Catalytic activity of Ru-Sn/Al₂O₃ in reduction reaction of pollutant 4-Nitrophenol

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Abstract. Ru-Sn/Al₂O₃ bimetallic nanocatalysts have been synthesized by using conventional and microwave impregnation methods. Structure and morphology of the samples were characterized using XRD, XPS, and TEM. XRD and XPS measurement have confirmed the presence of Ru and Sn in the samples. According to TEM results, the morphology of the catalyst strongly depends on the preparation route and stabilizing agent (i.e. PVP). The sample with PVP (polyvinylpyrrolidone) has better nanoparticles distribution over the support. A sample prepared by conventional method has an agglomeration of nanoparticles on the support. Catalytic activities of both samples were examined in the reduction reaction of pollutant, i.e. 4-nitrophenol. Catalytic examination showed that reaction rate of 4-nitrophenol reduction by using microwave-assisted sample has improved 3.5 times faster than conventional impregnation sample.

1. Introduction
Bimetallic nanoparticles have attracted much attention due to their unusual physical and chemical properties compared to monometallic. It has also been reported that they have broad applications in catalysis, photonics, electronics and drug delivery [1-3]. Ruthenium has been known to show very unique and interesting activity as the catalyst in many processes, including in ammonia synthesis [4], in hydrogenation reaction [5] and in wastewater treatment [6]. Ruthenium is a precious metal and its resources are limited and expensive. Therefore, Tin (Sn) is one of low-cost metal, abundantly available on earth. Effect of Sn has different response to its particular metal pair for certain application. In most hydrogenation process, addition of Sn to Ru are very promising, as it improves the chemoselectivity of the catalyst [7]. Metal oxides could be used to stabilize and anchor the nanoparticles to reduce the agglomeration of nanoparticles [8,9]. Compared to the conventional heating, microwave method is very promising. It has rapid volumetric heating, higher reaction rates and shorter reaction time [10]. Microwave radiation provides a quick, efficient, and uniform heating method that facilitates the formation of uniform nucleation centres [11].

In this paper, we report the preparation of Ru-Sn bimetallic nanoparticles via a microwave-polyol method and their use in the reduction of 4-nitrophenol. 4-nitrophenol (4-NP) is one of the frequently occurring by-products, which is toxic to the environment. These phenolic compounds are considered as priority pollutants since they are harmful to organisms even at low concentrations [12]. These samples were characterized by transmission electron microscope (TEM), X-Ray diffraction (XRD), and X-ray Photoelectron Spectroscopy (XPS). The samples were tested as a catalyst in a model
reaction process i.e. hydrogenation of 4-nitrophenol in aqueous solution at 20 °C. The catalytic reaction rate of microwave synthesis Ru-Sn catalysts was compared with impregnation prepared Ru-Sn catalyst.

2. Methods

2.1 Materials
Stannum chloride hydrate (SnCl₂·H₂O), Ruthenium trichloride dehydrate (RuCl₃·2H₂O), 4-Nitrophenol (4-NP), sodium borohydride (NaBH₄) were purchased from Sigma Aldrich. Ethylene glycol and PVP (40K) were supplied by Fluka, whereas ethanol, acetone, and methanol provided by the Sterm chemical. A domestic microwave SHARP model ShowerWave™ was used to carry out all the microwave-assisted reactions. All mixtures were irradiated with the power of 700W. Metal ratio and metal content on the support were kept (1:1) and 2 wt%, respectively.

2.2 Preparation of Ru-Sn bimetallic nanocatalyst
The synthesis of 2%(Ru₀.₅Sn₀.₅)/Al₂O₃ bimetallic nanoparticles was adopted from the method reported by [9,10] with some modifications in preparation steps and washing procedures [11]. Reduction time was previously determined by evaluating the UV-Vis spectra of diluted colloid every minute during irradiation.

The first catalyst was prepared by using microwave method by impregnation of PVP-stabilized Ru-Sn colloid onto Al₂O₃. Briefly, a certain amount of metal salts RuCl₃·3H₂O, SnCl₂·2H₂O (Ru/Sn = 1/1 mol/mol) and PVP (40K) were simultaneously reduced under microwave irradiation. The bimetallic solution was irradiated for 7 minutes. The irradiated solution was destabilized with acetone. After collected by centrifugation, the colloid was dried in vacuum at RT. 50 mg of the RuSn-PVP powder (from the colloid) was re-dispersed in methanol (20 ml), and then 1.95 g of the Al₂O₃ support was added under vigorous stirring to form a suspension. After methanol had been evaporated at RT, the homogeneous solid was obtained. This catalyst was denoted as RS-IM(MW). The second catalyst (co-reduction in-situ) was prepared by dissolving all precursor metal salt and Alumina simultaneously in 80 ml of EG without stabilizer. After stirred for 1 hr, the solution then was irradiated at the power of 700 W for 7 min. The suspension was then destabilized by excess acetone and collected by centrifugation. The powder then lets dry in a vacuum oven at 70°C for 12 h. This catalyst was denoted as RS-IS(MW).

