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Structural Characterization of Ni/ZrO₂/SiO₂ Nanocomposites Prepared by Wet Impregnation Route

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Structural Characterization of Ni/ZrO₂/SiO₂ Nanocomposites Prepared by Wet Impregnation Route

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Abstract. Investigation of hydrogenation catalytic application has become an interesting subject area by many experts, especially in nanoscience and nanotechnology. In general, metal-based SiO₂ and ZrO₂ composites become one of the promising materials to be applied as a hydrogenation support catalyst. In this work, we report the synthesis of Ni/SiO₂/ZrO₂ nanocomposites by using impregnation route. The characterization was done by means of XRD, XRF and SEM to investigate the structural, elemental compositional and morphological behaviors of the samples. Based on the data analysis, it showed that the presence of ZrO₂ during synthesis causes the crystallinity change of the SiO₂ from crystallite to amorphous phase. The addition of Ni loading altered the XRD pattern originating from amorphous SiO₂ and crystallite growth of the samples. Meanwhile, the elemental analysis exhibited that the change of metal composition in concomitant with the addition of Ni and Zr. Furthermore, the microscopy analysis showed that the samples have agglomerated shape in nanometric size. Therefore, the prepared Ni/ZrO₂/SiO₂ in this work opens the potential to be applied as hydrogenation catalyst.

Keywords: Catalyst, hydrogenation, nanocomposites, ZrO₂, SiO₂, nickel

1. Introduction

In general, the hydrogenation reaction is the reduction of the unsaturated compound into a saturated one in the presence of the catalyst and hydrogen gas. This reaction is very promising in several sophisticated applications, for example in the conversion of biomass into liquid fuel and chemicals [1]. Foraita *et al.* reported that the chemical properties of the catalyst controlled the reaction product [2]. Then, the preparation of the catalyst is predominant for directing the surface area as well as the shape morphology of the catalysts [3]. Since the catalyst become a crucial issue in the completion of many reactions, it becomes an interesting subject area for many experts in nanoscience and nanotechnology to develop a novel catalyst or nanocomposite for specific purposes.

Metal oxide catalysts- based, such as zirconia (ZrO₂) and silica (SiO₂) have interesting physical and chemical properties. In general, ZrO₂ has high hydrothermal stability and suppress carbon deposition on catalyst surface during the reaction. However, it has a lower surface area which promotes the decreasing of the product conversion and selectivity [4]. Meanwhile, SiO₂ has ability to enhance the surface area



of ZrO₂ by the formation of novel spherical and nano-layer shaped morphology [2]. Therefore, a deep fundamental studies as well as structure investigation of the blending composites of ZrO₂ and SiO₂ is important to be conducted. Such investigation is essential to expect a new characteristic, such as increasing the surface area, inducing the Brønsted acid sites, or the enhance of hydrothermal stability for hydrogenation reaction of bio-based compound in acidic, basic or neutral medium [2–5].

In the previous work, Li *et al.* reported the framework of the ZrO₂/SiO₂ combine with SO₄²⁻ ion gave a large surface area of composites. The ethane bridged moieties promote -Zr-O-Si-C-C-Si- linkages gave super-acid for high activity in the transesterification reaction. However, the presence of sulfur is contaminating the product [6]. In order to overcome such problem, the insertion of non-noble metal becomes a promising strategy to design hydrogenation catalyst compared with impregnation of noble-metal which is rather expensive [2,7].

Regarding the hydrogenation catalyst, nickel (Ni) has been widely reported as a metal precursor for hydrogenation reaction of lignin derivatives and hemicellulose for biofuels and chemicals synthesis [8–13]. Furthermore, the structural investigation of Ni supported on metal oxide is an important task since the rate-determining step in hydrogenation and/or deoxygenation reaction depends on the activation of H₂ by metal [14]. The oxide-based catalyst was also proposed to derive the reaction by oxygen chemisorption on unsaturated metal site, proton donation from a hydroxyl group and the desorption in the final step [7]. Based on the logical explanation above, therefore in this work, we investigate the structural characterization of metal oxide composites for catalytic performance.

2. Methods

2.1. Materials

The precursor used in this research were Ni(NO₃)₂·6H₂O, ZrOCl₂·8H₂O and SiO₂ purchased from Merck (Germany) in analytical grade. The solvent for wet impregnation route was demineralized water HYDROBAT (Indonesia) obtained from the local vendor and used as received. The NH₄OH (Merck, Germany) in analytical grade were used for precipitation of Zr(OH)₄ from ZrOCl₂·8H₂O. N₂ gas in >99.99% purity for calcination and Ultra-High-Purity (UHP) H₂ gas for reduction of the samples were supplied by PT. Tira Austenite Indonesia.

