# Effective utilization of glycerol for the synthesis of 2-methylpyrazine over ZnO- $ZnCr_2O_4$ catalyst

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**Abstract.** Bioglycerol an inevitable by-product in the production of biodiesel was effectively utilized for the synthesis of 2-methylpyrazine (2-MP) by vapour phase dehydrocyclization with ethylenediamine over ZnO-ZnCr<sub>2</sub>O<sub>4</sub>(Zn-Cr-O) mixed oxides. These Zn-Cr-O samples were obtained from hydrotalcite precursors synthesized by precipitation method at different pH ( $\sim$ 7 and 9) and calcination in air at 450°C. X-ray diffraction (XRD) and Fourier transform infrared (FT-IR) analysis confirmed the presence of ZnCr<sub>2</sub>O<sub>4</sub> species. Transmission electron microscopy (TEM) images indicated spherical particles with mean diameter of 35.8 and 24 nm for the Zn-Cr-O prepared at pH  $\sim$  7 and  $\sim$ 9, respectively. Surface Zn enrichment was observed in the near-surface region of Zn-Cr-O prepared at pH  $\sim$ 9. Differences in dehydrocyclization activity of Zn-Cr-O mixed oxides were established based on spectroscopic data that emphasized changes in structural properties of Zn-Cr-O obtained at different pH.

Keywords. Bio-glycerol; 2-methylpyrazine; TEM; FT-IR; ESR; ZnO-ZnCr<sub>2</sub>O<sub>4</sub>.

# 1. Introduction

Owing to diminution of fossil fuel sources with time, alternative energy resources are becoming increasingly important. In recent times, R&D has focussed on production of alternative fuels from renewable resources such as biomass-derived compounds, particularly biodiesel production from non-edible oils. Bio-diesel is an intriguing candidate because it is renewable, and carbon neutral.<sup>1-4</sup> A major drawback of this process is that about 10 wt% of bio-glycerol is obtained as a by-product during the process; as a result, surplus of inexpensive glycerol is produced. Hence, the cost of biodiesel is the constraint for commercialization of this product with ever-increasing production of biodiesel. Recovery and effective utilization of such bio-glycerol has been considered as one of the options to lower the overall cost of biodiesel production.

Production of alternative fuels from renewable resources is a crucial task. From an economical and environmental standpoint, utilization or safe disposal of by-products obtained in conversion/transformation of renewable resources is utmost important. Several alternatives are being explored to utilize bio-glycerol, and commercial plants have been established recently to produce propylene glycol from glycerol. Conversion of bio-glycerol into value-added compounds and fine chemicals have been extensively studied by several authors.<sup>5</sup> One such process is the production of 1,2-propanediol (a key compound in the synthesis of 2-methylpyrazine) by hydrogenolysis of bio-glycerol over supported noble metal catalysts at high pressures. 2-Methyl pyrazine is an intermediate compound for the synthesis of 2-amido pyrazine, a well-known bacteriostatic and antitubercular drug. Conventionally, 2methyl pyrazine is synthesized by dehydrocyclization of ethylenediamine (EDA) and 1,2-propanediol. Forni and Pollesel have studied a Pd-promoted zinc chromite catalyst for the synthesis of 2-methylpyrazine using EDA and 1,2-propanediol.<sup>6</sup>

The present study explores Zn–Cr hydrotalcite precursors that have been synthesized at pH  $\sim$  7 and  $\sim$  9, and catalytic activities were evaluated for the synthesis of 2-methylpyrazine by dehydrocyclization of EDA and aqueous glycerol. Fresh as well some of the used samples were characterized by BET-surface area, differential thermal and thermogravimetric analysis (DT/TGA), scanning electron microscope energy dispersive X-ray

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analysis (SEM-EDX), power X-ray diffraction analysis (XRD), X-ray photoelectron spectroscopy (XPS), electron spin resonance (ESR), transmission electron microscopy (TEM) and Fourier transformed infrared (FT-IR) spectroscopy.

