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Investigation of Structural and Catalytic Performance of Nano Crystalline Yttria Dopped Zirconia

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Nanocrystalline yttria doped zirconia (YZ) were prepared by sol-gel method and characterized by XRD, SEM, EDX, TGA and XPS techniques. The XRD results indicated the formation highly crystalline material with 2 to 4 nm in size. The tetragonal phase of the nanoparticles was confirmed by XRD analysis. Small amount of this catalysts was efficiently catalyzed acetylation of benzyl alcohol with acetic anhydride in short time under solvent free conditions. The 5 wt.% YZ gave best results at 120 ºC with 100% conversion of benzyl alcohol with 100% selectivity of the product. Different parameters were studied for optimization of acetylation, which proved the catalysts has excellent activity and can be used at large scale applications in industry.

Keywords: Mixed metal oxide, Sol gel, Acetylation reaction, Yttria, Zirconia, Green chemistry.

INTRODUCTION

Acetylation is one of the useful reactions in the synthesis of biologically active compounds as well as pharmaceutical products. In organic synthesis acetyl groups can be used for protection of many functional groups, which includes alcohols, amines, phenols and so on. [1]. To carry out acetylation, acid anhydrides and acyl halides were found in literature along with homogeneous and heterogeneous catalysts. Some synthetic procedures have been developed where a range of homogeneous catalysts such as $RuCl_3$ [2], $CeCl_3$ [3], $ZrCl_4$ [4], $La(NO_3)\cdot 6H_2O$ [5], $Al(OTf)_3$ [6], AgOTf [7], Co(II) salen complex [8], $NiCl_2$ [9], $CoCl_2$ [10], $Mg(NTf_2)_2$ [11], $H3[P(Mo_3O_{10})_4]\cdot nH_2O$ [12]. There has been also reported ionic liquids [13], ZnO [14,15], CuO-ZnO [16], nano-Fe_2O_3 [17], Fe_3O_4@PDA-SO_3H [18], polymer-supported $Gd(OTf)_3$ [19], silica-sulfonic acid [20], borated zirconia [21], $ZnAl_2O_4$ [22], P_2O_5/Al_2O_3 [23], as heterogeneous catalysts by different researchers. These reported reactions shown their respective advantages with few draw backs. Few researchers have been reported acetylation reactions under solvent and catalyst free conditions at moderate reaction temperature but with more reaction time.

Nanocrystalline mixed metal oxides are effective alternatives to conventional heterogeneous catalysts and it can be easily prepared from available and low-cost materials. This type of mixed oxides has shown advantages like higher acidity, reduced reaction time, higher selectivity with no formation of byproduct, easy workup, recyclability and also provide green reaction conditions. The sulfated yattria-zirconia catalyst used for the acylation of alcohols, amines and thiols and the acetylated products were resulted after longer reaction time with moderate yield [24].

Generally, ZrO_2 shows three different phases, such as monoclinic, tetragonal and cubic phase. Therefore, to stabilize the tetragonal phase at room temperature, yttrium is used as a dopant for ZrO_2. Furthermore, the tetragonal phase has strongly improved catalytic activity compared to cubic and monoclinic phase of ZrO_2 [25]. Herein, special efforts are investigated to meet the requirement for more efficient and selective methods. Hence, present work aims to provide an alternative and simple method to the previously reported procedures by developing an effective nanocrystalline mixed oxide yttria doped zirconia (YZ). Zirconia was doped with 1, 2, 3, 4 and 5 wt.% of yttria by sol-gel method. Under solvent free conditions, this method provided complete conversion of substrates with 100% selectivity of the desired products under reflux condition. Further reported about characterization of the catalyst by using techniques such as XRD, SEM, EDX, TGA and XPS studies.

EXPERIMENTAL

All the reagent *viz.* yttrium nitrate, zirconium but oxide, acetic anhydride, benzyl alcohol, diethyl ether and isopropyl alcohol used were of A.R. grade, and obtained from Merck chemicals, India.

