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Application of Subcritical Water for Production of ZnO Nano-Catalyst

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Abstract: The effect of process parameters (temperature and time) on preparation of ZnO nano catalyst using subcritical water was investigated. The amount of produced ZnO catalyst was dependent on temperature during subcritical water treatment. Increasing the temperature from 120 to 180 °C decreased the ZnO catalyst with particle size larger than 2.5 µm. In contrast the amount of nano sized ZnO catalyst increased rapidly when increasing the process temperature. Up to about 50 % nano sized ZnO catalyst could be produced at 180 °C and 4 h reaction time. In general the total produced ZnO catalyst using subcritical water was more than 2 times higher than conventionally prepared ZnO. Interestingly the ZnO catalyst prepared by subcritical water showed distinctly higher (up to 0.96 g/ml) bulk density compared to conventional prepared ZnO (about 0.47 g/ml). The Hemmet indicators have shown that the subcritical water prepared catalyst was higher basic strength than the conventionally prepared catalyst. The FTIR investigation of samples has shown that the subcritical water prepared catalyst has more impurities than the conventionally prepared ones. Additional experiments are necessary to determine the type of impurities in ZnO catalyst prepared by subcritical water method.

Keywords: Subcritical water, ZnO catalyst, Density, FTIR, Hemmet indicator

I. INTRODUCTION

A great deal of attention is being paid to metal oxide nano-particles of 1-10 nm in diameter. They are of interest in several fields ranging from material science and catalysis to biology. Their behavior is strongly related to the particle size. Nano-structured metal oxides are expected to have unusual electronic, optical, magnetic and chemical properties that differ from those of atomic or molecular species and bulk states [1]. Zinc oxide nanoparticles is one of the most studied metal oxide materials. That is because of multifunctional characteristics of ZnO and various options to tune its properties by controlling size and morphology. ZnO Nano-particles could be used in various areas such as electronics, gas sensors, UV photo detector materials, solar cells, cosmetics and other applications [2-3]. Due to the wide range of applications, enormous efforts have been made to explore expedient synthetic ways of producing ZnO nano particles with different particle sizes, various particle shapes and surface modification. In general, ZnO particles can be produced using precipitation [4], spray pyrolysis [5], thermal decomposition [6], and hydrothermal synthesis [7-9]. Ohara et al [10] have applied hydrothermal synthesis method to produce ZnO nano particle at 400 °C with a very short reaction time of 18 s. They have found that it is possible to produce ZnO nano particle with uniform particle size distribution and highly crystalline phase. The aim of this study was to study the effectiveness of the subcritical water method for production of ZnO nano catalysts and to investigate the physical properties of produced ZnO nano catalysts.

II. MATERIAL AND METHODS

A. Chemicals

Urea and Zinc acetate were purchased from Science Integration Company Limited (Thailand). Chemicals used for Hemmet indicator (Neutral red, Bromthymolblue, 2,4 Dinitroaniline, Phenolphthalein) were analytical grade.

B. Equipment

For production of ZnO nano particles using subcritical water method an own designed laboratory scale subcritical water equipment (max. operation pressure and temperature of 100 bars and 200 °C respectively) with about 1500 ml volume was applied (Fig. 1).

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Fig. 1: Subcritical water equipment for production of nano ZnO catalyst

