which can selectively hydrogenate carbonyl group in liquid phase hydrogenation. However, metal-free catalysts for these reactions are sparsely seen. On the other hand, a step forward in this hydrogenation reaction is the catalytic transfer hydrogenation (CTH) wherein

hydrogen obtained from donor molecule (usually alcohols) is used.^{15,16} A lot of metal oxides have been used for CTH reaction *via* Meerwein–Ponndorf–Verley (MPV) reaction.^{17–21} It is reported that acidic and basic sites play an important role in the MPV reaction. In this regard, Zirconium oxide is an amphoteric oxide with low cost and can be a potential candidate for this type of reactions as it is known for its CTH reactions.²² Several reports are available for CTH hydrogenation over ZrO_2 but none have shown to perform liquid phase study on this reaction to the best of our knowledge.^{23–25} Surface properties of zirconia have been thoroughly studied by different authors, and it has been reported that surface hydroxyl groups act as weak basic sites and the role of base sites has been proposed to help the formation of alkoxide species with acid sites by the deprotonation of alcohol molecules.^{26,27} The present work reported here exploited these properties of ZrO_2 which was calcined at different temperatures and tested for the conversion of FF to FFA *via* CTH with 2-propanol acting as solvent and as hydrogen donor in liquid phase conditions at atmospheric pressure.

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2. Experimental

2.1 Preparations of catalysts

Zirconia was prepared by a precipitation method using their chloride salt precursors. Required amount of $\text{ZrOCl}_2 \cdot 8\text{H}_2\text{O}$ (M/s. SD Fine chemicals, India, Purity- 98%) was dissolved in de-ionized water and precipitated with 5% NH_4OH (M/s. SD Fine chemicals, India) solution. Completion of precipitation has been confirmed by adding few drops of NH_4OH to the supernatant liquid. The resultant slurry was then aged for 24 h at room temperature. Later, the precipitate was filtered and washed several times with de-ionized water to remove chlorides completely (using AgNO_3 (M/s. SD Fine chemicals, Purity- 99%) test). Further, the solid mass was kept for drying at 393 K overnight, and then calcined at 573 K, 773 K and 973 K for 5 h taking separate amounts from the uncalcined mass. The prepared catalysts were designated as Z-573, Z-773 and Z-973, respectively.

2.2 Activity measurements

The catalytic transfer hydrogenation of furfural with 2-propanol was performed at atmospheric pressure in a 25 mL round bottom flask equipped with a reflux condenser. In a typical experiment, 0.2 g of catalyst, 10 mL of a mixture of FF: 2-propanol in molar ratio of 1:8 was added to the round bottom flask. The mixture was stirred at 383 K for 6 h. The obtained products were first confirmed by GCMS (QP-5050 (M/s. Shimadzu instruments, Japan) and quantified by a flame ionization detector (FID) equipped gas chromatography, GC-17A (M/s. Shimadzu Instruments, Japan) using with EB-5 MS capillary column (30 m $\times$ 0.25 mm $\times$ 0.25 m).

2.3 Catalyst characterization

Powder X-ray diffraction patterns of the catalysts were recorded on X-ray diffractometer (Ultima-IV, M/s. Rigaku Corporation, Japan) with $\text{Cu K}\alpha$ radiation. The BET surface area, pore volume and pore size were determined by N_2 sorption studies (M/s. Quantachrome Instruments, USA). Samples were degassed at 423 K for 2 h prior to N_2 adsorption at liquid N_2 temperature. The acidic and basic strength of the catalysts were analyzed by temperature programmed desorption of NH_3 and CO_2 , respectively on an AUTOSORB-iQ automated gas sorption analyser (M/s. Quantachrome Instruments, USA). In a typical desorption experiment, 50 mg of catalyst sample was placed in a quartz reactor and preheated in He flow (30 mL min^{-1}) at 573 K for 2 h. Later, the catalyst was saturated with 10% CO_2/He at 353 K for 0.5 h, followed by desorption in He for 0.5 h to remove any physisorbed CO_2 at the same temperature. Then, the temperature was raised to 950 K at a rate of 10 K min^{-1} in the presence of He (60 mL min^{-1}) and the desorbed CO_2 was monitored with the inbuilt thermal conductivity detector (TCD). NH_3 -TPD experiment was also performed by using a similar procedure mentioned above except that the probe gas is 10% NH_3/He

Figure 1. XRD pattern of, (a) Z-573; (b) Z-773; (c) Z-973; and (d) Regenerated catalyst.