For comparison, the third catalyst of 2%(Ru₀.₅Sn₀.₅)/Al₂O₃ was also prepared by conventional impregnation methods (named as RS-IM) as reported by Miyake et al. [13]. Typically, all metal salts were dissolved in distilled water in a glass flask. Then, the desired amount of support was added. The mixture was dried at 70°C under stirring. All samples were then reduced in H₂ flow at 350 °C for 4 h prior to use in the catalytic test.

2.3 Characterization
Morphology and structural investigations were performed using TEM and XRD method, respectively. For TEM characterization, RuSn colloid and RuSn/Al2O3 were re-dispersed in ethanol before dropped onto a copper grid. TEM images were recorded with a Phillips CM-12. The crystalline structure of the samples was analyzed by using powder X-ray diffractometer type BRUKERTM model D8 Advance using Cu Kα radiation at 40 kV and 20 mA. Ultraviolet-visible absorption spectral measurements were carried out with a UV-Vis spectrophotometer Perkin-Elmer model Lambda 35. X-ray photoelectron spectra (XPS) were acquired by KRATOS AXIS ULTRA spectrometer equipped with a hemispherical electron analyzer an Al Kα (E = 1486.4 eV, 1 eV = 1.6302 x 10⁻¹⁹ J) 300-W of the X-ray source. The powder sample was mounted on a double-sided copper adhesive tape and then placed on a sample rod in a pre-treatment chamber before transferred to the analysis chamber. The sample was maintained in the analysis chamber until a residual pressure of ca. 5x10⁻⁷ Nm⁻² was reached. The Al 2p line (74.4 eV) was used to calibrate the recorded spectra.

The catalytic activity of the composites towards the reduction of 4-nitrophenol (4-NP) by NaBH₄ was recorded by using Perkin Elmer UV-Vis spectrometer by the method as reported by [14]. The
initial molar ratio of (Ru+Sn)/4-NP/NaBH₄ was 1/15/22,500. 4 mg of catalyst (contained 1 wt% of metal (Ru+Sn), 4x10⁻⁷ mol) was previously dispersed in H₂O (8.0 mL). 4-NP (4.0x10⁻³ mM, 15 mL) aqueous solution was added. Then, a freshly prepared aqueous solution of NaBH₄ (1.28 M, 7 mL) was added. The reaction mixture (3.0 mL) was sampled at a fixed interval, without filtration. The absorption spectra of the solution were measured in the range of 250–500 nm. The rate constants of the reduction process were determined by measuring the change in absorbance at 400 nm as a function of time.

3. Result and Discussion

3.1 Reduction Process

In order to determine the irradiation time, the progressive reduction of Ru-Sn colloid was monitored by UV-Vis spectrophotometer. Figure 1 presents UV-Vis spectra of a Ru-Sn PVP-stabilized solution before and after the microwave-solothermal reaction. A broad absorption peak centered at 370 nm is assigned to the Ru³⁺ ions [9], [11] and a peak around 650 nm have resulted after addition of Sn²⁺. To examine Ru and Sn reduction simultaneously, sampling was done every 60 sec. Due to the in-oven system limitation, irradiation has to be stopped during sampling for 20 s. After irradiation for 5 minutes, the peaks vanished, which indicates that the Ru³⁺ and Sn²⁺ ions were completely reduced to Ru⁰ and Sn⁰ metals [11].

![Figure 1. UV-Vis absorption spectra of Ru-Sn colloidal solution stabilized by PVP during irradiation at power of 700 W](image)

The process of metal reduction actually can also be observed from the color change of the reaction mixture [11]. Before the irradiation, the mixture was green-blue color. After 2 minute irradiation, it was changed slightly into brownie colour, and finally, when the reduction was completed, it changed into dark brown color. The reduction of Ru-Sn was completed after 5 minutes at the power of 700 W.

The reaction process of metal salt in ethylene glycol follows the equation (1) to (3), as shown below:

$$2\text{CH}_2\text{OH} \rightarrow \text{CH}_3\text{CHO} + \text{H}_2\text{O}$$  \hspace{1cm} (1)

$$\text{M}^{n+} + \text{nH}_2\text{O} \rightarrow \text{M(OH)}_\text{n} + \text{nH}^+$$ \hspace{1cm} (2)

$$2\text{CH}_3\text{CHO} + \text{M(HO)}_\text{n} \rightarrow \text{CH}_3\text{–CO–CO–CH}_3 + \text{nH}_2\text{O} + \text{M}^0$$ \hspace{1cm} (3)

Microwave radiation promotes the decomposition of ethylene glycol primarily into acetaldehyde, the substance that promotes the reduction of Ru ions to generate metallic particles. The rapid and uniform microwave heating accelerates the reduction rate of metallic ions, forming metallic centers that could facilitate the formation of nanoparticles with a uniform size distribution.