C. ZnO Nano particle preparation methods

The conventional ZnO preparation method was carried out at boiling temperature and atmospheric pressure. 100 ml of 2 M Urea (12% w/v solution) and 100 ml of 1.27 M of Zinc acetate (37.75% w/v solution) were added to a 500 ml beaker and the beaker was placed in a water bath at boiling temperature (99 ± 2 °C). The beaker content was mixed during reaction time using a magnetic stirrer at 250 rpm. The reaction time was started after the temperature inside the beaker was 95 °C and the boiling was continued until the reaction was completed (0.5, 1, 2, 4hs). After that the beaker was removed from the water bath and the content was filtered on an ash less filter paper (Whatmann Nr. 44, pore size Of 2.5 μm , Germany). Finally the remaining solid on the filter paper (particle size larger than 2 μm) was dried in a hot air oven at 150 °C for 8 h. The dried sample was placed in clean and pre-weight crucible and sintered at 450 °C for 8 h. For production of nano ZnO catalyst using Subcritical water, 100 ml of 2 M Urea and 100 ml of 1.27 M of Zinc acetate were poured inside the vessel and the vessel was closed tightly. The Subcritical equipment was then fixed inside an oil bath on magnetic stirrer. The magnetic stirrer (250 rpm) and the heating elements were turned on. After the temperature inside the vessel achieved the treatment temperature (120, 140, 160, and 180 °C), the heat treatment at constant temperature was continued until the reaction was completed (0.5, 1, 2, 4hs). After that the vessel was removed from the oil bath, immersed in a large pot containing cold tap water, until the pressure inside the vessel dropped to atmospheric pressure. Finally the vessel was opened and the content poured inside a beaker. The beaker content was poured on a filter paper and filtered as described above. The ZnO on filter paper (particle size larger than 2 μm) was dried in a hot air oven at 150 °C for 8 h. The dried sample was placed in a clean and pre-weight crucible and sintered at 450 °C for 8 h.

The filtrate phases of each of the samples were kept at room temperature in a plastic bag for 3 weeks to measure the amount of nano sized ZnO particle passed through the filter paper (particle size less than 2 μm) during filtration.

The sediment production (ZnO nano particle agglomerate) during storage time (3 weeks) was filtered on filter paper with pore size of 2 μm and dried at 150 C for 8 hs. The weight of dried sample considered as nano ZnO particles (with particle size less than 2 μm) that produced during conventional and subcritical water treatment.

D. Analytical methods

Weight of ZnO nano particle was determined gravimetrically after drying in an oven (150 °C, 8 h) and after sinter (450 °C, 8 h).

The basic strength of produced ZnO nano particle before and after sinter was determined using the Hemmet indicator method with modifications. For each sample 4 test tubes containing 0.0500 g of ZnO nano particle were prepared. 4 ml dist water was added to each test tube. Finally, 1 ml of Hemmet indicator diluted in methanol (0.5 mM neutral

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red [$H_{\text{c}} = 6.8$], 2.5 mM Bromthymolblue [$H_{\text{c}} = 7.2$], 2.5 mM 2,4 Dinitroaniline [$H_{\text{c}} = 9.3$], 2.5 mM Phenolphthalein [$H_{\text{c}} = 15.0$]) was separately added inside the test tube. The color change of indicators in each test tube was observed and documented.

Fourier transmission infrared (FTIR) spectra were recorded in transmission mode using FTIR (MicoIET 6700, FTIR). All measurements were conducted at room temperature with wave numbers in the range $400\text{--}4000\text{ cm}^{-1}$ with 2 cm^{-1} resolution.

The true density of nano-catalyst was measured using Micromeritics Accupyc 1330. The gravimetric method was applied for measurement of bulk density of catalyst.

III. RESULTS AND DISCUSSIONS

A. *ZnO Production:* Production of ZnO nano catalyst (particle size larger than $2.5\text{ }\mu\text{m}$) during heat treatment at boiling temperature was dependent on reaction time. A nearly linear increasing of produced ZnO catalyst with increasing of reaction time was observed. Despite longer reaction time of 4 h the ZnO producing was low (5.42 g) (Fig. 2).

