

Mechanical alloying for green catalyst synthesis

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ABSTRACT

This work herewith presents mechanical alloying (MA) as an alternative catalyst synthesis pathway and the most practical technique, which is easy to handle, solvent free, and provides high productivity in both lab and commercial scales. Moreover, it is found that the mechanically alloyed (MAed) technique also results in new phases of intermetallics and produces small grains of materials that exhibit different thermodynamic properties.

The prepared catalysts were characterized and confirmed crystal structure of intermetallic catalysts by X-ray diffraction and the high resolution transmission electron micrographs with selected area electron diffraction. The MAed catalysts of Cu_aSn_b and Ni_aSn_b were tested for the phenol hydroxylation to observe their catalytic activity and the effect of the second metal on tin. The results showed that the mix crystal structure of Cu_6Sn_5 , $\text{Cu}_{41}\text{Sn}_{11}$, and Cu_3Sn provided the highest catalytic activity, giving conversion of 84% as catechol, hydroquinone, and benzoquinone whereas a single crystal structure of Ni_3Sn_4 gave less conversion of 42%, however, provided only hydroquinone (100%).

Keywords: Cu-Sn intermetallic, Ni-Sn intermetallic, Mechanical alloying, Phenol hydroxylation, strong acid sites

1 INTRODUCTION

Generally, the catalyst preparation was done by using a large number of solvents, base, acid, and many other organic compounds. Those chemicals are toxic to environment and need specific methods for treatment. Nowadays, the bimetallic catalysts were studied and showed the interestingly catalytic activity in many fields of chemistry (i.e. hydroxylation of benzen and phenol, selective hydrogenation of α,β -unsaturated aldehyde, hydrogenation of hydrocarbon, upgrading bio-oil, and partial oxidation) [1-4]. Bimetallic catalysts do not only reveal the combination of the properties related to the presence of two individual metals, but also generate new and distinctive properties due to synergetic effects between the two metals presence. However, their final structure strongly depends upon the composition, their synthesis method and conditions.

Evidently, the key factor for fabricating bimetallic catalyst was the energy which helped the second metal diffuse into the one another metal and create metal-metal bond to form bimetallic. The nature of the MA process consists of fracturing and welding [5], contributing to surface diffusion mechanism and resulting in the formation of more free surfaces and grain boundaries, surface diffusion which was driven by the reduction in surface area and radius of the crack tip [6-7]. For formation of a new crystal structure containing two different elements, the smaller diameter atoms penetrate to the interstitial site of the other to form solid solution, resulting in alloys or intermetallics. The diffusion process is very rapidly during mechanical alloying [8].

In this work, the catalysts were prepared by MA technique and studied their catalytic activity in phenol hydroxylation. The metal targets were tin (Sn), copper (Cu), nickel (Ni). Unfortunately, pure Cu and Ni did not give the satisfied results, showing over-oxidation to tar when using Cu [9] and low conversion when using Ni due to less hydroxyl radical generated [10]. Sn was revealed that it could enhance the hydrogen peroxide efficiency and prevent over oxidation of desired products [11]. The objective of this study was to provide a short review on series of Cu-Sn and Ni-Sn intermetallic catalysts synthesized by MA technique and their catalytic activity.

2 EXPERIMENTAL

2.1 Materials

Nickel (Ni, 99.99 %wt), Copper (Cu, 99.99 %wt) and tin (Sn, 99.99 % wt) powders were produced using gas atomization, as detailed in elsewhere [12]. Methanol (CH_3OH , 99.99%) was purchased from Labscan, Thailand; catechol (CAT, 99%), hydroquinone (HQ, 99%), 1,4-benzoquinone (BQ, 98%) from Sigma-Aldrich, USA; phenol detached crystals and hydrogen peroxide (H_2O_2 , 30 %w/v) from Fisher Scientific, UK. All chemicals were used without purification.

2.2 Synthesis of Cu_aSn_b and Ni_aSn_b intermetallic catalysts

Ni ($32 \leq \mu\text{m}$), Cu ($32 \leq \mu\text{m}$), and Sn ($32 \leq \mu\text{m}$) were used to prepare Cu_aSn_b and Ni_aSn_b nanoparticles, following

the papers cited elsewhere [9,13]. The Cu_aSn_b intermetallics were prepared by varying Sn contents (30, 50, and 70 %wt.) balanced with Cu powder. The Ni_aSn_b intermetallics were prepared by varying Sn contents (43, 58, and 73 %wt.) balanced with Ni powder. Elemental Cu and Sn powders and Ni and Sn powders were mechanically alloyed (Maed) in an attritor. The conditions were as follows: 5:1 ball-to-powder ratio, 300 rpm Ma speed, and 30h milling time. After that, the materials were heated in vacuum chamber in order to allowing metal diffusion. The Maed powders were further characterized using various techniques.