The synthesized catalysts were prepared by the sol-gel method and characterized by various spectroscopic and non-spectroscopic methods including X-ray diffraction (XRD), using Rigaku, Miniflex G-600 diffractometer with 2θ range from 10° to 80° and step width 0.01°. The crystalline size of the synthesized yttria doped on zirconia (YZ) nanocomposite were examined by XRD. Thermogravimetric analysis (TGA) was performed on Perkin-Elmer TGA7 under nitrogen between 25 to 850 ºC at a constant heating rate of 10 ºC/min. Scanning electron microscope coupled with EDX (a Philips XL-30 machine JEOL-JSM 6360A) was used for external surface of hybrid material. SEM and energy dispersive X-ray analysis detector (EDX) were got at accelerating voltage 20 keV. Sample were deposited on a sample holder with an adhesive carbon foil and sputtered with gold. The SEM images were obtained using a scanning electron microscope FEI. X-ray photoelectron spectroscopy (XPS) studies were carried out on a VSW scientific instrument using incident source with an energy of 1253 eV and a resolution of 0.9 eV vacuum of 10^{-8} torr was maintained in the sample analyzer chamber.

Preparation of Y_2O_3/ZrO_2 mixed metal oxide using sol-gel method: Yttria doped zirconia (YZ) were prepared with different wt.% of yttrium oxide concentration (1, 2, 3, 4, 5 wt.%) in a model procedure [26]. The 5 wt.% YZ catalyst was prepared by dissolving equimolar quantity of yttrium nitrate in 10 mL distilled water and zirconium butoxide in 20 mL IPA, which was sonicated for 30 min. The prepared aqueous solution of yttrium nitrate was added drop wise to zirconium butoxide solution with constant stirring. To the above mixture 3 wt.% dilute ammonia solution was added with continuous stirring. The resultant transparent gel was achieved, further dried overnight at room temperature and then heated in oven at 100 ºC for 10 h. Dried catalyst was calcined at 500 ºC for 4 h. Similarly, catalysts with 1, 2, 3 and 4 wt.% YZ were also prepared.

RESULTS AND DISCUSSION

XRD analysis: The structural properties of the synthesized various amount of yttria doped zirconia nanocomposites were investigated by X-ray diffraction studies over the 2θ values in the range of 10-80° (Fig. 1). For all YZ nanocomposites, the diffraction peak of 30.20°, 34.96°, 50.30°, 59.73°, 62.63° and 73.80° can be index to 111, 200, 220, 311, 222 and 400 planes, which confirmed the presence of yttrium zirconium oxide ($Y_{0.15}Zr_{0.85}O_{1.93}$). All peaks obtained by XRD analysis were assigned by comparison with data from the JCPDS card No. 01-084-2544). All the spectra of 1, 2, 3, 4 and 5 wt.% showed highly crystalline nature of the sample. The crystallite size obtained between 2 to 4 nm, calculated from the Debye Scherrer's equation:

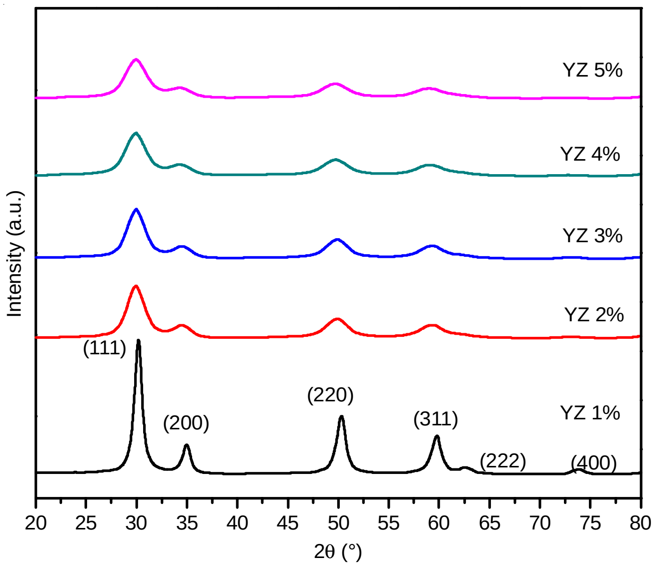


Fig. 1. X-ray diffraction pattern of YZ mixed oxides calcined at 500 °C

$$D = \frac{0.9\lambda}{\beta\cos\theta}$$

where D is the crystal size, λ is the wavelength of X-ray, θ is the Braggs angle in radians and β is the full width at half maximum of the peak in radians. As per the literature, tetragonal zirconia is indexed with all the diffraction peaks. Yttria dopped zirconia diffraction pattern could be attributed to the tetragonal phases [27]. As the amount of yttria was increased, the peaks slightly broadened.