# 2. Experimental

### 2.1 Preparation of catalysts

The Zn-Cr catalysts employed in this investigation were prepared by a simple co-precipitation method using  $Zn(NO_3)_2 \cdot 6H_2O$  and  $Cr(NO_3)_3 \cdot 9H_2O$  (Sigma-Aldrich, AR grade) with Zn:Cr = 2:1 (mole ratio), in order to obtain hydrotalcite structure.<sup>7</sup> Samples were prepared at two different pH, i.e., at pH 7 and 9 using a mixture of 2M NaOH+1M Na<sub>2</sub>CO<sub>3</sub> (base mixture) as precipitating agent. Gels were washed thoroughly, filtered and oven-dried for 12 h at 120°C, and subsequently, calcined in static air at 450°C for 5 h. The Zn-Cr samples prepared at pH  $\sim$  7 and  $\sim$  9 were denoted as ZC7 and ZC9, respectively. The bulk  $Cr_2O_3$ catalyst was prepared by precipitation method using Cr(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O (Sigma–Aldrich, AR grade) with similar composition of base mixture used here. All these samples were screened for dehydrocyclization of EDA and aqueous glycerol and some of the samples were characterized by various spectroscopic techniques.

### 2.2 Characterization of catalysts

Surface properties of the Zn-Cr-O samples were measured by  $N_2$  adsorption at  $-196^{\circ}C$  in an Autosorb 3000 physical adsorption apparatus. Specific surface areas were calculated applying BET method. Calcined forms of Zn-Cr-O catalysts were characterized by powder XRD analysis using a Rigaku Miniflex X-ray diffractometer using Ni-filtered Cu K<sub> $\alpha$ </sub> radiation ( $\lambda$  = 0.15406 nm) from  $2\theta = 20$  to  $80^\circ$ , at a scan rate of 2° min<sup>-1</sup> with beam voltage and beam current of 30 kV and 15 mA, respectively. SEM-EDX analysis was carried out using JEOL-JSM 5600 instrument. For TEM analysis, samples were dispersed in methanol solution and suspended on a 400-mesh; 3.5 mm diameter Cu grid and images were taken using JEOL JEM 2010 highresolution transmission electron microscope. XPS patterns were recorded using a Kratos Axis Ultra Imaging X-ray photoelectron spectrometer equipped with Mg anode and a multichannel detector. Charge referencing was done against adventitious carbon (C 1s, 284.8 eV). Shirley-type background was subtracted from the signals. Recorded spectra were always fitted using

Gauss–Lorentz curves to determine binding energies of different elements. Infrared spectra were recorded in KBr pellets using thermo Nicolet Nexus 670 spectrometer in the region of 4000-400 cm<sup>-1</sup>. The spectrum obtained after multiple scans was a plot of percentage transmittance against wave number. ESR analysis of Zn-Cr-O samples were performed at room temperature using JEOL/JES-FA200 spectrophotometer by X-band equipment with an operating frequency v = 9.029 GHz. DT/TGA of the oven-dried samples were recorded using a Leeds and Northup (USA) unit at a heating rate of 10°C/min, ranging from 30° to 1000°C under nitrogen flow.

#### 2.3 Activity measurements

Catalytic activities were carried out using -18/+23 sieved (BSS) catalyst particles. Carbon mass balance was done based on the inlet and outlet concentration of the organic moiety. Prior to the reaction, about 0.2 g of calcined catalyst (sieved particles -18/+23 BSS) was reduced in 5% H<sub>2</sub> (balance Ar) at 400°C for 5 h. Catalytic activities were measured under strict kinetic control. An aqueous glycerol solution (20 wt% in H<sub>2</sub>O) was used with a glycerol to EDA mole ratio of 1:1, and a flow rate of the reaction mixture of 5 mL h<sup>-1</sup>, with N<sub>2</sub> as the carrier gas at a flow rate of 1800 cc h<sup>-1</sup>. The reaction mixture contained a glycerol:EDA:H<sub>2</sub>O:N<sub>2</sub> = 1:1:20.4:7.4 mole ratio.

