



# Noble-metal-free bimetallic alloy nanoparticle-catalytic gasification of phenol in supercritical water



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## ABSTRACT

The exploration of non-noble-metal catalysts for high efficiency gasification of biomass in supercritical water (SCW) is of great significance for the sustainable development. A series of Ni–M (M = Co or Zn) bimetallic nanoparticles supported on graphitized carbon black were synthesized and examined as catalysts for gasification of phenol in SCW. It was found that a nearly complete gasification of phenol can be achieved even at a low temperature of 450 °C with the bimetallic nanoparticles catalysts. Kinetic study indicated the activation energy for phenol gasification were 20.4 ± 2.6 and 43.6 ± 2.6 kJ/mol for Ni<sub>20</sub>Zn<sub>15</sub> and Ni<sub>20</sub>Co<sub>15</sub> catalyst, respectively. XRD, XPS and TEM were further performed to characterize the catalysts and the results showed the formation of NiCo and NiZn alloy phase. Catalyst recycling experiments were also conducted to evaluate the stability of the catalysts. The characterization of used catalysts suggest that the severe agglomeration of nanoparticles leads to the decrease in catalytic activity.

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## 1. Introduction

Gasification of various organic materials in supercritical water (SCW) ( $T_c = 374$  °C,  $P_c = 22.1$  MPa) has attracted increasing attention as an efficient technology for energy production, especially for those with high moisture content, such as wet biomass [1,2], sludge [3,4], and lignite [5–7]. Under supercritical conditions, organic compounds become completely miscible in SCW, allowing for a high reaction rate due to the mass and heat transfer limitation free. In addition, SCW serves as both a reaction medium and a reactant during the gasification process [2], thus drying feedstock is not required compared to the conventional thermo chemical conversion process. In the process of supercritical water gasification (SCWG), elevated temperature is necessary to achieve a desirable conversion, which will inevitably leads to severe operation conditions. Therefore, an appropriate catalyst is generally employed to decrease the reaction temperature and enhance the yields of target products.

Various homogeneous catalysts (e.g., KOH, NaOH, K<sub>2</sub>CO<sub>3</sub> and Na<sub>2</sub>CO<sub>3</sub>) and heterogeneous catalysts supported on different car-

riers were widely reported in SCWG process [6–8]. The advantages of heterogeneous catalysts over homogeneous catalysts are recyclability and higher activity. Moreover, the potential corrosion caused by homogeneous catalysts such as alkali can be also relieved. Among various transition metal species, Ni-based and Ru-based catalysts are most commonly utilized as heterogeneous catalysts [2,7,9–13]. Ru catalyst supported on charcoal showed the highest activity compared to Rh, Pt, Pd and Ni in gasification of lignin at 400 °C [14]. In addition, noble metal Ru also showed excellent activity in the gasification of lignite [7] and phenol [12,13]. Compared to the noble metal catalysts, Ni is cheaper and easily available, the Ni-based catalysts have also attracted much attention. In order to improve the activity and stability of Ni catalyst, incorporating with other noble metal such as Ru, Pd and Pt were investigated [15–19]. Alloying Ni with other non-precious metals (such as Fe, Co, Zn, and Cu) also appears more attractive due to its low-cost and high performance, which is comparable or even better to that of noble metal catalyst [20,21]. Take Ni–Fe alloy nanoparticles as example, it exhibits excellent catalytic activity for the complete decomposition of hydrous hydrazine, which activity is comparable to that of Ni–M catalysts (M = noble metal) [20]. Ni–Zn alloy were also used for selective hydrogenation of acetylene [21] and conversion of cellulose for vicinal diols [22]. The Ni–Zn catalyst even had greater selectivity than the Pd–Ag catalyst in hydrogenation

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of acetylene [21]. These previous reports indicated that the performance of alloying Ni with other non-precious metals could be better to that of noble metal catalyst such as Pd, Pt, Rh.

However, for the process of SCWG, there are very few papers involved in the improvement of the second non-precious metals to Ni-based catalysts. Lee [9] added Y to Ni/activated charcoal (AC) by an incipient wetness method and found small amounts of Y enhanced the performance of Ni/AC catalyst. Because that Y seemed to prevent coking reaction to some extent. Guo et al. [23] also employed co-impregnation method to prepare Ni–Cu/ $\gamma$ -Al<sub>2</sub>O<sub>3</sub> catalyst and found that Cu can alleviate the sintering of Al<sub>2</sub>O<sub>3</sub> and thus an improved performance was obtained. But unfortunately, the above reports on the bimetal catalysts have not focused on the formation of alloy phase and certainly the effect of alloy phase nanoparticles on the SCWG was also not paid much attention. As stated in previous researches [20,21], once the alloy phase formed in nanometer-sized particles, the electronic properties of metal may be modified by the second metal and the surface of bimetallic alloy catalyst can significantly tune the interactions between the catalyst surface and reactants, as a result, a superior catalytic performance could be achieved.