3.2 Structure and Morphology

Al₂O₃ and series of Ru-Sn catalyst powder diffraction pattern are presented in Figure 2. The characteristic peak of Al₂O₃ denoted by its (hkl) matches to cubic Al₂O₃ standard pattern JCPDS no.
047-1308. According to XRD analysis, all samples exhibit similar XRD pattern to Al$_2$O$_3$ standard (JCPDS No. 047-1308) with peaks slightly shifted. Peaks shift to higher 2Theta indicates that lattice parameter of Al$_2$O$_3$ has also shifted to a higher value. The absence of any reflections from the metal phase can be assumed that bimetallic Ru-Sn forms very small particles dispersed on the support and very low content of Ru-Sn on the support [9]. It also probably due to the high affinity of Sn and alumina [7]. From XRD pattern, the average crystallite sizes $D$ (nm) of the as-prepared samples are estimated using Scherrer’s formula:

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

where $\lambda$ is the X-ray wavelength of the Cu-K$\alpha$ radiation source (=0.15418 nm), $\beta$ (in rad) is the full width at half maximum (FWHM) intensity of the diffraction peak located at $2\theta$, and $\theta$ is the Bragg angle. The average crystallite sizes of all samples were estimated from the FWHM value of the most intense peak, i.e. [401] peak and calculated using Scherrer’s equation.

![XRD pattern](image)

**Figure 2.** XRD pattern of (a) pure Al$_2$O$_3$, (b) RS-IM(mw), (c) RS-IS(mw) and (d) RS-IM.

To verify the presence of Ru and Sn, the samples are then characterized by the wide scanning and narrow scanning of X-Ray Photoelectron Spectrometer (XPS) for selected samples. The XPS wide scan for the microwave samples as shown in Figure 3. From the wide scan results, the presence of elements Ru and Sn are visible. Chlorine content is also still detected in all samples. This is due to chlorine content derived from the precursor material. The precise information about the chemical state of the element, a narrow scan was necessary. The narrow scan of XPS spectra will not be reported here. Percentage of Ru and Sn were determined quantitatively using XPS wide scan as reported in Table 1.

![XPS wide scan](image)

**Figure 3.** Wide scanning XPS result of 2%(Ru$_{1/2}$Sn$_{1/2}$)/Al$_2$O$_3$ (RS-IS(MW))

According to quantitative analysis of XPS, the atomic concentration of Ru and Sn for RS-IM (MW) sample are slightly reduced compared to RS-IS(MW). This might due long washing procedure during preparation. From XPS analysis, all samples contain ruthenium in the metal phase. It has the properties of Ru 3p$_{3/2}$ ~ 461.0 ± 0.2 eV [9]. Other signs of higher binding energy were given to higher oxidation number of ruthenium (Ru$^{4+}$ and Ru$^{6+}$) of 463.1 ± 0.1 eV and 466 ± 0.2 eV. The XPS peak of
Sn 3d\textsubscript{5/2} at \textasciitilde 486.5 eV may be given to Sn(II) and/or Sn(IV) since Sn(II) and Sn(IV) are indistinguishable [15].

| Peak   | Position BE (eV) | Atomic Mass | Atomic Conc. % RS-IM(MW) | Atomic Conc. % RS-IS(MW) |
|--------|-----------------|-------------|---------------------------|--------------------------|
| Al 2p  | 74.4            | 26.98       | 30.49                     | 30.92                    |
| O 1s   | 529             | 15.99       | 64.68                     | 64.78                    |
| Ru 3p  | 461.0           | 101.07      | 1.52                      | 1.97                     |
| Sn 3d  | 484.1           | 118.74      | 1.32                      | 1.56                     |

Figure 4 shows typical TEM images of supported bimetallic nanoparticles prepared by (a) microwave and (b) conventional method. For sample RS-IS(MW) (Figure 4a), a large amount of well dispersed small nanoparticles of size around 2 nm is evident. The geometrical average of RS-IM(MW) and RS-IS(MW) bimetallic grain sizes are 2.0 ± 0.2 nm and 2.5± 0.36 nm, respectively. Parallel to that previously observed, the presence of the support in reduction process is sufficient to limit the metal particles aggregation [13]. For impregnation sample RS-IM, bimetallic particles were appeared covering the alumina as shown in Figure 4b.

