Supercritical water synthesis of nano-particle catalyst on TiO₂ and its application in supercritical water gasification of biomass

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ABSTRACT
Hydrogen production by catalytic gasification in supercritical water (SCW) is a promising way to utilise biomass resource. Supercritical water not only provides homogeneous and rapid reaction environment for the biomass gasification but also causes catalyst agglomeration problems. In order to prepare activity and stable catalyst for biomass gasification in supercritical water, supercritical water synthesis method was utilised and the preparation method was investigated. Ni, Co, Zn and Cu metal elements were loaded on TiO₂ particles which was proved to be hythothermally steady in supercritical water. And nano-particles were successfully made. Based on gas chromatography/mass spectrometer (GC/MS), scanning electron microscopy, energy dispersive spectrometer (EDS) and X-ray diffraction analysis methods, it turned out that metal catalysts have a uniform spherical structure with diameter around 30 nm. Metal catalysts synthesised with supercritical hydrothermal method showed certain catalytic effects. Ni catalyst had the best performance in stability while Zn catalyst possessed highest hydrogen yield.

1. Introduction
There are abundant biofuels of different kinds all around the world. However, present utilisation of direct combustion causes severe environmental pollution, moreover, the efficiency of combustion is relatively low [1,2]. During combustion of biofuel, it is necessary to provide enough air because combustion needs a gaseous phase, therefore, great amount of inert N₂ lowers overall thermal efficiency. On the other hand, it dilutes concentration of pollutants, which causes expensive cost of centralised processing and collection. For fuels, which contain oxygen themselves, would significantly reduce the demanded quantity for air. As a result, it is easier to control pollution and emission, and improves thermal efficiency. Therefore, depolymerisation has great potential for the production of oxygenated fuels from biomass [3–6].

In the process of depolymerisation of biofuels, massive hydrogen is indispensable. It has great practical significance to produce hydrogen by gasification of depolymerisation wastes to make the whole conversion system independent. Among all the gasification
methods, supercritical water (SCW) gasification takes the advantages of the unique physical and chemical properties of SCW, is suitable for the gasification of depolymerisation wastes because the high energy consuming drying process is not necessary [7–11].

The key for a more economical system relies on a proper catalyst with fine abilities in SCW [12,13]. Considering that normal catalysts are very easy to sinter and then lose their catalytic effects in SCW, right method to prepare catalyst is of great importance [14–18]. Hydrothermal synthesis in SCW has been a hot spot for SCW catalysts. Because since catalysts are made in the environment of SCW, catalysts have already been tested for stability during the synthesis [19–23]. Meanwhile, without any organic solvent evolved, it is definitely a green and sustainable chemical way. Because of unique physical and chemical properties of SCW, some oxides, which are hard to synthesise in normal ways, have a better way to synthesise. Not only what we get is single phase, but also it is possible to develop a uniform morphology and structure. In addition, through temperature and pressure adjustment, morphology can be directionally controlled [24–27].

In this paper, four metal elements, Zn, Ni, Cu and Co were loaded on TiO₂ particles by supercritical water synthesis. The influence of preparation temperature upon catalyst topography was investigated. Multiple analysis methods such as scanning electron microscopy (SEM), X-ray diffraction (XRD) and energy dispersive spectrometer (EDS) were conducted for the catalysts before and after reaction. Furfural was selected as the model compound of depolymerisation wastes. Based on gasification results of furfural in SCW, different metal catalysts were discussed and compared.

2. Experimental section

2.1. Apparatus and procedure

The synthesis and gasification processes were conducted in a high-throughput batch reactor system with six subsystems. The reactor was fabricated from Inconel 625 and was designed with a maximum temperature and pressure of 750 °C and 30 MPa, respectively. The system contained a batch reactor, an electric furnace and a data acquisition station (DAS) of temperature and pressure. With a temperature controller, the electric furnace can operate at a desired temperature. The DAS can monitor and record the temperature inside the reactor using a thermocouple inserted inside the reactor [8,28,29].

First, metal salt solution was injected into the reactor with desired amount of TiO₂ particles. Calculated amount of deionised water was injected into the reactor with a syringe in order that desired supercritical water condition can be obtained. After that, a purging process was conducted to avoid influence of air or other gases. Next, the metal catalysts extracted from the reactor were dried in a small stove. Then, these metal catalysts were used in gasification of furfural in SCW for the evaluation of the catalysts.

2.2. Materials

Reagents are commercial products bought from special companies and their content information is listed in Table 1. Titanium sulphate was bought from Tianjin Guangfu Fine Chemical Research Institute with the content within 15.0%–20.0%. TiO₂ was used as
catalyst carrier and was obtained from Northwest Institute for Non-ferrous Metal Research.