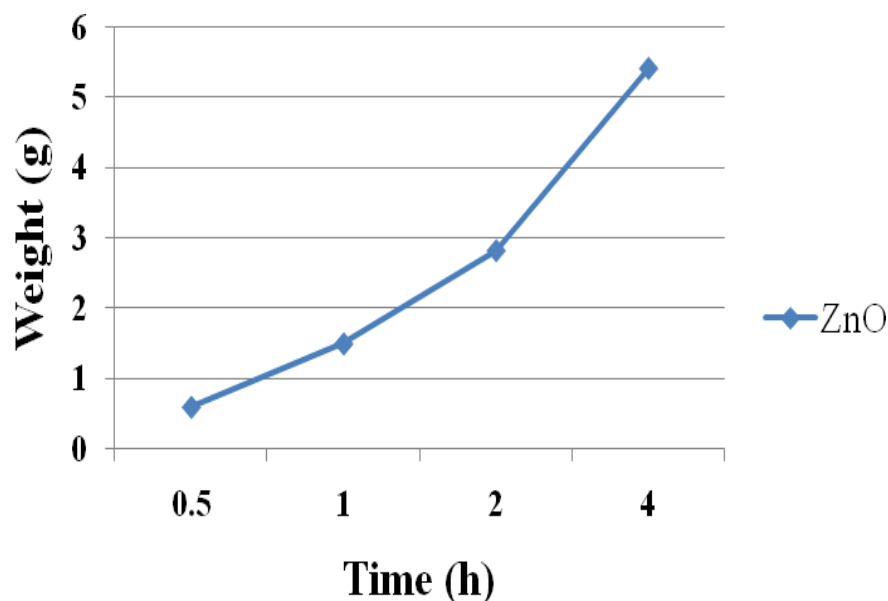


Fig. 2: Effect of reaction time on ZnO production (with particle size $\geq 2.5\text{ }\mu\text{m}$) using conventional boiling method

Fig. 3 demonstrates the effect of temperature during ZnO preparation using conventional boiling and subcritical water method and 4 hour reaction time. In general the weight of produced ZnO particle (particle size larger than $2\text{ }\mu\text{m}$) in the case of subcritical water treatment was distinctly higher than the conventionally produced ZnO. With increasing the process temperature during subcritical treatment a slight decreasing of ZnO amount was obvious. Interestingly, the reaction time showed only a negligible effect on the amount of ZnO (Fig. 4). This may be because of higher partial amount of nano sized ZnO particles that could pass through the filter paper during the filtration. The measurement of ZnO content in filtrate confirmed this hypothesis (Table 1). After 0.5h subcritical water treatment at $180\text{ }^{\circ}\text{C}$ a higher amount ($\square 7.6\text{ g}$) of ZnO could be produced (Fig. 4) than after 4h using the conventional method (5.5 g). This indicated that the subcritical water treatment not only decreased the reaction time but also increased the ZnO yield. Sintering of dried ZnO led to a distinct decreasing of sample weight (up to 25 % on the basis of weight before sinter) in the case of subcritical water treated samples. In contrast the conventionally produced ZnO showed only slight weight decreasing (about 4%) during sintering (Fig.5). The higher weight loss of subcritical water treated ZnO during sintering is probably because of higher amounts of impurity in the sample. It seems the reaction path

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way during ZnO production using conventional method (boiling) and subcritical water treatment is different. Whereas during reaction of urea and zinc acetate at boiling temperatures mainly ZnO will be produced, the reaction at subcritical conditions may be too complex with molecules containing complex structures of ZnO, urea and acetate. The measurement of pH in filtrate of subcritical water treated samples indicated distinctly higher pH values compared to the pH of filtrate in the case of the conventional method (Table 2). To confirm this hypothesis additional experiments such as XRD and TEM analysis are necessary.