EDX-SEM: The chemical composition of resulting Y_2O_3/ZrO_2 composite has been analyzed by EDX (Fig. 2). In this pattern, Yt, O and Zr peaks were clearly seen, which confirmed the purity and content of the synthesized sample clearly. The Yt:Zr ratio obtained from the EDX analysis agreed well with the original used for the synthesis.

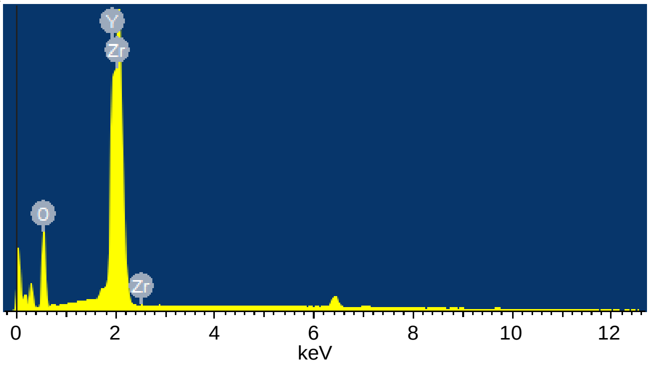


Fig. 2. EDX spectrum of representative samples of 4 wt.% YZ

The surface morphology of Y_2O_3/ZrO_2 nanocomposites were investigated by SEM microscopy. Fig. 3 showed the SEM images of yttria doped zirconia nanocomposites are spherically shaped with uniform distribution of yttria on zirconia. In

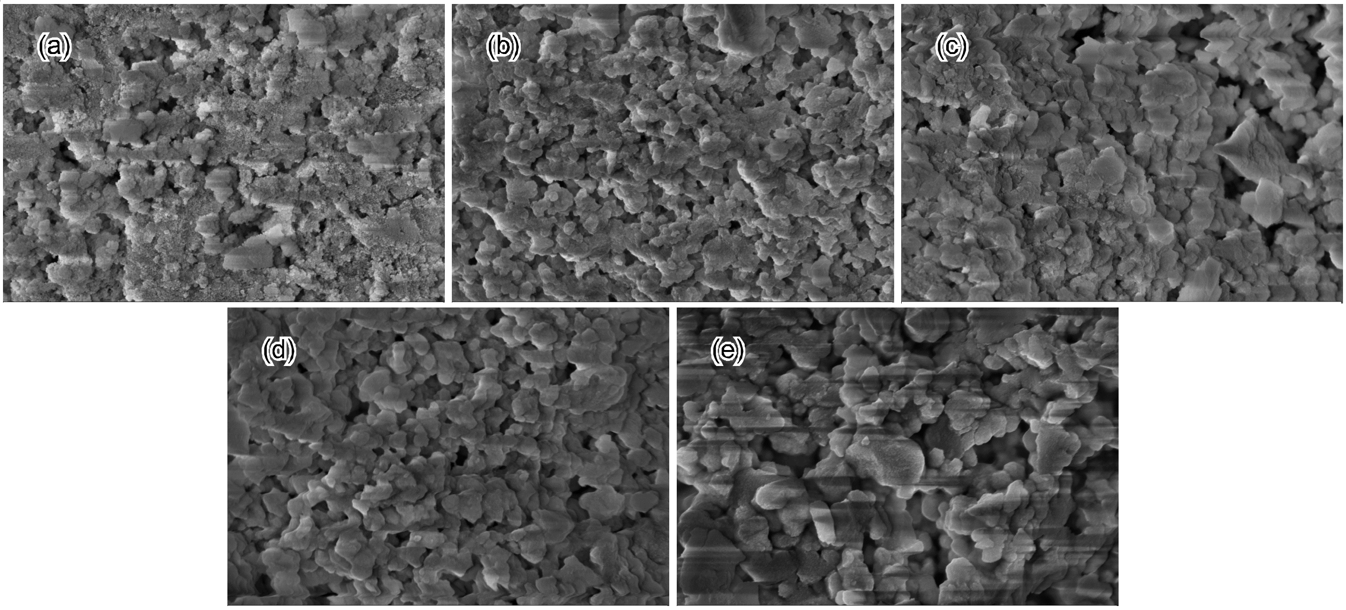


Fig. 3. SEM images of (a) 1 wt.% YZ, (b) 2 wt.% YZ, (c) 3 wt.% YZ, (d) 4 wt.% YZ, (e) 5 wt.% YZ

addition, they confirmed excellent morphology for smaller nanoparticles size (2-4 nm). The results seen that equiaxial particles, uniform in size and shape, with a relative affinity of agglomeration. Uniform distribution and nanocrystallite size were added advantage for the best catalytic activity.