2.3. Characterisation and analytical methods

All samples were characterised by XRD using a PANalytical X\textsuperscript{pert} MPD Pro X automatic diffractometer, with the $\lambda_{\text{CuK}a} = 1.541836$ Å radiation. The volt and current is 40 kV and 40 mA, respectively. Powders were observed by SEM, which were conducted on a JEOL JSM-7800F electron microscope coupled with an energy dispersive spectroscope. The composition of the gaseous products was analysed by gas chromatography (Agilent 7890A) with thermal conductivity detectors. High-purity argon was used as the carrier gas.

2.4. Data interpretation

CE, GE, HE and YH\textsubscript{2} were used for the evaluation of the gasification results \cite{10} in every catalytic situation.

$\text{CE} = \frac{\text{total carbon in the gaseous products}}{\text{total carbon in furfural}} \times 100\%$

$\text{GE} = \frac{\text{mass of the gaseous products}}{\text{mass of furfural}} \times 100\%$

$\text{HE} = \frac{\text{total hydrogen in the gaseous products}}{\text{total hydrogen in furfural}} \times 100\%$

$\text{YH}_2$ (Yield of H\textsubscript{2}) $= \text{molar amount of H}_2 \text{ after reaction/mass of furfural (mol/kg)}$

3. Results and discussion

TiO\textsubscript{2} was a common used catalyst carrier in supercritical water \cite{30–33}. In order to synthesise TiO\textsubscript{2}-based catalyst particles in SCW, titanium sulphate was used as the precursor and the main pathway was showed as follows \cite{34,35}:

\begin{align*}
\text{Ti(SO}_4\text{)}_2 + 4\text{H}_2\text{O} & \rightarrow \text{Ti(OH)}_4 + 2\text{H}_2\text{SO}_4 \\
\text{Ti(OH)}_4 & \rightarrow \text{TiO}_2 + 2\text{H}_2\text{O}
\end{align*}

Since we choose TiO\textsubscript{2} as our carrier of metal catalyst, it is necessary to explore the stability under different temperature. To realise it, we put TiO\textsubscript{2} into reactor for 20 min under different temperatures: 400, 500, 600 and 700 °C.

Figure 1 shows the SEM images of TiO\textsubscript{2} particles under different temperature. It can be seen that in a temperature range of 400–600 °C, TiO\textsubscript{2} particles remained spheroidal and nano-sized while they suddenly changed to have a massive laminar structure with less surface area at 700 °C. It is possible to result in the devitalisation of the catalyst. Moreover,
when it comes to economy, lower operating temperature often means lower energy for catalyst preparation.

From Equation (1), sulphuric acid was formed after hydrolysis of Ti(SO$_4$)$_2$. This kind of strong acid will lead to severe damage of reactor and thermal couple, especially at higher temperature. XRD and EDS analysis at 700 °C also showed that there was element Fe on the surface of carrier. Therefore, acetic salts seemed to be a better option and acetic salts were used as the catalyst precursor in the following experiments.

The hydrothermal stability of TiO$_2$ was tested in supercritical water with the temperature of 400 °C in autoclave for 20 min as seen in Figure 2. SEM images show a comparison of TiO$_2$ particles before and after exposure to supercritical water. Generally, there was almost no obvious difference in TiO$_2$ particle structure.

Acetic slats are our choice to be loaded on TiO$_2$ particles. The reaction pathway is shown as Equations (3)–(5). Through three steps, metal element can be dispersed on TiO$_2$ particle surface in the form of oxides. For quantification, mass of metal in acetic salt is 20 wt% of TiO$_2$. Then we did XRD analysis to investigate the crystalline phase on TiO$_2$.
particles as seen in Figure 3. Elements Zn and Ni existed in the form ZnO and NiO, respectively as expected. It is surprising to that Cu$_2$O was generated instead of CuO. It can be explained by atomic orbit theory that 3d$^{10}$ structure is more stable in SCW. For the element Co, two kinds of cobalt titanate were produced.

\[
\text{MCH}_2\text{COOH} + \text{H}_2\text{O} \rightarrow \text{MOH} + \text{CH}_3\text{COOH}
\]

\[
\text{CH}_3\text{COOH} + \text{H}_2\text{O} \rightarrow \text{CO}_2 + \text{H}_2
\]

\[
2\text{MOH} \rightarrow \text{M}_2\text{O} + \text{H}_2\text{O}
\]

Supercritical water gasification in autoclaves was conducted to evaluate the catalyst prepared. Furfural was selected as the model compound of the depolymerisation wastes. Mass of furfural and deionised water was 0.5 and 5 g, respectively. Mass of TiO$_2$ was 0.25 g and residence time was 20 min. After filtration and drying, residues are analysed by multiple characterisation methods.

![Figure 2. SEM images of TiO$_2$ particles. (a) Pure TiO$_2$ particles; (b) TiO$_2$ particles after 20 min in SCW at 400 °C.](image)

![Figure 3. XRD plot of different metal elements loaded on TiO$_2$ particles in SCW.](image)
As we can see in Figure 4, the catalyst crystalline phase was ZnO and zinc titanate after reaction for the Zn situation. NiO remained stable through the SCW gasification. And Cu$_2$O is all turned into elementary Cu. At the same time, two kinds of cobalt titanate become Co$_2$TiO$_4$ only. Table 2 lists all changes for every element. In summary, except for Cu, it occurred to all the elements that chemical valence remained unchanged.