mixture. Amount of carbonaceous species was obtained by CHNS analysis on VARIO MICRO CUBE (M/s. Elementar Analysen systeme GmbH, Germany). The sample weighed in milligrams housed in a tin capsule is dropped into a quartz tube kept at 1293 K temperature with constant He flow. The pyridine adsorption studies were carried out in the diffuse reflectance infrared Fourier transform (DRIFT) mode. In a typical experiment the catalyst was degassed under vacuum at 473 K for 3 h followed by suspending dry pyridine. Then, the excess pyridine was removed by heating the sample at 393 K for 1 h. After cooling the sample to room temperature in N_2 flow, FTIR spectra of the pyridine-adsorbed samples were recorded. FTIR spectra were recorded on a GX spectrometer (M/s. PerkinElmer, Germany) in a scan range of 4000–400 cm^{-1} with a resolution of 4 cm^{-1} , and averaging 20 scans per spectrum. The samples were finely ground in the ratio 1: 10 (sample: KBr) and pelletized to obtain a wafer which was used to record the FT- IR spectra.

3. Results and Discussion

3.1 X-ray diffraction analysis and physico-chemical properties

A series of characterization techniques were used to understand the physico-chemical properties of ZrO_2 calcined at different temperatures. XRD patterns of ZrO_2 catalysts are given in Figure 1. It can be seen that Z-573 is mostly amorphous phase. When the calcination temperature was increased to 773 K, we observed the presence of both monoclinic and tetragonal phases. However, monoclinic phase was observed in major

amount (Table 1). Further increase in the calcination temperature (973 K), resulted only in monoclinic phase of ZrO₂ with 2θ values at 24.4, 28.1, 31.4, 35, 40.6, 50.1 and 60° (PCPDF No-861415).

The phase composition in the catalysts was calculated from the following equations proposed by Toraya.²⁸

$$X_m(\%) = [I_m(111) + I_m(-111)/I_m(111) + I_m(-111) + I_t(101)] \times 100 \quad (1)$$

$$X_t(\%) = 7[I_t(101)/I_m(111) + I_m(-111) + I_t(101)] \times 100 \quad (2)$$

Here, $I_m(111)$ and $I_m(-111)$ are the intensities of monoclinic zirconia phase (at 2θ of 28.2° and 31.1°) and $I_t(101)$ is the intensities of tetragonal zirconia phase (at 2θ 30.1°).

BET surface area, N₂ sorption details of the catalysts are presented in Table 1. A similar trend is found in the N₂ sorption isotherms of all the samples (Figure 2) with type IV isotherm and H2 type hysteresis loop which indicates mesoporous structure.²⁹ Z-573 has high surface area and pore volume compared to Z-773 and Z-973 (values shown in Table 1). Increase in calcination temperature enhanced the pore diameter from 4.9 nm in Z-573 to 7.4 nm in Z-973 (calculated by NLDFT method, Figure 2, inset).²⁹ High temperatures aid the growth and perfection of ZrO₂ crystals, which resulted in the increase of the particle sizes and the decrease of the surface area and pore volume.

3.2 Temperature programmed desorption of carbon dioxide

CO₂-TPD profiles of the catalysts were displayed in Figure 3. The desorption peak was observed in similar temperature region in all the catalysts which indicate the presence of only weak basic sites. However, the area under the peak decreased significantly as the calcination temperature increased (Table 1). This is because of the sintering of the particles which destroys the basic sites (surface -OH groups). A similar decreasing trend of CO₂ desorption amount with increasing calcination temperature of ZrO₂ was reported.³⁰

3.3 Temperature programmed desorption of ammonia

The acidic strength is classified as weak (<400 K), medium (400–700 K), and strong (>700 K) acidic sites.³¹ In the NH₃-TPD patterns (Figure 4) desorption peak at 440 K and a broad desorption peak at 635 K, which can be assigned to weak and medium acidic sites, respectively, was detected in the Z-573 catalyst. A broad peak observed in Z-773 at 690 K can be attributed to the

Table 1. Physico-chemical properties of various samples.

Catalysts	Phase composition (%) ^a	Crystallite size (nm) ^b	S _{BET} (m ² /g) ^c	Basicity (m mol/g) ^d	Acidity (mmol/g) ^e	V _t (cc/g)	D ^g (nm)
Z-573	Amorphous	Amorphous	210	0.285	0.228	0.50	4.9
Z-773	71 (m), 29 (t)	11.6 (m), 17 (t)	80	0.103	0.188	0.38	6
Z-973	100 (m)	21.55 (m)	30	0.072	0.105	0.15	7.4
Z-573-R ^f	Amorphous	Amorphous	170	—	—	—	—

^aPhase composition obtained from equations 1 and 2, m - monoclinic phase; t - tetragonal phase, ^bDetermined from Scherrer equation, ^cBET surface area determined from N₂ sorption, ^dDetermined from CO₂ TPD areas, ^eDetermined from NH₃-TPD peak areas, ^fTotal pore volume, ^gAverage pore size, ^hRegenerated catalyst.