2.2. Synthesis procedures

The synthesis of Ni/ZrO₂/SiO₂ composites was followed to Zhang *et al* with modification [8,13]. The SiO₂ is provided from the commercial silica gel 60 Merck Germany with particle size 0.063-0.200 mm, and ZrO₂ was prepared by precipitation of ZrOCl₂·8H₂O. The ZrO₂/SiO₂ was prepared in the ratio of 1:1 (wt/wt). Amount of ZrOCl₂·8H₂O was dissolved in water then added with ammonia solution until a white precipitate appeared (pH = 8). Amount of SiO₂ was added to the slurry and continue to stir for 12 hours by heating the solution at 75 °C. The filtration of the slurry gave a white solid then dried at 120 °C for 12 hours. Calcination of the solid at 500 °C in the N₂ gas followed by reduction at 500 °C for 5 hours gave ZrO₂/SiO₂ composites. After the preparation of the SiO₂/ZrO₂ support, nickel (Ni) was introduced into the composites by wet impregnation routes. The synthesis of Ni/ZrO₂/SiO₂ was prepared using Ni(NO₃)₂·6H₂O salt and dissolved in free-ion water (10% and 20% by weight), then aging with the slurry of ZrO₂/SiO₂ for 12 hours at ambient condition. After calcination using N₂ and reduction using H₂ at 500 °C for 5 hours, the samples were evaluated for the crystallinity and Ni content.

2.3. Structural characterizations of Ni/ZrO₂/SiO₂ composites

The phases and crystal structure of Ni/ZrO₂/SiO₂ composites were characterized by X-Ray Diffractometer PHILIPS PW 1800, Cu-K α radiation 1.5406 Å at 40 kV and 40 mA scanned at 2-theta = 20° – 80° with a scan rate of 1°/min. The elemental composition of the composites was recorded by X-Ray Fluorescence PAN analytical MiniPal 4. Meanwhile, the particle size and surface morphology were investigated by Scanning Electron Microscopy (SEM) Phenom.

3. Results and Discussion

Figure 1 shows X-ray diffraction patterns of the SiO_2 and $\text{ZrO}_2/\text{SiO}_2$ prepared by wet impregnation route. Based on the Figure 1 (a), the diffraction pattern of SiO_2 before impregnated with ZrO_2 reveals the crystalline phase of alpha- SiO_2 with specific diffraction at 2-theta = 20.89° (100), 26.72° (011), 36.63° (110), 39.54° (102), 42.49° (200), 50.21° (112), 60.00° (121), and 67.78° (031). In more detail, the alpha- SiO_2 has trigonal structure with the space group number of $P3_221$ (No. 154). In general, SiO_2 constructs a framework structure of SiO_4 tetrahedra. In this structure, the Si atoms are linked by shared 'corner' oxygens as shown in Figure 2.

In this work, the interesting data occurred after the impregnation process with ZrO_2 , where the broad peak appears at 2-theta in the range of 25°–35° originated from the presence of SiO_2 in the amorphous phase. In means that the crystalline state transforms to amorphous state initiated from impregnation process. Therefore, it is difficult to calculate the particle size from the Scherrer equation. Physically, such compound constructed composite system from ZrO_2 and SiO_2 as shown in Figure 1 (b). The changes of the crystallinity of SiO_2 in this work is also in line as reported in the previous work [8] and the obtained x-ray diffraction pattern is also similar to the reported data [8]. Additionally, Morimoto *et al.* reported that the oxide, for example ZrO_2 , suppressed surface crystallization and reduce the crystal growth rate [15]. Furthermore, Dennis and co-workers reported that such changes might due to the temperature reaction when impregnation using metal ion is performed [16]. By this reason, the formation of amorphous SiO_2 after the impregnation and calcination can be explained by crystal growth formation theory [17].