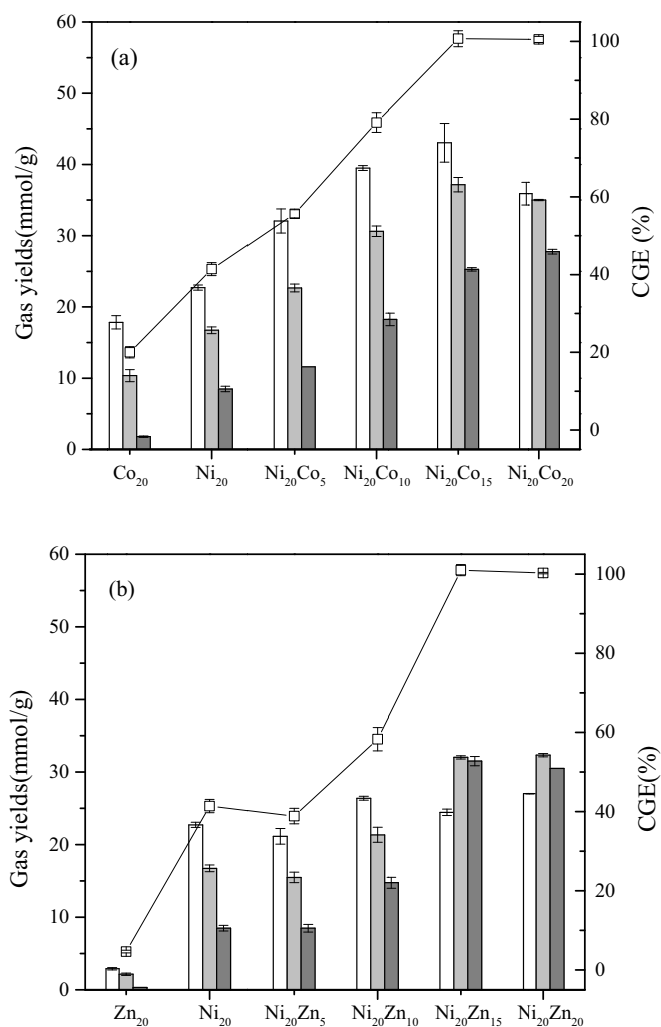
Apart from the metal species of catalyst, the stability of catalyst support also plays a critical role in SCWG as the catalyst stability problems are widely observed in hot compressed water. As shown in our previous study [13], the graphitized carbon black (GCB) with a high degree of graphitization is very stable as a support for Ru catalyst in the SCWG of phenol. In addition, phenol was often selected as a model compound in the SCWG of biomass due to its important structural features of lignin [24,25]. Phenol has also been described as one of the last hurdles to complete gasification of biomass, because it is long-lived and ubiquitous intermediates in SCWG [26]. Therefore, it would be beneficial to investigate the application of noble-metal-free alloy bimetallic nanoparticle supported on GCB for catalytic gasification of phenol in SCWG.

To our best knowledge, this is the first research on the application of noble-metal-free bimetallic alloy nanoparticles in the SCWG. In this work, a series of Ni–Co and Ni–Zn alloy catalysts were prepared by surfactant-aided polyol reduction method and tested in SCWG of phenol. Effect of temperature, reaction time and the contents of Co and Zn on the gasification results were examined. In addition, multiple techniques such as XRD, XPS and TEM were performed to prove the formation of alloy nanoparticles. The stability of the catalysts was also investigated.

## 2. Materials and methods

### 2.1. Catalyst preparation and characterization

The catalysts were synthesized using the surfactant-aided polyol reduction method as described in references [27,28]. Ethylene glycol (EG) was used as the solvent, reducing agent as well as protecting agent and the GCB (Shanghai Pantian powder material Co. Ltd.) used as catalyst support without any treatment. The details of the procedure are as follows: 160 ml of EG and 6.4 g of polyvinylpyrrolidone (PVP, MW = 30,000) were introduced to a beaker. 0.4 g of GCB was dispersed into EG by magnetic stirring after complete dissolution of the PVP. 1.92 g of NaOH and the metal precursors i.e., Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O and Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O or Zn(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O with a given weight ratio were added into the above mixture. After the complete dissolution of the precursors, a given volume of chloroplatinic acid solution (8 wt%) was also added into the mixture as the heterogeneous nucleation seed. It should be noted that the mole ratio of Pt/(Pt + Ni + Co (or Zn)) in the mixture was quite low (0.8%). Subsequently, the mixture was transferred into an oil bath and the reduction was carried out at 180 °C for 4 h under continuous



**Fig. 1.** Effect of metal contents on the SCWG of phenol (a) effect of Co content and (b) effect of Zn content. □—H<sub>2</sub>, ■—CO<sub>2</sub>, ■—CH<sub>4</sub>, —□—CGE (500 °C, 32 min, 5.2 wt% phenol, 0.1 g/cm<sup>3</sup> water density and 1 g/g catalyst loading).

magnetic stirring. After cooling to room temperature, the mixture was filtered and thoroughly washed with hot water and ethanol. The resulting catalyst was dried at 105 °C overnight using an oven. For convenience, the catalysts were denoted as Ni xMy/GCB (M = Co or Zn), where x and y repetitively represent the weight percents of Ni and M in the catalysts. For comparison, the corresponding monometallic catalysts Ni<sub>20</sub>/GCB, Co<sub>20</sub>/GCB and Zn<sub>20</sub>/GCB were also prepared using the same process as bimetal catalyst.

Powder X-ray diffraction (XRD) patterns of catalysts were conducted on a Bruker D8 Advance diffractometer system, with Cu K $\alpha$  radiation (1.5406 Å) and a graphite monochromator. Surface areas of the catalysts were measured applying the Brunauer–Emmett–Teller (BET) method on a Micromeritics Tristar II 3020 analyzer. X-ray photoelectron spectrum (XPS) analysis was done using an ULVAC PHI 5000 Versa Probe-II equipment. The morphology and structure were observed using high resolution transmission electron microscopy (HR-TEM) performed on a FEI Tecnai G<sup>2</sup> TF30 S-Twin transmission electron microscope with an energy-dispersive X-ray spectroscopy (EDS). Thermo gravimetric analysis (TGA DTG-60H, Shimadzu) was performed to roughly estimate the metal content in the catalysts, with a heating rate of 10 °C min<sup>-1</sup> under an air flow of 50 ml min<sup>-1</sup>.

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