SEM and EDS analysis were used to investigate the microstructure of synthesised catalyst. Synthesised catalyst particles have an excellent dispersity under the scope of 100,000 times magnified view in Figure 5. The diameters of the catalysts were roughly 30 nm which was almost the same as the original TiO$_2$.

Take Figure 5 (d) for example, energy spectrum analysis is listed in Table 3. As can be seen in Table 3, elements Ti and O were observed to have the most amount on the surface. Meanwhile, element Co was successfully loaded on TiO$_2$ particles uniformly and supercritical water synthesis method was proved to be successful.

Figure 6 shows SEM images of metal catalysts particles collected after furfural gasification in SCW, and the magnification was 5000 times. There appeared to be some bigger spherical particles on the surface of catalysts. EDS analysis was conducted to figure out that the content was mainly carbon as seen in Table 4. It could be that metal catalyst accelerates the precursor of coke during the gasification of furfural in SCW. This kind of precursor probably grows up to coke particles centred on metal

Table 2. Differences of metal elements between before and after reaction.

| Element | Before reaction | After reaction |
|---------|----------------|---------------|
| Zn      | ZnO            | ZnO, Zn$_2$TiO$_4$ |
| Ni      | NiO            | NiO           |
| Cu      | Cu$_2$O        | Cu            |
| Co      | CoTiO$_3$, Co$_2$TiO$_4$ | Co$_2$TiO$_4$ |

Figure 4. XRD plot of different metal elements loaded on TiO$_2$ particles after reaction in SCW.
catalyst particles. According to SEM image, diameter of coke particles is around 1 micrometre.

**Figure 5.** SEM images of different metal elements loaded on TiO₂ particles in SCW (a) Ni, 20wt% (b) Zn, 20wt% (c) Cu, 20wt% (d) Co, 20wt%.

**Table 3.** EDS analysis results of catalyst surface (Co loaded on TiO₂, 20wt%, 400 °C).

| Element | Mass percentage (%) | Atom percentage (%) |
|---------|---------------------|---------------------|
| O       | 39.33               | 66.59               |
| Ti      | 52.15               | 29.49               |
| Co      | 8.51                | 3.91                |

**Figure 7** shows the gasification results of furfural with and without different metal elements catalysts. The fraction of H₂ in gaseous products was only 6.34% and there appeared to be no methane without catalyst. In comparison, each catalyst improved HE vastly and some metal catalysts showed unique effect. At the same time, all catalysts
helped to produce methane although the ratio was around 3%–5%. Moreover, all catalysts reduced the ratio of CO₂.

When metal elements were Zn, Cu, Ni and Co, fractions of H₂ are 21.89%, 12.47%, 9.59% and 13.50%. This group of number tells us that element Zn performed best on H₂ selectivity. Simultaneously, ratio of CO₂ dropped from 82.29% without catalyst to 64.56% with Zn. HE increased most to 11.74% compared with 4.26% without catalyst and around 6% using any other catalyst. Yield of H₂ increased up to 17.38 mol/kg with Zn catalyst.

Table 4. EDS analysis results of partial spherical particles (Co loaded on TiO₂, 20wt%, 400 °C).

| Element | Mass percentage | Atom percentage |
|---------|----------------|----------------|
| C       | 74.99          | 80.34          |
| O       | 24.19          | 19.46          |
| Ti      | 0.57           | 0.15           |
| Co      | 0.24           | 0.05           |

Figure 6. SEM images of metal element loaded on TiO₂ particles after reaction in SCW (a) Ni, 20wt% (b) Cu, 20wt% (c) Co, 20wt%.
4. Conclusions

Nano metal catalysts based on TiO\textsubscript{2} particles were successfully prepared by supercritical water synthesis. 400 °C was approved to be the optimal preparation temperature because it can promote the generation of catalyst and reduce energy consumption. The stability of catalysts was tested over 20 min in supercritical water and Zn, Ni, Cu, and Co were proved to be dispersed on the surface of TiO\textsubscript{2} particles. According to XRD analysis, Ni performed the best stability without crystalline phase change. Although there happened to be some coke covered on the catalyst particles, gasification results of furfural in SCW were still much better than those without catalyst. By comparison, zinc catalyst showed best catalytic effects among all catalysts. Single metal catalysts carried on TiO\textsubscript{2} can be successful prepared by supercritical water synthesis and performed catalytic effect for furfural gasification in supercritical water.

Disclosure statement

No potential conflict of interest was reported by the authors.

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Figure 7. Gasification results of furfural with different metal elements catalysts (furfural 10 wt%, residence time 20 min).
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