Thermal studies: TGA spectra of 5 wt.% Yr_2O_3/ZrO_2 of uncalcined samples have been recorded in temperature range from room temperature to 1000 ºC performed on Perkin-Elmer TGA7, under nitrogen between 25 to 850 ºC at a constant heating rate of 10 ºC/min. TGA curves of yttria dopped zirconia nanopowder are given in Fig. 4. It was observed from the TGA curve that dominant weight loss of the sample occurred in temperature region between 100 and 525 ºC. There was almost no weight loss above 550 ºC. The percentage weight loss observed near 150 ºC (20.01%) was considered due to the moisture content present in the sample. The organics present over the surface of then nanoparticles decomposed in temperature range of 150-525 ºC (32.81%). Overall, the TGA results show a loss of ~52%. This indicated the stability of the catalyst and selection of calcination temperature for the mixed oxides.

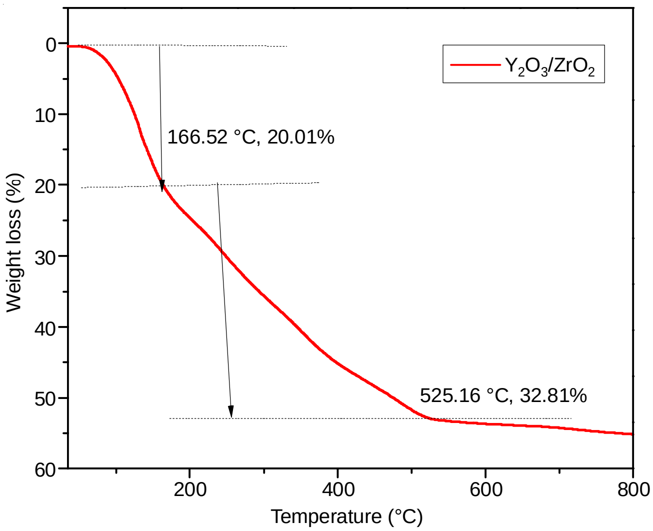


Fig. 4. TGA of 5 wt% YZ mixed oxides uncalcined material

X-ray photoelectron spectroscopy (XPS) studies: Mixed metal oxides of yttria doped zirconia (YZ) were prepared by sol-gel method. To study surface compositions and oxidation states X-ray photoelectron spectroscopy studies were carried out on yttria doped on zirconia. On the surface enrichment of zirconium is more than yttrium, which takes to assumption of core-shell like structure of this nanomaterial. To evaluate oxidation state is challenging task for bimetallic nanomaterials but for zirconium it was found a characteristic peak of $3d_{5/2}$ and $3d_{3/2}$ resolves the confusion. Similarly for yttrium it is $3d_{3/2}$ which also characteristic peak. The corresponding calibrated energy scale for O1s peak with broad nature is at 533.3 eV. After calibration of broadness on both equal sides of this peak then end up with two values 532.5 and 534.5 eV which can be assigned for minor contributions from ZrO_2 and Y_2O_3 respectively [28]. Fig. 5. Showed two peaks at 187.6 and 185.9 eV corresponding to $3d_{3/2}$ and $3d_{5/2}$ peaks of Zr which are very good agreement with literature data of ZrO_2 [29,30]. These two peaks are good agreement with Zr^{4+} oxidation state but need to consider FWHM values to check suboxide formation in this samples. However relatively narrow FWHM of around 2.3 eV for both Zr $3d_{3/2}$ and $3d_{5/2}$ lines supported formation of Zr^{4+} in compounds. Another method can be used to calculate average oxidation state by using energy difference between O1s and 3d lines of the metals in oxides. In this sample difference between $3d_{5/2}$ peak line of Zr is at (185.9 eV) and main O1s line is at (533.3 eV) is 347.4 eV and which is matching with pure ZrO_2 [29,31]. So XPS confirmed formation of Y_2O_3 and ZrO_2 formation with oxidation state Zr^{4+} and Y^{3+} in this sample.