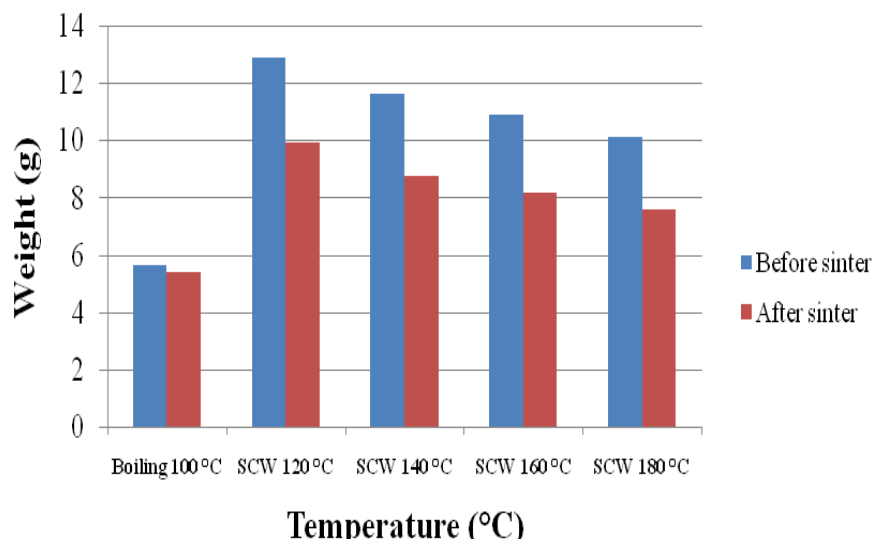


Fig. 3: Effect of process temperature during ZnO production using conventional boiling and subcritical water method on amount of ZnO

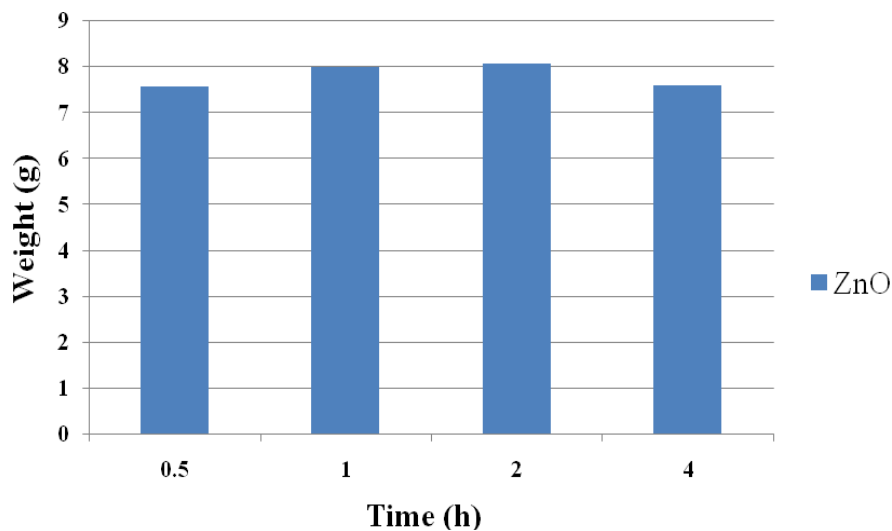


Fig. 4: Effect of process time during ZnO production using subcritical water method at 180 °C

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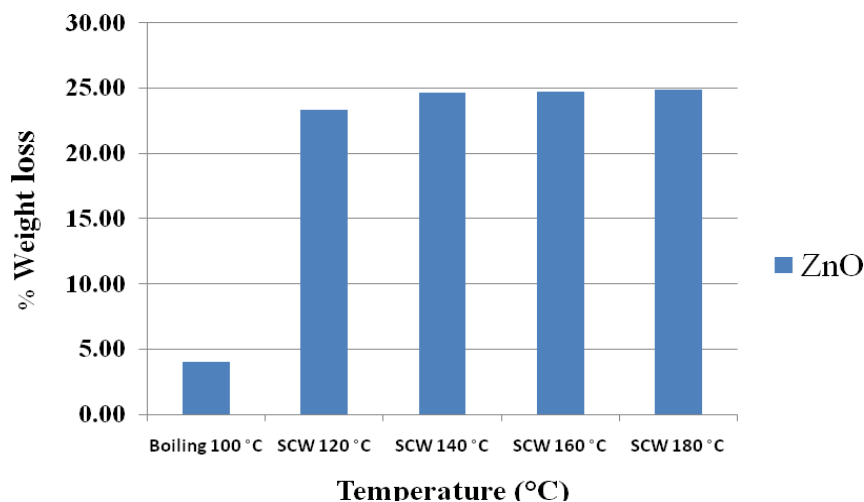


Fig. 5: The relationship between % Weight loss of produced ZnO during sintering and the process temperature during ZnO production.