# 2.4 Product analysis

Samples were analysed by gas chromatograph (Shimadzu, GC-17A) via a flame ionization detector (FID) using a ZB-5 capillary column at a ramping rate of 10°C min<sup>-1</sup> from 60° to 280°C. Mass balance for all the measurements was >95%. Samples were analysed by GC-MS (QP5050A Shimadzu) using a ZB-5 capillary column with EI mode. Mass spectra confirmed product distribution and corresponding m/zvalues for methylpyrazine: M+. m/z: 94, (M-HCN) +. m/z: 67, (M-CH<sub>3</sub>CN) +. m/z: 53, (M-C<sub>3</sub>H<sub>4</sub>N) +. *m/z*: 40; pyrazine: M+. *m/z*: 80, (M-HCN) +. *m/z*: 53; EDA: (M-H) + m/z: 59,  $(M-NH_3) + ... m/z$ : 43; glycerol:  $(M-CH_2OH)+. m/z$ : 61;  $\{M-(CH_2OH, H_2O)\}+.$ m/z: 43; 2,5-dimethylpyrazine: M+. m/z: 108; (M-CH<sub>3</sub>)+. *m/z*: 93; (M-HCN) +. *m/z*: 81; (M-CH<sub>3</sub>CN) +. m/z: 67; (M-C<sub>3</sub>H<sub>6</sub>N)+. m/z: 52; (M-C<sub>4</sub>H<sub>4</sub>N) +. m/z: 42; pyrazinealdehyde: M+. m/z: 108; (M-H)+. m/z: 107; (M-CO)+. m/z: 80; (M-C<sub>2</sub>N<sub>2</sub>)+. m/z: 56; {M- $(H,CO,C_2H_2)$  +. *m/z*: 53; and 2,3-dimethylpyrazine: M+. m/z: 108; (M-CH<sub>3</sub>CN)+. m/z: 67; (M-C<sub>4</sub>H<sub>6</sub>N)+. m/z: 40. Methylpyrazine was isolated and analysed by <sup>1</sup>H NMR spectra which revealed <sup>1</sup>H NMR (CDCl<sub>3</sub>,

200 MHz):  $\delta = 8.32-8.5$  (m, 3 H); 2.56 (s, 3 H), attributed to methylpyrazine.<sup>7</sup>

%Conversion of Ethylenediamine =	$[moles_{Ethylenediaminein} - moles_{Ethylenediamineout} / moles_{Ethylenediaminein}] \times 100$
%Conversion of Glycerol =	$[moles_{Glycerol.in} - moles_{Glycerol.out} / moles_{Glycerol.in}] \times 100$
$Yield_{2MP} =$	$[Conversion_{Glycerol} \times Selectivity_{2MP}]/100$
$Yield_{2-pyrazinylmethanol} =$	$[Conversion_{Glycerol} \times Sel_{2-pyrazinylmethanol}]/100$
$r_{\rm 2MP} =$	[(Yield <sub>2MP</sub> ) × (Ethylenediamine + Glycerol) flow rate/ $S_{\text{BET surface area}}$ × Weight of the catalyst.]
$r_{2-pyrazinylmethanol} =$	[(Yield <sub>2-pyrazinylmethanol</sub> ) × (Ethylenediamine + Glycerol)flow rate/ $S_{\text{BET surface area}}$ × Weight of the catalyst]

# 3. Results and discussion

# 3.1 Powder XRD analysis

The XRD patterns of oven-dried samples are reported in figure 1. The Zn-Cr hydrotalcite-like structure is confirmed by presence of HT phase layered double hydroxide (LDH) which is decomposed to form ZnO and ZnCr<sub>2</sub>O<sub>4</sub> phases<sup>8</sup> upon calcination in air at 450°C for 5 h. Lattice parameters corresponding to the HT structure are found to be a = 3.10 and c = 22.5 for Zn– Cr LDH. Basal spacing is calculated from the average of (001) peaks ( $d\sim0.775$  nm), while the 'a' dimension is calculated as twice the position of the (110) peaks ( $a \sim 0.3106$  nm). This is in good agreement with literature value.<sup>9</sup>

# 3.2 DT/TGA analysis of oven-dried ZC7 and ZC9 samples

Hydrotalcite-type materials decompose in three consecutive steps, resulting in plateaus in the TGA diagram and endothermic peaks in the DTA pattern. There are three endothermic peaks (figure 2) in the DTA patterns of ZC samples prepared at different pH levels (7 and 9) located at 110°C, 200°C and 320°C. In the TGA analyses, the first stage started as soon as heating commenced, and ceased at 170°C. The resulting weak and broad endothermic peak is due to the removal of weakly adsorbed water molecules, most likely on the external surface of the particles. The next stage starts immediately upon completion of the first step and results in minima at 200°C in DTA pattern and remains up to 250°C. This peak is possibly due to removal of water of crystallization accompanied with dehydroxylation of hydroxyl groups from brucite-like layered structure. The third and last stage starts with completion of second stage, resulting in an endothermic peak at 320°C in the DTA pattern and ceases at 455°C. This is ascribed to the removal of carbon dioxide from the interlayer



Figure 1. XRD patterns of the (a) oven-dried and (b) calcined ZC7 and ZC9 samples.