Catalytic activity: Various amount of yttria dopped zirconia (YZ) nanocomposite were used as catalyst in acetylation reaction using acetic anhydride as acetylating reagent. Different derivatives of acetate were synthesized by using alcohol,

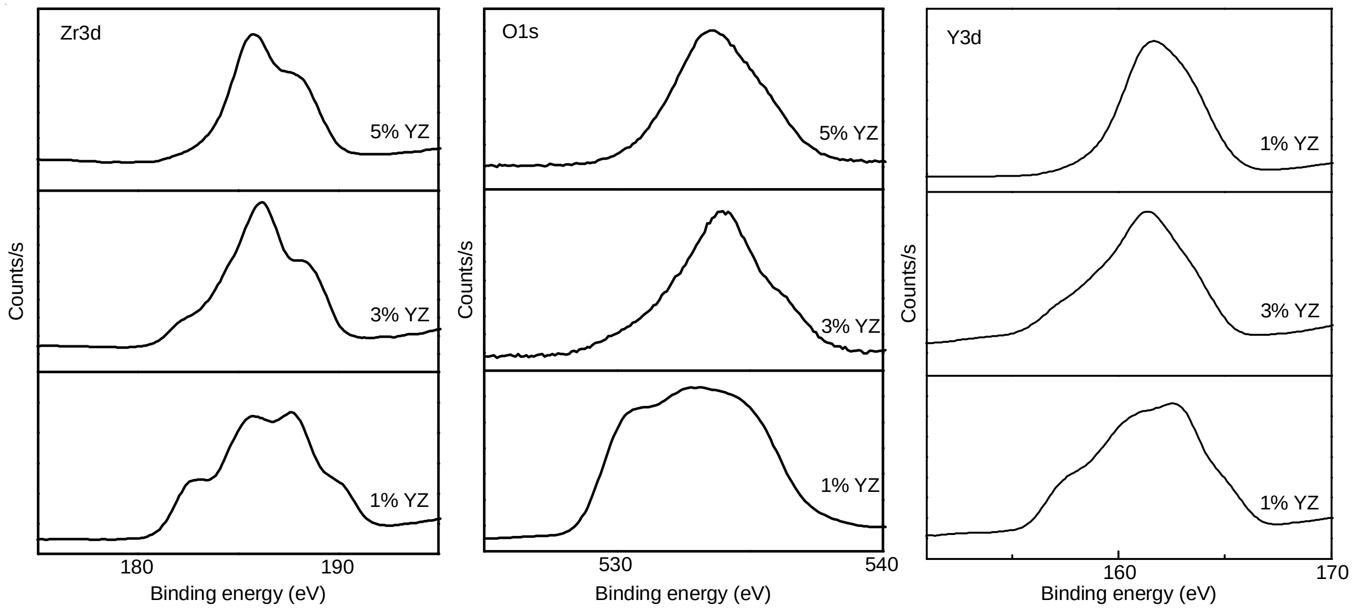


Fig. 5. XPS of yttria doped zirconia

phenol and amine in presence of YZ catalysts. The experimental procedure of acetylation reaction as below:

General procedure for the acetylation under solvent-free conditions: Acetylation reaction was carried out in a two necked round bottom flask which is attached with water condenser. In a reaction, round-bottom flask was charged with 1 mmol of substrate followed by the addition of 3 mmol acetic anhydride and the mixture was mixed well and then 0.1 g YZ catalyst was added which is previously activated at 200 °C and then placed in an oil bath with maintained temperature at 120 °C. A small amount of sample was taken from the reaction mixture at different time intervals and diluted with diethyl ether to monitor the progress of the reaction by gas chromatography. Products were identified by comparing them with standard samples. After completion of the reaction, the mixed oxide catalyst was removed easily by simple filtration. The catalyst was reactivated by simple washing with water and then with acetone respectively and then calcined at 500 °C. To optimize the reaction conditions, the effect of various amount of yttria doped on zirconia, effect of temperature, time, molar ratio and amount of catalyst were studied in a model reaction between benzyl alcohol and acetic anhydride and presented the results. By following same protocol, the acetylation of phenol and anime was also carried out and results are presented in Table-1. A wide range of alcohols, phenols and amines were subjected to acetylation with acetic anhydride by this procedure. Furthermore, acetylation of amines took place in short time compared to alcohols and phenols. However, aliphatic molecule cyclohexanol completed acetylation in 10 min, while aromatic in 30 min of time.