The measurement of the ZnO in filtrate (after 3 weeks storage at room temperature and subsequent filtration on filter paper) made clear that the subcritical water is a suitable method to produce ZnO nano particles with particle size less than 2 μm. Whereas the amount of nano ZnO in the case of conventional boiling method was very low (1.6% on total ZnO weight basis), the amount of produced nano sized ZnO in the case of subcritical water treatment was very high (up to 50 % of total produced ZnO) (Table 3). Considering only the weight of nano sized ZnO, it could be shown that the amount of nano sized ZnO using subcritical water was much higher than the total amount of ZnO produced by conventional method (Table 3).

TABLE 2 PH-value of filtrate from conventional and subcritical water treatment samples

Treatment methods	pH of filtrate
180 °C, 0.5 h	8.56
180 °C, 1 h	8.62
180 °C, 2 h	8.55
180 °C, 4 h	8.61
160 °C, 4 h	7.64
140 °C, 4 h	7.08
120 °C, 4 h	6.65
Boiling 4h	--
Boiling 2h	5.64
boiling 1h	5.65
boiling 0.5 h	5.62

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TABLE 3 Amount of ZnO on filter paper (particle size larger than 2.5µm) and in filtrate of conventional and subcritical treated samples

Treatment methods	Weight of ZnO on Filter paper (g)	Weight of ZnO in Filtrate (g)	Total ZnO production (g)	% ZnO nano-particle (less than 2 µm size)
180 °C. 0.5 h	10.18	4.03	14.21	28.38
180 °C. 1 h	10.50	4.77	15.27	31.21
180 °C. 2 h	10.57	5.75	14.32	40.16
180 °C. 4 h	10.12	9.76	19.88	49.07
160 °C. 4 h	10.87	8.41	19.28	43.62
140 °C. 4 h	11.64	0.11	11.75	0.96
120 °C. 4 h	12.90	0.01	12.96	0.04
Boiling 0.5h	0.61	0.26	0.87	29.94
Boiling 1h	1.53	0.26	1.79	14.52
boiling 2h	2.88	0.15	1.68	8.94
boiling 4 h	5.65	0.09	5.74	1.61

B. *Hemmet indicator results:* The results of Hemmet indicator have shown that in general the ZnO nano catalysts prepared using subcritical water have higher basic strength than the samples prepared at boiling temperature of water. Basic strength of catalysts prepared at 120, 140, 160 and 180 °C was high ($H_{-}=8.2$ and $H_{-}=15$) (color change of phenolphthaleine), whereas the basic strength of catalysts prepared at boiling temperature of water (95 °C) was less than $H_{-}= 8.2$ (no color change of phenolphthaleine). This indicated that using subcritical water method it is possible to produce ZnO catalyst with higher catalytic activity due to higher basic strength.

TABLE 4 Basic strength of ZnO nano catalyst prepared at different temperature

ZnO	Neutral red ($H_{-} = 6.8$)		Bromthymolblu ^e ($H_{-} = 7.2$)		phenonpthalein ($H_{-} = 8.2$)		2,4-dinitroaniline ($H_{-} = 15$)	
	Befor e sinter	After sinte r	Befor e sinter	After sinte r	Befor e sinter	After sinte r	Befor e sinter	After sinte r
Boiling, 0.5 h	+	+	+	+	-	-	-	-
Boiling, 1 h	+	+	+	+	-	-	-	-
Boiling, 2 h	+	+	+	+	-	-	-	-
Boiling, 4 h	+	+	+	+	-	-	-	-
SCW 120 °C, 4 h	+	+	+	+	+	+	-	-
SCW 140 °C, 4 h	+	+	+	+	+	+	-	-
SCW 160 °C, 4 h	+	+	+	+	+	+	-	-
SCW 180 °C, 4 h	+	+	+	+	+	+	-	-
SCW 180 °C, 0.5 h	+	+	+	+	+	+	-	-
SCW 180 °C, 1 h	+	+	+	+	+	+	-	-
SCW 180 °C, 2 h	+	+	+	+	+	+	-	-
SCW 180 °C, 4 h	+	+	+	+	+	+	-	-