2.3 Characterization

X-ray diffractometry (XRD) patterns were recorded on a Rigaku X-ray diffractometer with $\text{CuK}\alpha$ radiation and the crystallite sizes were determined using MDI JADE 9 software, relating to the Scherrer formula, with a residual error of less than 10% [14-16] and the high resolution transmission electron micrographs (HRTEM) with selected area electron diffraction (SAED). The samples were analyzed by a UFLC Shimadzu high performance liquid chromatography (HPLC) equipped with a C-18 reverse-phase column (Inertsil ODS-3) and a UV detector (SPD-M20A Shimadzu). The products were further confirmed by comparing the HPLC of pure CAT, BQ, and HQ. All reactions were performed in triplicate and average values were used in the data presentation.

2.4 Catalytic activity study

Phenol hydroxylation was carried out to study the activity of the synthesized catalysts by adding phenol (1.88g, 20mmol), H_2O_2 (6.84g, 60 mmol), and water (10 ml) into a 250 ml two-necked round bottom flask fitted with a condenser. The catalytic activity results of Cu_aSn_b intermetallics before and after heat treatment were compared at 70 degree 50mg of catalyst phenol:hydrogen peroxide ratio 1:3 by considering the rate constant of phenol, CAT, HQ, BQ, and conversion.

3 RESULTS AND DISCUSSION

3.1 Characterization of MAed Cu_aSn_b and MAed Ni_aSn_b intermetallic catalysts

The catalysts prepared by Maed technique were characterized to observe the change in the crystal structure and orientation of Cu_aSn_b and Ni_aSn_b intermetallic catalysts. Series of MAed Cu-Sn intermetallic catalysts showed XRD patterns, belonging to MAed $\text{Cu}_{30}\text{Sn}_{70}$ (JCPDS card No. 45-1488 of monoclinic Cu_6Sn_5), MAed $\text{Cu}_{50}\text{Sn}_{50}$ (JCPDS card No. 65-7047 of cubic $\text{Cu}_{41}\text{Sn}_{11}$ (52.4%), JCPDS card No. 65-5721 of orthorhombic Cu_3Sn (35.5%), and JCPDS card No. 45-1488 of monoclinic Cu_6Sn_5 (12.1%)), and MAed $\text{Cu}_{70}\text{Sn}_{30}$ (JCPDS card No. 65-7047 of cubic $\text{Cu}_{41}\text{Sn}_{11}$), respectively. XRD patterns of series of Ni-Sn intermetallic

catalysts indicated MAed $\text{Ni}_{57}\text{Sn}_{43}$ (JCPDS Card No. 035-1362 of hexagonal Ni_3Sn), MAed $\text{Ni}_{42}\text{Sn}_{58}$ (JCPDS Card No. 065-1315 of orthorhombic Ni_3Sn_2), MAed $\text{Ni}_{27}\text{Sn}_{73}$ (JCPDS Card No. 004-0845 of monoclinic Ni_3Sn_4), respectively. The results were informed that the crystal structure of all catalysts were changed from parent metals since Sn diffused into the interstitial site and created the new metal-metal bond, resulting in new crystal structure [9,13].

TPD- NH_3 analysis for determining the acid strength and the amount of acid of all MAed Ni-Sn and Cu-Sn intermetallic catalysts were investigated by Wongkasemjit's research group [13]. It was found that strong acid sites of MAed Ni_3Sn , MAed Ni_3Sn_2 , and MAed Ni_3Sn_4 were 0.0307, 0.0835, and 0.4773 mmol/g, respectively, indicating that the more Sn content resulted in the higher value of the acid strength. The strong acid sites of MAed $\text{Cu}_{70}\text{Sn}_{30}$, MAed $\text{Cu}_{50}\text{Sn}_{50}$, and MAed $\text{Cu}_{30}\text{Sn}_{70}$ were 0.01695, 0.17956, and 0.0561 mmol/g, respectively, showing that the crystal structure of $\text{Cu}_{50}\text{Sn}_{50}$ had the highest number of the acid site.

3.2 Catalytic activities

A good catalytic activity in phenol hydroxylation could be reached by a large number of hydroxyl radical species and phenol absorption [17]. Relatively, the acid sites on surface catalyst was revealed that they could both prevent hydrogen peroxide scavenging to H_2O and O_2 [18] and increase phenol absorption on its surface. The catalyst characterization results also showed that the added Sn into Ni and Cu succeeded improving acidity on the catalyst and gave the strong acid sites on the catalyst. Moreover, the relative research revealed that a number of strong acid sites had an effect on the catalytic activity since it enhanced the reaction [19].