To optimize the acetylation reaction, following parameters were studied. The reaction was carried out in the presence of 1, 2, 3, 4 and 5 wt.% YZ catalyst at 120 °C for 30 min with molar ratio of benzyl alcohol to acetic anhydride maintained 1:3. In this work, it was found that the acetylation reaction of benzyl alcohol could proceed more efficiently with 5 wt.% YZ. On rising the catalyst concentration from 1 to 5 wt.%, conversion increased to 100% with 5 wt.% YZ while at 1 wt.% to 4 wt.% YZ catalyst showed less conversion. These results were also compared with literature (Table-2) as acetylating agent like acetic anhydride and acetic acid. YZ catalysts first time used for solvent free acetylation with 100% conversion. As increased amount of yttria help to increase the conversion as well as selectivity of the product, this may be due to increased acidity of mixed oxide.

The reaction temperature was an important parameter, which was affected the acetylation of organic compound. Hence, a series of experiments were performed at room temperature, 60, 80, 100 and 120 °C, the conversion of benzyl alcohol increased from 0.91% to 100%. Results are shown in Table-3. Lower conversion of 0.91% obtained at room temperature with lower selectivity for substituted acetate. Therefore, further experiments were carried out at temperature (120 °C) with magnetic stirring in oil bath to accomplish complete conversion of benzyl alcohol within a short reaction time. With these optimized conditions in hand benzyl alcohol with electron donating and electro withdrawing substituents were examined and achieved more than 99% conversions with 100% selectivity of the corresponding acetylated products after 10 min. The conversion increased considerably when temperature of reaction mixture was increased to 120 °C, it showed increase in selectivity to 100% as well as conversion of benzyl alcohol to 100%. This may due to the rate of formation of carbocation was more at 120 °C than lower temperature. Therefore, as the temperature increased further selectivity decreased, so reaction was optimized at 120 °C and for next study temperature was kept constant. Reaction was carried out up to 1 h but maximum conversion was obtained after 0.5 h.

This work also investigated the effect of the amount of catalyst on the reaction conversion. It was already reported that for the Friedel Crafts acylation reaction using traditional catalysts, an excess over stoichiometric amounts of the Lewis

TABLE-1
ACETYLATION OF ALCOHOLS, PHENOLS AND AMINE USING ACETIC ANHYDRIDE IN THE PRESENCE OF A CATALYTIC AMOUNT OF YTTRIA DOPPED ZIRCONIA

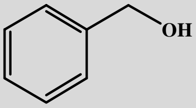
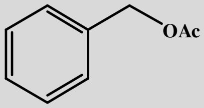
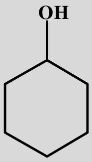
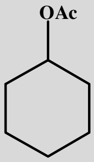
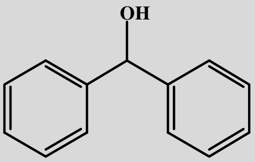
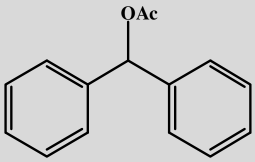
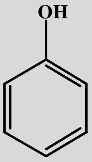
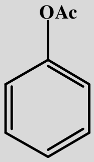
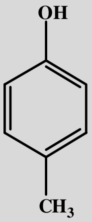
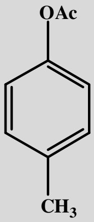
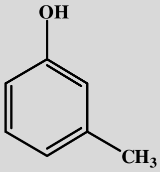
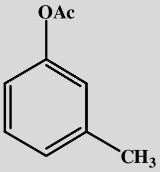
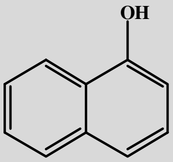
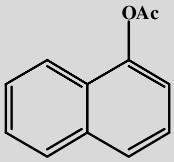
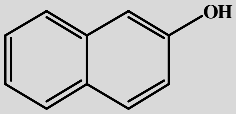
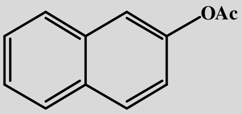
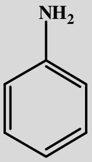
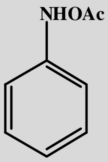
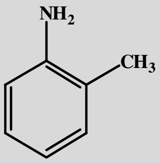
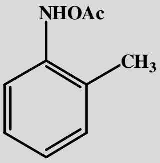
Entry	Substrate	Product	Time (min)	Conversion (%)
Alcohol				
1			30	100
2			10	99
3			30	95
Phenol				
4			30	88.67
5			30	100
6			30	76.23
7			30	90
8			30	99.57
Amines				
9			10	100
10			10	67