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- = color of indicator doesn't change

+ = color change

C. *Density:* The results of density measurement of sintered ZnO catalyst are shown in Table 4. Generally the true density of subcritical water prepared ZnO was negligibly higher than conventionally prepared ZnO. In contrast the subcritical water prepared ZnO showed distinctly higher bulk density compared to conventionally prepared ZnO. The highest bulk density (0.9648 g/ml) was observed for subcritical water treated samples at 180 °C for 4 h. This indicated that the Subcritical water prepared ZnO has a compact structure. Within the subcritical treated samples the bulk density increased with increasing the treatment temperature. The bulk density of conventionally prepared ZnO was distinctly lower than using subcritical water prepared ZnO and ranged between 0.4678 and 0.4072 g/ml.

TABLE 5 Effect of conventional and subcritical water treatment on true and bulk density of sintered ZnO

Treatment methods	True Density (g/ml)	Bulk Density (g/ml)
180 °C, 0.5 h	5.8577±0.0614	0.7621±0.0218
180 °C, 1 h	5.8218±0.0314	0.8773±0.0253
180 °C, 2 h	5.9860±0.0712	0.9241±0.0147
180 °C, 4 h	6.0368±0.0549	0.9648±0.0143
160 °C, 4 h	5.7065±0.0416	0.9004±0.0126
140 °C, 4 h	5.6541±0.0282	0.9199±0.0385
120 °C, 4 h	5.6246±0.0568	0.6700±0.0156
Boiling 4h	5.2116±0.0303	0.4678±0.0363
Boiling 2h	5.1477±0.1191	0.4072±0.0256
boiling 1h	5.3823±0.4235	0.4574±0.0340
boiling 0.5 h	5.9627±0.4897	---

D. *FTIR- results:* From Figures 6 and 7 the zinc nitrate and urea have different FTIR spectra. Zn-acetate has 2 main peaks at wave lengths of 3335 and 1326 cm⁻¹. In addition, two small peaks at 1625, 1047 and 819 cm⁻¹ were obvious. In the case of urea 4 main peaks at 3427, 3330, 1589 and 1458 cm⁻¹ can be indicated. Additional small peaks at 1674 and 1149 cm⁻¹ could be observed. The FTIR spectra of using conventional method and subcritical water prepared ZnO was distinctly different. Whereas the FTIR spectra of conventionally produced ZnO (before sinter) showed only two main peaks (Fig. 8) at 1371 and 3483 cm⁻¹, in the case of at 120 and 140 °C subcritical water treated samples three main peaks at 1328, 1496 and 3348 cm⁻¹ were obvious (data not shown). With increasing the temperature higher than 140 °C an additional peak at 1550 cm⁻¹ appeared (Fig. 9). The position of these three peaks in subcritical water treated samples were nearly similar to position of peaks in urea (1589, 1458 cm⁻¹) and zinc nitrate (1329 cm⁻¹). It seems that in the case of subcritical treated samples both of zinc nitrate and urea as impurities (maybe as complex molecules) exist in the produced ZnO. Interestingly, sintered samples don't show any peaks at 1589, 1458 cm⁻¹ and 1329 cm⁻¹ (data not shown). This is may be because of degradation of complex molecules containing residual of urea and zinc nitrate during sintering.