Figure 1 shows the catalytic activity of MAed Ni-Sn intermetallic catalysts on the phenol hydroxylation, giving the TON values of MAed $\text{Ni}_{67}\text{Sn}_{33}$, MAed $\text{Ni}_{42}\text{Sn}_{58}$, and MAed $\text{Ni}_{27}\text{Sn}_{73}$ intermetallic catalysts (34, 36, and 140, respectively) [13]. As can be seen, when the content of Sn increased to 73% wt, the TON significantly increased due to its strong acid sites. The higher number of the strong acid sites prevents the scavenging of hydrogen peroxide [18], meaning that the system could produce more hydroxyl radicals and gave a higher TON number. In addition, more phenol was absorbed on the catalyst surface and reacted with hydroxyl radicals to give dihydroxybenzenes. Surprisingly, MAed $\text{Ni}_{27}\text{Sn}_{73}$ (Ni_3Sn_4) gave only HQ as a product.

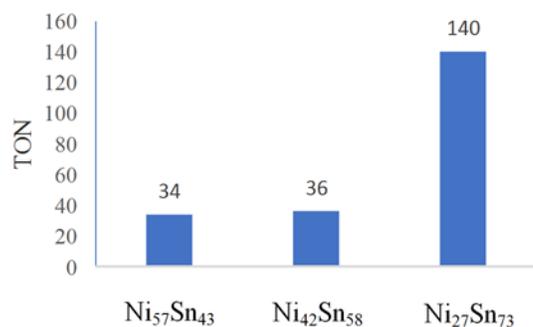


Fig.1 TONs values of MAed Ni-Sn intermetallic catalysts in phenol hydroxylation, using 1:3 H₂O₂:phenol, 50 mg of catalyst, and 10 ml of H₂O for 24 min

Figure 2 shows how Cu influence the TON value, especially, when the Cu content was increased to 50%, giving an impressive increase to almost 800 [20]. The results revealed that the mixed phases of Cu₅₀Sn₅₀ showed the highest number of acid sites among those catalysts and could generate more hydroxy radicals that resulted in the highest TON value. Surprisingly, MAed Cu₅₀Sn₅₀ did not give any BQ while the Cu₃₀Sn₇₀ and Cu₇₀Sn₃₀ gave 12.1 and 8.9%, respectively. In addition, the yields of HQ of MAed Cu₅₀Sn₅₀, MAed Cu₃₀Sn₇₀, and MAed Cu₇₀Sn₃₀ were 36.2, 16.6, and 11.9 %, respectively. Moreover, the highest CAT yield was obtained when using MAed Cu₅₀Sn₅₀, again, due to the presence of the more strong acid sites.

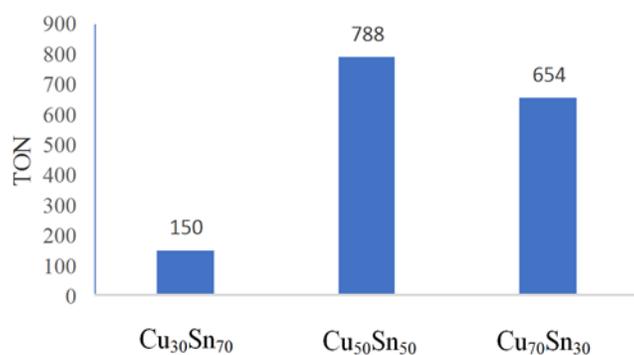


Fig.2 TONs values of MAed Cu-Sn intermetallic catalysts in phenol hydroxylation, using 1:3 H₂O₂:phenol, 50 mg of catalyst, and 10 ml of H₂O for 24 min,

4 CONCLUSIONS

Series of MAed Ni-Sn and MAed Cu-Sn intermetallic catalysts were prepared successfully using mechanical alloying technique which is a green. Series of MAed Ni-Sn intermetallic catalysts gave only single phase intermetallics and their catalytic activity showed that the more Sn content gave the more strong acid sites. Among MAed Ni-Sn intermetallic catalysts the MAed Ni₁₅₇Sn₄₃ and MAed

Ni₂₇Sn₇₃ intermetallic catalysts gave only HQ as a product while MAed Ni₂₇Sn₇₃ intermetallic catalyst show the higher TON. Series of MAed Cu-Sn intermetallic catalysts showed that both MAed Cu₃₀Sn₇₀ and MAed Cu₇₀Sn₃₀ gave a single phase whereas MAed Cu₅₀Sn₅₀ gave the mixed phases. The catalytic activity revealed that Cu₅₀Sn₅₀ showed not only the highest the number of strong acid sites but also the best of TON value.

ACKNOWLEDGEMENTS

The authors gratefully acknowledge the mutual supports or the partial scholarship from Thailand Graduate Institute of Science and Technology (TGIST-TG-33-09-58-058D), Ratchadaphiseksompot Endowment Fund, Chulalongkorn University, The Petroleum and Petrochemical College, Chulalongkorn University, and Powder Metallurgy Research and Development Unit (PM_RDU) of the National Metal and Materials Technology Center (MTEC).

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