**Figure 2.** DT/TGA patterns of the oven-dried ZC7 and ZC9 samples.

carbonate anion. In the present investigation, TG analysis of Zn-Cr hydrotalcite precursors revealed that this is responsible for approximately 30% of the weight loss. End products from this decomposition process are ZnO and ZnCr<sub>2</sub>O<sub>4</sub> mixed metal oxides which were identified by powder XRD analysis.<sup>7,8</sup>

### 3.3 FT-IR analysis of the calcined Zn-Cr-O samples

FTIR spectra of calcined catalysts (ZC7 and ZC9) are shown in figure 3. Absorption band near 3400 cm<sup>-1</sup> is due to O-H bond vibration modes of hydroxyl groups and water molecules. Absorption band present close to 1629 cm<sup>-1</sup> is ascribed to the hydroxyl deformation mode of water. Weak bands near 1496 cm<sup>-1</sup> could be



**Figure 3.** FT-IR spectra of calcined ZC7 and ZC9 catalysts.

attributed to carbonate species adsorbed on the external surface of crystallites, observed only in the ZC7 catalyst. Bands below 1000 cm<sup>-1</sup> are lattice absorptions due to Zn-O, Cr-O, Zn-O-Cr vibration modes. IR spectra of spinels are characterized by four bands which originate due to  $F_{1u}$  symmetry. Shapes and exact positions of high frequency IR bands,  $v_1$  and  $v_2$  essentially depend on trivalent cations and thus are related to vibration of lattice octahedral groups. The band recorded at approximately 623 cm<sup>-1</sup> in both ZC7 and ZC9 samples is due to the  $v_1$  mode, and a less sharp band at 501 cm<sup>-1</sup> is due to the  $v_2$  mode of ZnCr<sub>2</sub>O<sub>4</sub>. Bands due to modes  $v_3$  and  $v_4$ are not observed, as they are expected between 250 and  $150 \text{ cm}^{-1}$ . The broad band at 945 cm<sup>-1</sup> present in both samples is assigned to a Zn-O deformation mode.<sup>10,11</sup> Appearance of bands in the region of 900 to  $1100 \text{ cm}^{-1}$ is an evidence of M=O link present in the lattice.<sup>12</sup>

### 3.4 TEM analysis of calcined Zn-Cr-O samples

The TEM images of fresh calcined ZC7 and ZC9 catalysts are displayed in figure 4. About 20 particles are chosen in order to measure the average particle size of the catalysts. Particles are almost spherical in shape with an average mean particle diameter of 35.8 and 24.0 nm for (table 1) ZC7 and ZC9 catalysts, respectively. These results suggest that pH has a significant influence on the synthesis of Zn-Cr hydrotalcite precursors that produced ZnO-ZnCr<sub>2</sub>O<sub>4</sub> mixed oxide nanoparticles.

# 3.5 ESR analysis of the calcined Zn-Cr-O samples

Figure 5 shows the room temperature ESR spectra of calcined, reduced and used Cr2O3 and Zn-Cr-O catalysts. Clustered  $Cr^{3+}$  ions of the bulk or  $\beta$ -phase resonance exhibit a broad, symmetric resonance absorption line with a peak-to-peak line width of  $(\Delta H_{pp})$  of 50 to 300 mT.<sup>13</sup> Oxidized phase of Cr<sub>2</sub>O<sub>3</sub> usually contains coupled Cr<sup>3+</sup> and Cr<sup>6+</sup> species only, and these species are highly stable (in the calcination temperature range of 200° to 600°C) when compared to  $Cr^{3+}$ or Cr<sup>6+</sup> species alone. The spectra are broad and symmetrical (figure 5a) and  $\Delta H_{pp}$  is varied (table 1) where ZC7 exhibits a peak-to-peak line width of 161 mT and 130 mT in case of ZC9 catalyst showing differences in structural properties of ZnO-ZnCr<sub>2</sub>O<sub>4</sub> mixed oxides synthesized from Zn-Cr hydrotalcite precursors as a result of pH dependency. A comparative ESR spectrum of bulk Cr<sub>2</sub>O<sub>3</sub> exhibited a peak-to-peak line width  $(\Delta H_{pp})$  of 114 mT. Peak widths of the reduced (figure 5b) samples are found to be  $\Delta H_{pp} = 44$ and 61 mT for the ZC7 and ZC9 catalysts, respectively. ESR spectra of the used catalysts are reported in