3.3 Catalytic Analysis
The catalytic performance of samples for the reduction of 4-nitrophenol (4-NP) to 4-aminophenol (4-AP) was tested as a model reaction with an excess amount of NaBH\textsubscript{4}. After adding NaBH\textsubscript{4} into the aqueous solution of 4-NP, the color of the solution changed from light yellow to dark yellow due to the formation of the 4-nitrophenolate ion. Without the addition of a catalyst, the reduction of 4-NP by NaBH\textsubscript{4} will not proceed. As evidence, peak belongs to 4-nitrophenolate have not reduced after 120 min, as shown in Figure 5.

However, after the addition of Ru-Sn/Al\textsubscript{2}O\textsubscript{3} (4.0 mg), the color of the 4-nitrophenolate ions faded with time which indicates the hydrogenation reaction occurs. The progress of the reaction was monitored by UV–vis spectroscopy. The characteristic peak of 4-NP at 400 nm decreased, while at 290 nm a new peak appeared which were assigned to 4-aminophenol (4-AP) (Figure 6).
Figure 5. Reduction process of 4-nitrophenol without catalyst

The rate constant $k_{\text{app}}$ was obtained by plotting the logarithmic ratio of $(c_t/c_0)$ to time $t$. On the curve, it appears that at a very short interval at the start of the reaction, absorption does not occur. This condition is called induction time ($t_0$) [16,17]. The induction period is also interpreted as the time required for the reactants to blend into the surface of the particles. The degree of conversion can be directly read off from this curve, and the ratio of the concentration of 4-nitrophenol at time $t$ to its value $C_0$ at $t = 0$ is given directly by the ratio of the respective absorbance. From the graphical analysis, the reaction follows the pseudo first order reaction kinetics [17].

Figure 6. UV-Vis absorption spectra for the reduction of 4-NP over 2%$(\text{Ru}_{0.5}\text{Sn}_{0.5})/\text{Al}_2\text{O}_3$ (MW)

The reaction catalyzed by RS-IM(MW) and RS-IS(MW) was finished within 400 s and 600 s at 15-20 °C. Eventually, in presence of catalyst RS-IM, the reaction was finished even longer. The pseudo-first-order rate constant ($k$) at 293 K was calculated from the slope. The highest to the lowest rate constant is represented by RS-IM(MW)>RS-IS(MW)>RS-IM. The rate constant in the presence of catalyst RS-IM(MW), RS-IS(MW), RS-IM are $(8.07\pm 0.82)\times 10^{-3}$ s$^{-1}$, $(4.84\pm 0.77)\times 10^{-3}$ s$^{-1}$, and $(3.02\pm 0.99)\times 10^{-3}$ s$^{-1}$, respectively. From this result, the PVP-stabilized nanoparticle has the highest rate constant (Figure 7).

Table 2 below summarizes RuSn/Al$_2$O$_3$ properties obtained via microwave method and conventional heating. It shows that the crystallite size of the synthesized Ru-Sn nanostructures varied the preparation route. Particle size and distribution of bimetallic nanoparticles were obtained by TEM measurement.
Table 2 Summary of RuSn samples properties

| Sample   | Crystallite size (Scherrer) (nm) | Nanoparticles size (TEM) (nm) | Reaction rate constant (s⁻¹) |
|----------|----------------------------------|-------------------------------|-------------------------------|
| Al₂O₃    | 9.54                             | NA                            | NA                            |
| RS-IM(MW) | 11.21                           | 2.0 ± 0.2                     | (8.07 ± 0.82) x 10⁻³           |
| RS-IS(MW) | 11.93                           | 2.0 ± 0.28                    | (4.84 ± 0.77) x 10⁻³           |
| RS-IM    | 10.60                           | NA                            | (3.02 ± 0.99) x 10⁻³           |

4. Conclusion
Preparation route has a strong influence on the structure, morphology and the activity of Ru-Sn catalyst. PVP-stabilized catalyst RS-IM(MW) is proven to have the highest activity in the hydrogenation of 4-nitrophenol by an excess amount of NaBH₄. Bimetallic particles size can be controlled up to less than 2 nm with narrow size distribution. PVP has an important role to limit the nanoparticles aggregation and at the same time might improve the catalyst activity. In-situ reduction process, alumina has been proved to be able to control and immobilize the bimetallic nanoparticles on the support. The catalytic tests showed that the activity is strongly enhanced by the interaction between metals, Al₂O₃, and PVP. The highest to lowest of the pseudo-first-order rates constant of RS-IM(MW), RS-IS(MW), RS-IM are (8.07 ± 0.82)x10⁻³ s⁻¹, (4.84 ± 0.77)x10⁻³ s⁻¹, and (3.02 ± 0.99)x10⁻³ s⁻¹, respectively. According to the results from this study, PVP-stabilized Ru-Sn/Al₂O₃ obtained via microwave-polylol method is potential to be used in another hydrogenation process, such as hydrogenation of fatty acid to fatty alcohol.

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