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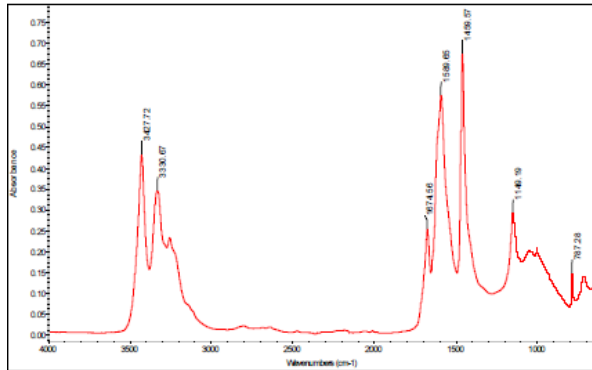


Fig. 6: FTIR spectra of Urea

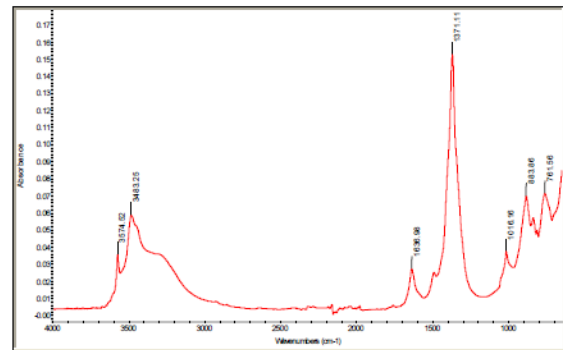


Fig. 8: FTIR spectra of conventional prepared ZnO (before sintering)

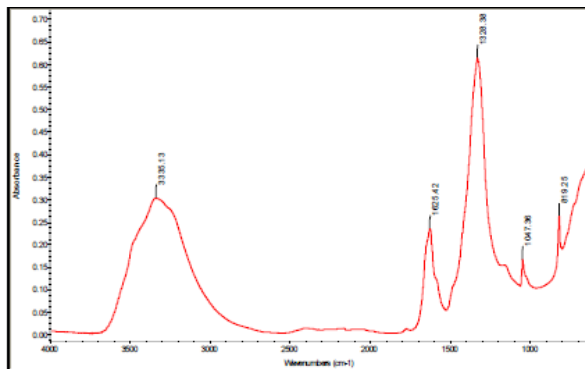


Fig. 7: FTIR spectra of Zinc nitrate

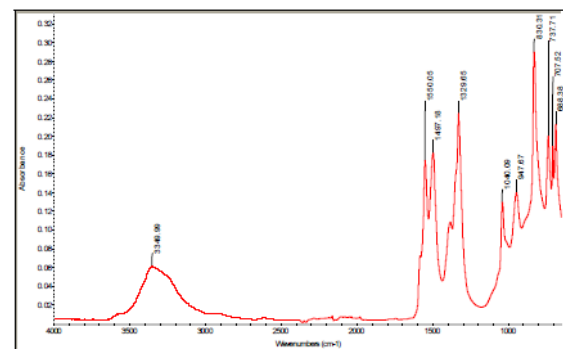


Fig. 9: Subcritical water prepared ZnO (before sintering)

IV. CONCLUSION

The application of subcritical water for preparation of ZnO catalyst was investigated in this study. In addition the performance of subcritical water prepared ZnO catalyst was compared with conventionally prepared ZnO catalyst. The results of this study have indicated that using the subcritical water method distinctly higher ZnO could be produced compared to the conventional boiling method. Whereas the amount of produced ZnO during conventional method was strongly dependent on the reaction time, the amount of produced ZnO using subcritical water was nearly independent of the reaction time. The bulk density of subcritical water prepared ZnO catalyst was distinctly higher than conventionally prepared ZnO (0.40 - 0.46 g/ml) and ranged between 0.67 - 0.96 g/ml. Sintering of subcritical prepared ZnO resulted in up to 25 % weight loss (on sample weight basis before sintering) compared to about 4% for conventionally prepared catalyst. The FTIR investigation of samples has shown that the subcritical water prepared catalysts have more impurities than the conventionally prepared samples. Additional experiments are necessary to determine the type of impurities in ZnO catalysts prepared by the subcritical water method.

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