Figure 4. TEM images of Zn-Cr-O prepared at (a) pH = 7 and (b) pH = 9.

figure 5c. Line widths show dramatic changes (table 1) when compared to the reduced catalysts. Figure 5c suggests the presence of amorphous carbon for the Cr<sub>2</sub>O<sub>3</sub> (used) catalyst with  $\Delta H_{pp} = 0.88 \text{ mT.}^{14}$  Decrease in line width of the reduced and used catalysts are probably due to exchange coupling between the Cr<sup>3+</sup> ions, which results in an exchange narrowing of the resonance line. Fresh calcined (ZC7 and ZC9) samples show broad symmetric lines with near-Lorentzian shapes, centred at g = 1.98, characteristic of magnetically interacting  $\beta$ -phase Cr<sup>3+</sup> species. Whereas bulkamorphous chromia displayed a symmetric ESR signal centred at g = 2.242 with  $\Delta H_{\rm pp}$  of 114 mT is attributed to clustered Cr<sup>3+</sup> ions.<sup>15</sup> A significant change is observed in line widths upon treatment with H<sub>2</sub> (table 1). Changes in ESR spectral shape could be due to variations in the geometry of the compound.<sup>16</sup> The  $\beta$ -phase Cr<sup>3+</sup> ESR line width was reported to vary from about 80 to 200 mT with chromia-alumina catalysts reduced in H<sub>2</sub> at 500°C.<sup>15</sup> Antiferromagnetic ZnCr<sub>2</sub>O<sub>4</sub> with a normal spinel structure shows line width less than 30 mT broad over the temperature range of  $-173^{\circ}$ C to  $23^{\circ}$ C.<sup>17</sup> Forni and Oliva have observed the ESR line width ranging between 65 and 39 mT with ZnO-ZnCr<sub>2</sub>O<sub>4</sub> catalysts.<sup>18</sup> The observed results in this investigation are analogous to those reported by Forni and Oliva<sup>18</sup> The broad line width ESR signals of ZnO- ZnCr<sub>2</sub>O<sub>4</sub> mixed oxides of fresh calcined (ZC7 and ZC9) catalysts could be explained based on strong spin–spin exchange dipolar broadening and the decrease in line widths of the reduced and used ZC7 and ZC9 catalysts are possibly due to spin–spin exchange narrowing. Fresh and reduced ZC7 and ZC9 samples did not show any signals attributed to  $Cr^{5+}$  species.

### 3.6 Surface and bulk analysis of Zn-Cr-O samples

XPS analysis of Zn-Cr-O samples revealed Zn enrichment at the near-surface region on ZC9 sample (table 2). Surface oxygen density is slightly lower on ZC9 than ZC7 sample. Our earlier investigations of  $O_2$  pulse chemisorption studies on Zn-Cr-O further confirmed the relatively high surface oxygen density on Zn-Cr-O that was prepared at lower pH  $\sim$ 7. EDX analysis (table 3) showed that the bulk is enriched with chromium than Zn in ZC7 compared to ZC9 sample. In contrast, a reverse trend is observed in the XPS analysis of ZC7 and ZC9 samples.

### 3.7 Dehydrocyclization activity measurements

Dehydrocyclization activity data on Zn-Cr-O samples is reported in table 4. Rate of 2MP is lower on ZC7 and almost twice on ZC9 sample. Slightly higher rate

**Table 1.** Bulk and surface compositions and ESR line widths of ZC7 and ZC9catalysts.

Sample	Compo Nominal	sition (Z EDX	Zn/Cr) XPS	$\frac{\mathrm{Cr}^{3+} \mathrm{ES}}{\mathrm{Calcined}}_{\Delta H_{\mathrm{pp}}}$	$\frac{SR \text{ line widt}}{\text{Reduced}}$ $\frac{\Delta H_{\text{pp}}}{\Delta H_{\text{pp}}}$	$\frac{\text{ths (mT)}}{\text{Used}} \\ \Delta H_{\text{pp}}$	TEM Mean particle size (nm) Calcined
ZC7 ZC9 Cr <sub>2</sub> O <sub>3</sub>	2:1 2:1 _	4.7 3.2 -	1.59 2.01 -	161 130 114	44 61 - 0.88	34 49 202	35.8 24.0