TABLE-2
ACETYLATION REACTION RESULTS WITH REPORTED LITERATURE

Catalyst	Reaction conditions	% Conversion/Yield	Ref.
Maghemite-ZnO	Benzyl alcohol, acetic acid, 3 h, room temperature	94	[32]
CuO-ZnO	Benzyl alcohol, acetic acid, DCM, 15 min, room temperature	92	[16]
P_2O_5/Al_2O_3	Benzyl alcohol, acetic acid, Solvent free, 20 min, room temperature	97	[23]
Borated Zirconia	Benzyl alcohol, acetic acid, 14 h, 110 °C	69	[21]
$ZnAl_2O_4@SiO_2$	Benzyl alcohol, acetic acid, solvent free 20 min, 75 °C	92	[33]
5 wt.% YZ	Benzyl alcohol, acetic acid, solvent free, 30 min, 120 °C	100	Present work

TABLE-3
EFFECT OF TEMPERATURE ON CONVERSION OF BENZYL ALCOHOL USING YZ AS CATALYST

Temp. (°C)	Conversion of benzyl alcohol (%)	Selectivity (%)
Room temp.	0.91	99.56
60	27.89	100
80	71.07	100
100	97.68	100
120	100	100

Reaction condition: Benzyl alcohol (1 mmol), acetic anhydride (3 mmol), catalyst: Yt/Zr5 wt.% 0.1 g, Time: 0.5 h

acid can be required, for the formation of aryl products in significant amounts. The catalyst concentration can be reduced for the reaction. The catalyst amount was increased from 0.05, 0.1 to 0.20 g respectively by keeping other conditions constant. The conversion of acetate product was increased from 95.43% to 100% (Table-4). With increase in amount of catalyst there was small decreased in conversion of acetate. By comparing obtained results, it is concluded that the best results of acetylation of benzyl alcohol were obtained with 0.1 g of catalyst, may be due to the nanocrystalline size of catalyst. Therefore, more surface area helps to improve the catalytic activity. In absence of catalyst showed conversion 22.28% and also selectivity was lowered as compared to the solid acid catalyst.

TABLE-4
EFFECT OF CATALYST AMOUNT ON CONVERSION OF BENZYL ALCOHOL

Catalyst amount (g)	Conversion of benzyl alcohol (%)	Selectivity (%)
Without catalyst	22.28	100
0.05	97.24	100
0.10	100.00	100
0.20	95.43	100

Reaction condition: Benzyl alcohol (1 mmol), acetic anhydride (3 mmol), Temp.: 120 °C, catalyst: YZ 5 wt.%, Time: 30 min

The reaction of benzyl alcohol to benzyl acetate was carried out by keeping constant amount of benzyl alcohol with different amount of acetylating agent acetic anhydride ratio from 1:1, 1:2 and 1:3. The result data simplified that the conversion of alcohol increased from 93% to 100% (Table-5). As the amount of acetic anhydride was increased with respect to ratio, there was decreased selectivity and also conversion of the product. Thus, from the above observations, maximum conversion of benzyl alcohol and selectivity of product was obtained with 1:3 molar ratio.