Figure 2. N_2 sorption isotherms of, (a) Z-573; (b) Z-773; (c) Z-973 and pore size distribution (inset figure).

Figure 3. CO_2 TPD of (a) Z-573; (b) Z-773; (c) Z-973.

medium acidic sites. Z-973 catalyst displays desorption peak at 540 K, which can be ascribed to medium acidic sites. As can be seen from Figures 3 and 4, higher amount of acidic and basic sites were observed over Z-573 catalyst compared to other catalysts. At higher calcination temperatures, agglomeration of ZrO_2 particles caused lower specific surface areas in the catalysts Z-773 and Z-973 leading to possess fewer numbers of acid and base sites. The trend in the acidic and basic site strengths of these catalysts in the present study is in line with the literature.³⁰

Figure 4. NH_3 -TPD profiles of (a) Z-573; (b) Z-773; (c) Z-973.

3.4 FTIR Analysis

The FTIR spectra of ZrO_2 catalysts are shown in Figure 5. The broad band in the region of $3500\text{--}3600\text{ cm}^{-1}$ is due to the stretching vibration of the hydroxyl groups. The band at 1625 cm^{-1} can be assigned to the coordinated the water molecule. The peak centered at around 1365 and 1125 cm^{-1} can be attributed to the bending vibration of $Zr\text{-OH}$ groups.^{32,33} It is evident that in all the catalysts OH groups are present on the surface. However, the intensity of all these bands decreased as the sample was heated to higher temperatures.

3.4a Pyridine-FTIR: The type of acidity on the surface of catalyst was analyzed by FTIR using Pyridine as a probe molecule (Figure 6). The pyridine-adsorbed DRIFT spectra showed characteristic peaks in the range $1700\text{--}1350\text{ cm}^{-1}$. The bands at around 1440 cm^{-1} and 1585 cm^{-1} indicated the presence of pyridine bound to Lewis acid sites and the peak appeared at 1640 cm^{-1} is assigned to the pyridine interacted with Bronsted acid sites.^{31,34} It can be observed that, increasing the calcination temperature decreased the intensity of surface Bronsted acidic site peak. It is noteworthy that the Bronsted acidity observed in Pyridine-FTIR patterns is not seen in NH_3 -TPD profiles. We suspect that the catalyst has weak bronsted acidity. Because of this reason, we did not observe any peak at high temperature in NH_3 -TPD profiles, but seen in Pyridine FTIR as it was recorded at room temperature.

Figure 5. FTIR spectra of (a) Z-573 (b) Z-773 (c) Z-973.

Figure 6. Pyridine-FTIR spectra of the catalysts. (a) Z-573; (b) Z-773; (c) Z-973. (B- Bronsted acid sites, L- Lewis acid sites).

3.5 Activity studies

3.5a Effect of ZrO_2 calcination temperature: Zirconia calcined at different temperatures has been tested for conversion of FF to FFA at 383 K with 2-propanol and the results are shown in Table 2.

It can be seen that the conversion of furfural decreased significantly with increase in calcination temperature. Increase in calcination temperature decreased the surface area, number of surface hydroxyl groups which resulted in decrease in density of acidic-basic sites of the

catalysts in which surface hydroxyl groups are important in the MPV reaction. Chuah *et al.*,²⁶ proposed that in the MPV reaction of cinnamaldehyde on hydrous zirconia, Zr-OH groups (weak Bronsted acid sites) act as activation centers for ligand exchange with 2-propanol on the catalyst. From the Figure 4, it is clear that calcination temperature has a significant effect on the amount of acid-base sites present in ZrO_2 . These results indicate that the catalytic activity depends on Zr-OH groups.

3.5b Effect of reaction time: The effect of reaction time on the conversion of FF to FFA over Z-573 catalyst was studied and the results are shown in Table 3.

As shown from the Table 3, FF was completely converted into FFA by 360 min and no by-products were observed in transfer hydrogenation at longer reaction times. The by-products at the lower reaction times are dimerized products of furfuryl alcohol and aldol condensation products of acetone and furfural. These products are not observed at longer reaction times because of the fact that aldol condensation is reversible. A preliminary kinetic analysis shows that the reaction is zero order with respect to furfural and the rate constant is 3×10^{-5} M/s at 383 K (Figure S4, supplementary information).

3.5c Effect of reaction temperature: The effect of temperature on FF to FFA was examined in the range of 343–403 K over Z-573 and the results are presented in Figure 7. A significant change in the conversion is observed, as expected, when the reaction temperature increased from 343 to 383 K and levels off thereafter and a modest change is observed in the selectivity.