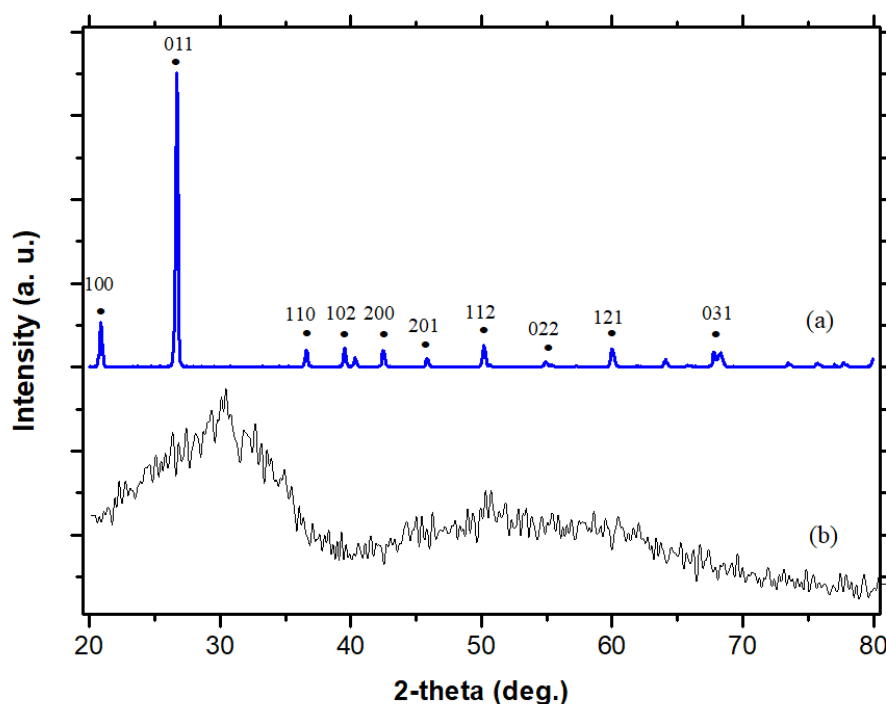


Figure 1. XRD spectra of (a) SiO_2 and (b) $\text{ZrO}_2/\text{SiO}_2$

The presence of Ni in the catalyst is detected from the X-ray diffraction data at 2-theta = 44.45° (111), 51.81° (200), and 76.27° (202) which is in line with the data of JCPDS 96-210-2279. In both composites, the absent of NiO peak at 2-theta = 37°, 43°, and 64° showed that the reduction at the temperature of 500 °C completely reduced Ni^{2+} into Ni^0 [9]. The diffraction intensity of Ni in Figure 3 (b) is higher than those of Figure 3 (a) by the different Ni loading. To support this data, the elemental analysis obtained from X-ray fluorescence characterization is tabulated in Table 1. The actual Ni content for 10% Ni/ $\text{SiO}_2/\text{ZrO}_2$ is 9.77% and 20% Ni/ $\text{SiO}_2/\text{ZrO}_2$ is 17.1%. The interesting phenomenon is the

amorphous SiO_2 become crystalline again after Ni impregnation. The formation of SiZrO_4 spinel is recorded on XRD at $2\text{-theta} = 26.99^\circ$. In our knowledge, this is the first report for SiO_2 crystallinity changing by Ni insertion using wet impregnation route. Then, analysis of Zr/Si ratio in the composites is revealed 10:1 by XRF.

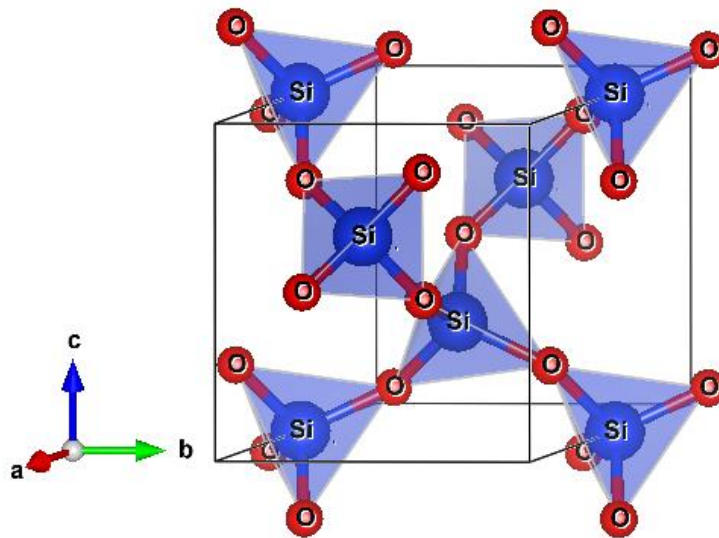


Figure 2. Crystal structure of SiO_2

Table 1. Elemental composition of Ni/ZrO₂/SiO₂ as determined by X-ray fluorescence

Sample	Element content (% weight)							
	Zr	Si	Ni	Ca	Mn	Fe	Cu	Y
10Ni/SiO ₂ /ZrO ₂	76.7	7.48	9.77	0.19	0.13	4.60	0.74	0.23
20Ni/SiO ₂ /ZrO ₂	70.7	7.15	17.1	0.20	0.26	5.09	-	0.48