**Figure 5.** ESR spectra of (**a**) calcined Cr<sub>2</sub>O<sub>3</sub>, ZC7 and ZC9, (**b**) reduced ZC7 and ZC9, (**c**) used Cr<sub>2</sub>O<sub>3</sub>, ZC7 and ZC9 catalysts, (**c1**) Magnification of Figure 5c from 175 to 425 mT.

**Table 2.** Surface composition obtained from XPS analysis of calcined fresh ZC7and ZC9 catalysts.

Catalyst	Zn	Cr	0	Zn/Cr	O/Zn	O/Cr	O/(Zn+Cr)
ZC7	23.37	14.68	61.95	1.59	2.65	4.22	1.63
ZC9	30.68	15.26	54.05	2.01	1.76	3.54	1.17

 Table 3.
 Bulk compositions of calcined fresh and used ZC7 and ZC9 catalysts obtained from EDX analysis.

Catalyst	Zn	Cr	0	Zn/Cr	O/Zn	O/Cr
ZC7fresh	61.58	13.08	25.34	4.7	0.41	1.93
ZC7used	62.26	13.76	23.98	4.5	0.38	1.74
ZC9fresh	63.01	19.56	17.43	3.2	0.27	0.89
ZC9used	63.3	18.90	17.8	3.3	0.28	0.94

**Table 4.** Comparison of dehydrocyclization activities at a reaction temperature of 400 °C over ZC7 and ZC9 catalysts.

Catalyst	Spec		
	2-Methylpyrazine	2-Pyrazinylmethanol	Others <sup>b</sup>
ZC7 ZC9	2.91 5.89	1.33 1.73	0.56 0.45

<sup>a</sup>Specific rates of 2-methylpyrazine and 2-pyrazinylmethanol measured with respect to 2MP and 2-pyrazinylmethanol yields normalized by  $S_{\text{BET}}$ 

<sup>b</sup>Others include pyrazine, 2-pyrazinaldehyde and (-2,6; -2,5; -2,3)-dimethylpyrazines

of 2-pyrazinylmethanol is observed on ZC9 compared to ZC7. Formation of 2MP occurs by homo-coupling of 2-pyrazinylmethanol which undergoes a cyclic transition state.<sup>7</sup> A marginal difference is observed in the rate of 2-pyrazinylmethanol over ZC7 and ZC9 compared to the rate of 2MP ( $^{2MP}r_{ZC9}$ : $^{2MP}r_{ZC7} = 2$ ) suggesting higher cyclization activity of ZC9 than the ZC7 sample.

# 4. Conclusion

Hydrotalcite precursors of Zn-Cr synthesized at pH = 7 and 9 produced a mixed oxide of  $ZnO-ZnCr_2O_4$  upon calcination in air at 450°C. XRD and FT-IR analysis of Zn-Cr-O indicated the presence of both ZnO and  $ZnCr_2O_4$  species. Presence of stabilized  $Cr^{3+}$  species in both ZC7 and ZC9 samples was observed in ESR investigations. Decrease in peak to peak width ratio was huge in the case of ZC7 which is attributed to the presence of large size particles. TEM studies revealed the formation of large size particles in Zn-Cr-O obtained at low pH. Compositions obtained from EDX analysis showed chromium enrichment in the bulk of the Zn-Cr-O sample. In contrast, XPS analysis indicated that Zn-Cr-O synthesized at higher pH ( $\sim$ 9) is found to have Zn enrichment at the near-surface region. High dehydrocyclization activity of Zn-Cr-O synthesized at pH =9 was explained as due to small-sized Zn-Cr-O particles and Zn-enriched Zn-Cr-O surface. Finally, it can be concluded that nano-sized mixed oxide ZnO-ZnCr<sub>2</sub>O<sub>4</sub> catalyst derived from HT precursor synthesized at pH  $\sim$ 9 is found to be highly efficient in the conversion of bioglycerol to 2-methylpyrazine. Thus, this process can be extended to utilize bio-glycerol for the industrially important anti-TB drug intermediate.

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