3.5d Effect of 2-propanol molar ratio: The influence of different molar ratio between FF and 2-propanol (4–10), on the activity was studied over Z-573 catalyst and results are depicted in the Figure 8. With increasing 2-propanol molar ratio from 4 to 6, FF conversion increased from 82% to 95% and selectivities are 80 and 92%. At lower ratio FF readily undergoes polymerization to form oligomeric products.³⁵ To avoid such polymerization, a higher amount of 2-propanol was needed. Further increasing the molar ratio of 2-propanol complete conversion and selectivity are obtained. At higher molar ratio (10), there is no considerable change in conversion and selectivity which suggests that the optimal ratio is 1:8.

3.5e Effect of catalyst amount: The effect of catalyst amount on the conversion of FF to FFA over Z-573 catalyst was studied for different amounts of catalyst loading from 0.05 to 0.3 g and the results are shown in Figure 9. FF conversion decreased from 80% to 65%

Table 2. Catalytic transfer hydrogenation of Furfural into FFA catalyzed by Zirconia at different calcination temperatures.

Catalyst	Conversion (%) of FF	Selectivity (%) to FFA
Z-573	> 99	100
Z-773	70	> 99
Z-973	60	> 99

Reaction conditions: catalyst amount = 0.2 g, FF: 2-propanol molar ratio = 1:8, temperature = 383 K, time = 6 h.

Table 3. Effect of reaction time: Reaction conditions: catalyst amount = 0.2 g, FF: 2-propanol = 1:8 (mol/mol), temperature = 383 K.

Catalyst	Run no.	Temperature (K)	Time (min)	FF conversion (%)	Selectivity (%)	
					FFA	By products
Z-573	1	383	60	43	71	28
	2	383	120	56	79	20.7
	3	383	180	63	83	16.4
	4	383	240	78	87	13
	5	383	300	90	91	8.7
	6	383	360	100	> 99	–

Figure 7. Effect of temperature on catalytic transfer hydrogenation of Furfural. Reaction conditions: catalyst amount = 0.2 g, FF: 2-propanol = 1:8 (mol/mol), time = 5 h.

with decrease in catalyst loading from 0.1 to 0.05 g, obviously due to insufficient active sites. When catalyst loading was increased to 0.2 g, we observed almost complete conversion of FF and selectivity to FFA.

3.5f Catalyst recyclability: The recyclability of the Z-573 catalyst was examined in the transfer

Figure 8. Effect of 2-propanol molar ratio on catalytic transfer hydrogenation of Furfural. Reaction conditions: catalyst amount = 0.2 g, temperature = 383 K, time = 5 h.

hydrogenation of FF under the optimized conditions and the results are displayed in Figure 10. After the catalytic reaction, the catalyst was recovered by centrifugation, then thoroughly washed with methanol and dried at 373 K for 3 h before using in the next catalytic

Figure 9. Effect of catalyst amount on catalytic transfer hydrogenation of Furfural. Reaction conditions: FF: 2-propanol = 1:8 (mol/mol), temperature = 383 K, time = 5 h.

Figure 10. Catalyst recyclability in catalytic transfer hydrogenation of Furfural. Reaction conditions: catalyst amount = 0.2 g, FF: 2-propanol = 1:8 (mol/mol), temperature = 383 K, time = 5 h.

run. As can be seen from Figure 10, there is no change in conversion of FF for at least four repeated cycles, while no significant loss of selectivity to FFA was observed. The stability of the catalyst was also proved by XRD patterns of fresh and reused catalysts. XRD patterns of

fresh and reused catalysts (after 4th cycle) were found to be identical (Figure 1(d)). On the other hand, BET surface area decrease from 210 to 170 m²g⁻¹ was observed after use, which can be assigned to pore blockage by the residual reactants or products, which may be responsible for the decrease in the catalytic activity in further cycles.

4. Conclusions

In this work, we present an efficient method for the production of furfuryl alcohol from catalytic transfer hydrogenation of furfural *via* MPV reduction, with 2-propanol acting as solvent and as hydrogen donor over ZrO₂ calcined at lower temperature (573 K) with complete conversion and selectivity at 383 K. The Z-573 catalyst can be reused for up to four cycles, with only a small drop in selectivity to FFA due to decline in the surface area of the catalyst. Higher calcination temperatures resulted in a decrease in the amount of acid-base sites which effected negatively in the catalytic reaction.

Supplementary Information (SI)

Separately, gas phase experiments were also performed and included in the supplementary information along with preliminary kinetics analysis graph (Figure S4). Supplementary Information is available at www.ias.ac.in/chemsci.

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