TABLE-5
EFFECT OF MOLAR RATIO ON CONVERSION OF BENZYL ALCOHOL

Mole ratio (Benzyl alcohol:Acetic acid)	Conversion of benzyl alcohol (%)	Selectivity (%)
1:1	93.43	99.99
1:3	100	100
1:4	96.11	100

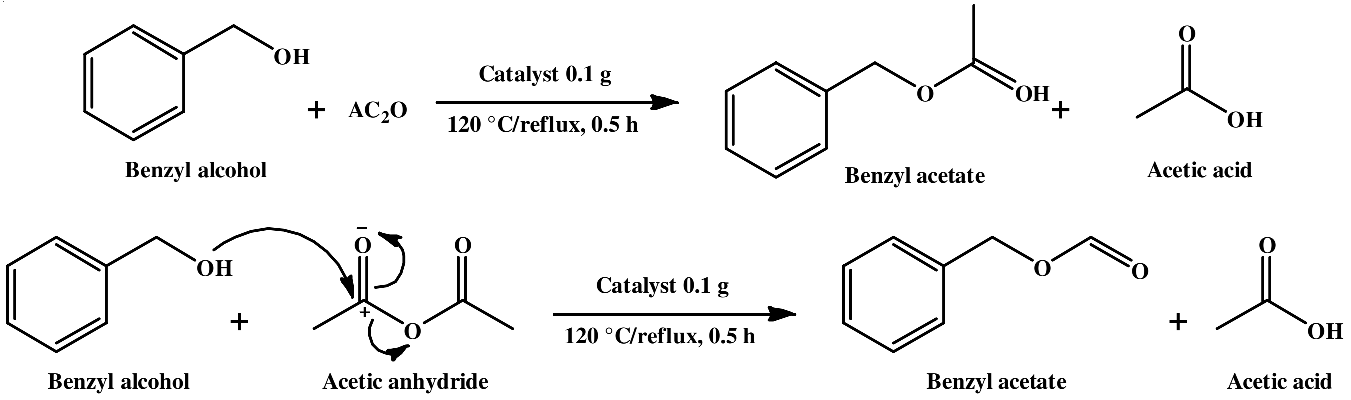
Reaction condition: Temp.: 120 °C, Time: 0.5 h, catalyst: YZ 5 wt.% (0.1 g)

Recycle and reuse of catalyst: To study the recyclability of the synthesized catalyst, the YZ catalyst was recovered from the reaction mixture and reused. After each use in reaction, the catalyst was removed from the reaction mixture by simple filtration method, washed successively with acetone and water and dried at 100 ºC for 3 h and then activated at 500 ºC for 4 h. Reaction with fresh catalyst showed conversion of benzyl alcohol was 94.81% after second and third recycle of the catalyst gave the conversion 91.07% and 88.08%, respectively. The small loss catalytic activity was indicated by the catalysts. Therefore, it accomplished that the catalyst can be reused for more runs with minor loss in activity.

Reaction mechanism: The proposed mechanism of acetylation of benzyl alcohol with acetic anhydride is given in **Scheme-I**. As previously mentioned, acetylation reaction is electrophilic substitution mechanism of reaction in which formation of carbocation group takes place by complexing with acetylating agent in presence of catalyst. In acetylation reaction, the carbocation species generated and attack on aromatic species. Thus, formation of this carbocation was mainly important during acetylation reaction.

Conclusion

By using sol gel method, yttria doped zirconia (YZ) catalysts with various loading were synthesized and characterized by XRD, SEM, EDX, TGA and XPS techniques. The results of SEM and EDX data revealed that all the catalysts were in nanocrystalline form, it was also confirmed from XRD results. In most of the prepared catalyst, effective tetragonal phase geometry was found to be more effective for the catalytic study. Acetylation of benzyl alcohol was carried in the presence of synthesized catalysts gave higher conversion as well as selectivity. The optimized conditions for the reaction were benzyl alcohol (1 mmol), acetic anhydride (3 mmol), 5 wt.% YZ catalyst (0.1 g), at 120 ºC for 30 min. 5 wt.% YZ catalyst gave maximum results due to nanocrystallite size as well as doping of yttria. Y_2O_3 doped ZrO_2 catalyst was non-corrosive, inexpensive, environmental benign catalysts and can be reused by



Scheme-I: Reaction mechanism for acetylation reaction of benzyl alcohol

simple filtration method without significant degradation in the catalytic performance and gave excellent conversion of reactant and selectivity of product.

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CONFLICT OF INTEREST

The authors declare that there is no conflict of interests regarding the publication of this article.

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