XPS and TPR studies of 2\%(Ru_{1/2}-Sn_{1/2})/Al_{2}O_{3} catalyst synthesized by microwave techniques

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Abstract. X-Ray photoelectron spectroscopy (XPS) and Temperature-programmed Reduction (TPR) of 2\%(Ru_{1/2}-Sn_{1/2})/Al_{2}O_{3} prepared by the microwave-assisted method have been studied. 2\%(Ru_{1/2}-Sn_{1/2})/Al_{2}O_{3} have previously been evaluated as a catalyst in the reduction reaction of 4-nitrophenol. XPS and TPR studies of 2\%(Ru_{1/2}-Sn_{1/2})/Al_{2}O_{3} was performed to confirm the metal state of Ru and Sn and reducibility of the sample, respectively. XPS data suggested that the formation of metal Ru(0) and Sn(0) in all samples. The XPS spectra of Ru 3p\textsubscript{3/2} and Sn 3d\textsubscript{5/2} shows binding energy peak at \( \sim 461.0 \pm 0.2 \text{ eV} \) and \( \sim 484.1 \text{ eV} \), respectively. The correlation of TPR and XPS characterization will be discussed further.

Keywords: XPS, TPR, microwave, nanoparticles, catalyst

1. Introduction

Nitro-aromatic compounds such as 4-nitrophenol are the most important class of industrial chemicals which is widely used as intermediates for synthesis of dyes, polymers, pesticides, and pharmaceuticals [1] which has led to environmental contamination of soil and groundwater. US Environmental Protection Agency has listed the aromatic compound as dangerous pollutant for environment [2]. Hydrogenation of 4-nitrophenol catalyzed by metal nanoparticles has received increasing attention [3], [4]. This reaction can be performed in aqueous solutions under mild condition. Bimetallic nanoparticles possess significantly new physicals and chemical properties in comparison to bulk metals.

Many works have done to improve and study catalytic activities of mono and bimetallic nanoparticles. Nevertheless, studies on the structure and catalytic activities correlation of bimetallic nanocatalyst are still rare. The characteristics and the structures of photocatalysts were depended on the preparation processes [5]. Various Ru-Sn/Al\textsubscript{2}O\textsubscript{3} catalysts which had been prepared according to different metal reduction sequences under microwave irradiation was evaluated in the process of 4-nitrophenol hydrogenation [6]. The results of catalytic measurements obtained at room temperature revealed that differently prepared catalysts and the physical mixture containing Ru-Sn/Al\textsubscript{2}O\textsubscript{3} with the same Ru/Sn ratio exhibited different activities [6]. The structure and reducibility of Ru-Sn bimetallic catalysts prepared by microwave irradiation method has not been discussed.
In this paper, Ru-Sn based nanocatalyst was characterized by XPS and TPR to examine the oxidation states of metals prepared in a different route to reveal the real mixture containing in the sample according to its coordination number. By these characterizations, the effect of preparation route on the nature of the surfaces exposed by the active phases can be explained.

2. Methodology

2.1. Materials
Stannum chloride hydrate (SnCl₂.xH₂O), Ruthenium trichloride dehydrate (RuCl₃.2H₂O), 4-Nitrophenol (4-NP), sodium borohydride (NaBH₄) were purchased from Sigma Aldrich. Ethylene glycol and PVP (40K) was supplied by Fluka, whereas ethanol, acetone, and methanol provided by Stern chemical. A domestic microwave SHARP model ShowerWaveTM was used to carry out all the microwave-assisted reactions. All mixtures were irradiated under a power of 700W. Metal ratio and metal content on the support were kept (1:1) and 2 wt%, respectively.

2.2. Methods

2.2.1. Sample Preparation
The synthesis of 2%(Ru₀.₅Sn₀.₅)/Al₂O₃ bimetallic nanoparticles follows the method reported [7], [8] with some modifications in preparation steps and washing procedures [9]. In detail, sample preparation procedures were previously reported elsewhere[6].

2.2.2. X-ray Photoelectron Spectroscopy (XPS) and TPR characterization
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 and then transferred to the analysis chamber. Before recording the spectra, the sample was maintained in the analysis chamber until a residual pressure of ca. 5x10⁻⁷ Nm⁻² was reached. The narrow scan spectra of the particular element were collected at the pass energy of 20 eV.

Normally, the binding energy of C1s was used as a standard for calibration. In this study, we examined Ru 3p instead of Ru 3d because the Ru 3d spectra are overlapped with the region of C1s [8], [9]. For that reason, we also calibrated the reading using Al³⁺ binding energy (74.4 eV) as reference [10]. Spectral background calibration used Shirley or Linear method for every peak and adjusted using the Gaussian function.

The characterization of the sample using TPR is done using ThermoFinnigan TPD/R/O 1100 apparatus. Before being characterized, the sample was treated in a flow N₂ gas stream with a flow rate of 5 cc/min for 5min at room temperature. Then the temperature was raised at a warming rate of 10 °C/min to a temperature of 150°C and held for 5 min. At the time of TPR characterization, 5% hydrogen gas in argon with flow rate (25 cc/min) flowed into the sample at a temperature rate of 10 °C/min to 450 °C. H₂ gas consumption is read at every temperature increase.