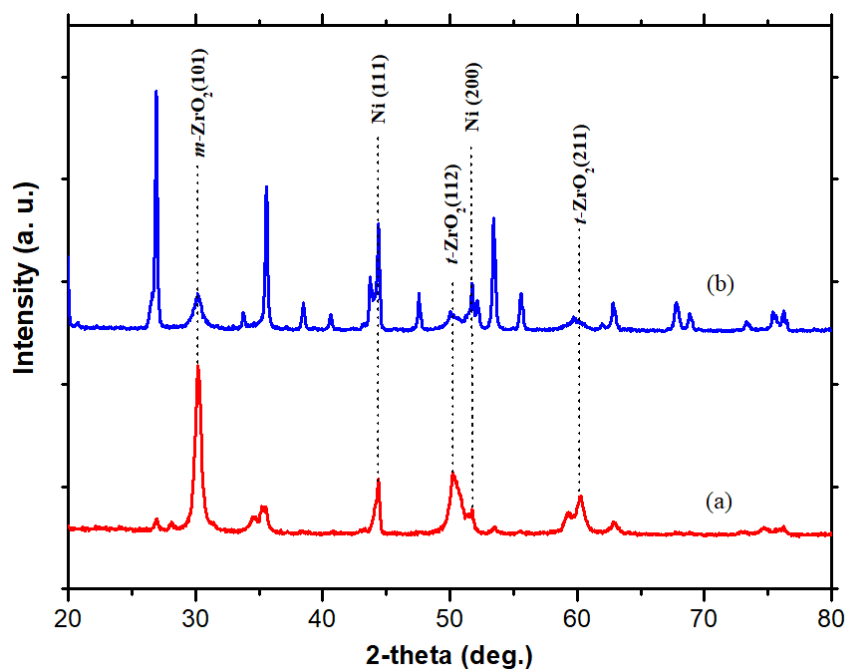


Figure 3. XRD spectra of (a) 10% Ni/ZrO₂/SiO₂ and (b) 20% Ni/ZrO₂/SiO₂

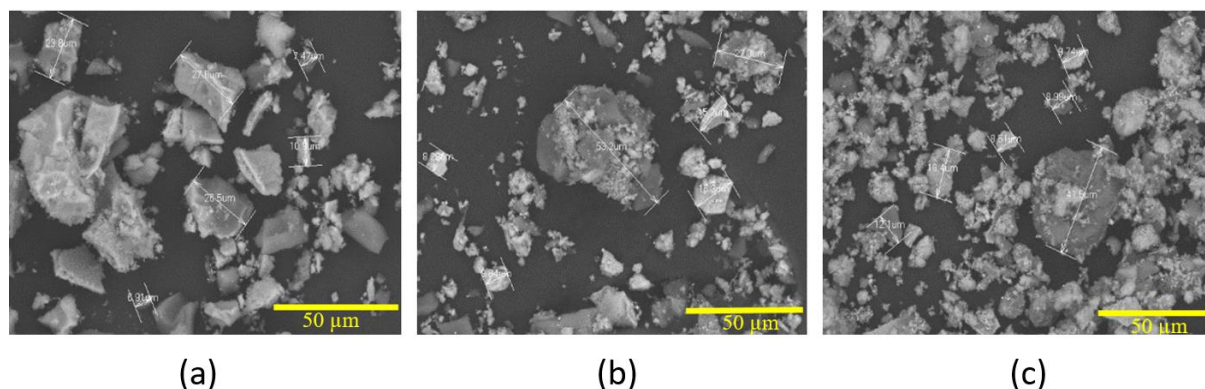


Figure 4. SEM images of (a) $\text{SiO}_2/\text{ZrO}_2$, (b) $10\text{Ni}/\text{SiO}_2/\text{ZrO}_2$, and (c) $20\text{Ni}/\text{SiO}_2/\text{ZrO}_2$

The morphology of $\text{Ni}/\text{ZrO}_2/\text{SiO}_2$ by SEM is depicted in Figure 4. Before impregnation as shown in Figure 4 (a), the particle size is distributed within 6.91–27.8 μm . After impregnation of 10% Ni as shown in Figure 4 (b) and 20% Ni in Figure 4 (c), the reducing particle size is observed. The insertion of Ni into $\text{ZrO}_2/\text{SiO}_2$ broke the support and gave irregular shape. The EDX analysis was also confirmed that Ni is distributed on the composites. Another phenomenon is the agglomeration processed which is detected by the formation of a particle in the size of 41.5–53.2 μm after Ni impregnation. In correlation with this work, Rahemi *et al.* reported that wet impregnation methods easily promote the aggregation of the metal and the oxide by rigorous contact in the solution [18]. Furthermore, since the distribution of the samples is in nanometric size, the samples are promising for catalytic reaction application.

4. Conclusion

The characterization of $\text{Ni}/\text{ZrO}_2/\text{SiO}_2$ composites was determined by XRD, XRF, and SEM analysis showed that the wet impregnation routes can be used for Ni deposition into $\text{ZrO}_2/\text{SiO}_2$. In the first step, the crystallinity of SiO_2 was changed into amorphous by the addition of ZrO_2 . Then, the addition of Ni restored the crystallinity of SiO_2 by the formation of SiZrO_4 . Increasing of Ni loading into $\text{ZrO}_2/\text{SiO}_2$ influence the morphology of the composites and particle size gave potential application as a hydrogenation catalyst.

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