3. Result and Discussion

3.1. X-Ray Spectroscopy
To confirm the reduction of Ru and Sn, the irradiated samples were characterized by X-ray Photoelectron Spectrometer as shown in Figure 1. From XPS analysis, all samples contain ruthenium in its metallic state. It is characterized by the binding energy of Ru 3p₃/₂ ~ 461.0±0.2 eV [8]. Other signals at higher binding energy were assigned to the higher oxidation states of ruthenium (Ru⁴⁺ and Ru⁶⁺) i.e. 463.1±0.1 eV and 466±0.2 eV. The surface oxidation of ruthenium was actually possible
because of ambient condition exposure for a few minutes [8], [9]. A narrow scan of the Sn 3d$_{5/2}$ XPS spectra provides some information. Sn at metallic oxidation state was detected for RS-2 and RS-3 samples which are noticed at 484.1 eV. However, Sn(II) and Sn (IV) are unable to be differentiated [11]. According to literature, Sn 3d$_{5/2}$ peak of Sn at ~ 486.5 might be assigned to Sn(II) and/or Sn(IV) [10]. The peak at ~ 484.1 eV corresponds to Sn$^0$. The RS-1 sample shows two Sn 3d$_{5/2}$ peaks centered around 484.1 eV and 486.8 eV. The first peak is most probably due to tin Sn$^0$ species.

According to the literature [10], [12], this binding energy is not much different from the binding energy of Sn(II) ~ 484.8 eV [12]. The results were contrary with the results observed from uncalcined Ru-Sn bimetallic prepared by the co-impregnation technique where the metallic tin cannot be observed [10]. In our work, the as-prepared sample obtained by microwave irradiation technique exhibits Sn in the metallic state for all samples as listed in Table 1. From the results, as we can see from XPS analysis, bimetallic PVP-stabilized Ru-Sn/Al$_2$O$_3$ catalyst obtained via microwave irradiation are majority composed of ruthenium and Sn(II) species. In all samples, the oxidation state of Sn is in major concentration. The tin is tightly bonded (via oxygen) in the outer surface of the $\gamma$-Al$_2$O$_3$ particles and may act as electronic promoter.
Figure 1. XPS narrow scan spectra of Ru 3p and Sn 3d of (a) RS-1 (b) RS-2 (c) RS-3

Table 1. The XPS qualitative analysis of 2%(Ru-Sn)/Al₂O₃ samples and its reaction rate.

| Binding Energy (eV) | XPS analysis | Reaction rate$^{(2)}$, 10⁻³ |
|---------------------|--------------|-------------------------------|
| Ru⁰ 3p              | Ru⁺⁺ 3p      | Ru⁰/Ru⁺⁺              | Sn⁰/Sn⁺⁺              | Cl/(Ru+Sn)            |                  |
| RS-1 461.2          | 463.5        | 1.7                      | 0.31                   | 0.25                  | (8.07±0.82)       |
| RS-2 461.2          | 463.6        | 1.03                     | 0.23                   | 0.07                  | (4.84±0.77)       |
| RS-3 461.2          | 463.1        | 0.97                      | 0.10                   | 0.07                  | (3.02±0.99)       |

3.2. Temperature-Programmed Reduction

The XPS results were then correlated with the characterization of TPR. The effect of the preparation route to the TPR profile of the Ru-Sn catalyst sample is supported with Sn/Ru atom ratio of 1.0 and compared with Sn / Ru = 0 sample shown in Figure 2. The differences in H₂ use patterns for different samples after preparation indicate a change in decline behavior. The emergence of a peak of hydrogen use was seen in the 1% Ru/Al₂O₃ TPR pattern at temperatures around (~ 223 °C). The intensity is related to the free Ru (0) formed in support [10]. TPR sample RS-1 samples show peak intake of H₂ at around ~ 140 °C with a reduction rate of 160-190 °C. There is also a peak at 330 °C and another peak above 450 °C. The peak at 140 °C is the reduction in RuCl₃ [13]. It also implies that there is still chlorine content in the sample, in accordance with the analysis using XPS in Table 1. The decrease in hydrogen consumption after temperatures around 160 and 200 °C is derived from the reduction of Ruthenium oxychloride and Ruthenium oxide. Other tops at around 300 °C indicate a decrease in Sn (II) and Sn metal [13]. The peak above the 450 °C temperature comes from Sn (IV) which does not interact with Ru (0) [10], [14].
The previous studies showed that the Ru-Sn preparation route drastically alters 2%(Ru-Sn)/Al$_2$O$_3$ catalytic properties [6]. In the case of RS-2 catalysts, provided by a consecutive reduction, the peak of the TPR reading was observed near 100 °C due to the reduction of ruthenium oxide (RuO$_2$) to the Ru metal [15]. Another small peak seen at 180 °C is also due to RuO$_2$ [16]. The use of low hydrogen by RS-2 sample shows that it can be easily reduced. This is contrary to other findings in conventional Ru-Sn cases that found that Sn prevented access to hydrogen for reduced ruthenium [17]. Sample prepared from in-situ reduction of metal salts with the presence of Al$_2$O$_3$ and ethylene glycol (RS-3) has a similar profile with RS-2. It exhibits a wide peak at 179 °C given to RuO$_2$ [16]. The RS-2 and RS-3 profiles of hydrogen use temperature decline at the range of approximately 270 °C. The peak at 270 °C comes from another Ru$^{n+}$ with interactions to Sn$^{n+}$ [10]. Low-temperature reduction of RS-2 and RS-3 samples from low peaks also show a strong interaction of Ru and Sn species to alumina support [17].

4. Conclusions
XPS studies of 2%(Ru-Sn)/Al$_2$O$_3$ by three different preparation route under microwave irradiation, contain ruthenium and tin at their metallic state. Ruthenium and Tin exist majorly in an oxidation state of Ru(0) and Sn(II) on the surface of reduced samples, respectively. TPR studies of the catalysts showed the most reactive sample most probably due to its high content of Ru(0) with no interaction with Sn.

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