

Effect of supercritical water gasification conditions on properties of ZrO₂

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Highlights

- Monoclinic and tetragonal ZrO₂ was synthesized with sol-gel method
- Monoclinic phase composition of ZrO₂ is both stable and active for SCWG.
- The highest percentage of hydrogen was obtained in the presence of monoclinic ZrO₂.
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1. Introduction

Catalytic supercritical water gasification (CSCWG) is an important technique for converting biomass into gaseous biofuels (such as H₂ and CH₄) and, in contrast to supercritical water gasification (SCWG), is carried out at low to moderate temperatures (around 400 °C). For this purpose, metal oxides are a promising catalyst for the SCWG of organic waste and biomass, as they are inexpensive, resistant to high temperatures, easily transportable and regenerable. However, these catalysts often undergo instability and mechanical structural changes in supercritical water (SCW), leading to phenomena such as agglomeration, phase transformation, formation of solid solutions and dissolution of components. The extent of these changes is influenced by the composition of the catalyst, the preparation method and the reaction conditions. Therefore, it is necessary to specify the phase composition and particle morphology which, among other properties, ensure the stability of the catalysts under SCW conditions.

Zirconium oxide (ZrO₂) is a very special metal oxide that has both redox and acid-base properties and has cubic, tetragonal, and monoclinic phases. The physical properties of ZrO₂ are greatly influenced by these crystal phases [1,2]. Comparing monoclinic ZrO₂ to tetragonal ZrO₂, the former exhibits a higher Brönsted Zr-OH group concentration and a higher Lewis acidity of Zr⁴⁺ ions and Lewis basicity of O²⁻ ions. The reactants activation is significantly influenced by the properties of the ZrO₂ crystal phase.

The aim of this study is to determine the activity, selectivity and stability of the ZrO₂ catalyst in relation to the gasification of formaldehyde in a supercritical water environment. The sol-gel technique was used for the synthesis of monoclinic and tetragonal ZrO₂ as it is inexpensive, simple, reusable, reliable and provides extremely mild synthesis conditions. The morphological and structural changes of the ZrO₂ catalyst prepared by sol-gel and removed from the reactor after the gasification tests were characterized by zeta potential, XRD, BET, TPR, TPD, TGA, SEM, TPO and FTIR. We analyzed and compared the gaseous and liquid products formed during supercritical formaldehyde gasification with and without ZrO₂ catalyst.

2. Methods

Zirconium oxide synthesis was carried out with 70% (vol/vol) zirconium n-propoxide solution according to Ward and Ko [3]. The samples were calcined at 500, 900 and 1400 °C for 2 hours. The synthesized samples are abbreviated as ZrO₂-X-SJ, where x stands for the calcination temperature and SJ for the sol-gel method. XRD, BET, TPR, TPD, TGA, SEM, TPO and FTIR for all samples were performed for all samples as in our previous studies [4,5].

Catalytic gasification of formaldehyde in supercritical water was carried out using a batch reactor (Parr 4591) with an internal volume of 100 mL. On the efficiency of SCW gasification of formaldehyde with ZrO₂ catalysts, varying catalyst amount (0.5- 1.0 g), temperature (375- 425 °C), input concentration (10 and 20 %) and retention time (15- 60 min) were investigated. After reaction, gas, liquid and solid products were analyzed using on-line GC, HPLC and total organic carbon analyzer.

3. Results and discussion

XRD results show that ZrO₂ samples calcined at 500 and 1400 °C mostly have monoclinic and tetragonal phase, respectively and have nano-sized particles. The surface area and porosity of samples prepared with the sol-gel increased significantly in catalytic gasification of formaldehyde in SCW, but decreased in commercial ZrO₂. The increase in surface area and porosity may be explained by the formation of defects by dissolution of material under hydrothermal conditions. As observed in the SEM results of the material under hydrothermal conditions, the reduction in the surface area of the commercial ZrO₂ sample may be a consequence of significant amount of agglomeration and coking. The thermal stability study of ZrO₂ catalysts by thermogravimetric method showed that the ZrO₂ sample calcined at 1400 °C with high crystal size has high thermal stability. Based on the zeta potential results, SCW-exposed ZrO₂ samples under atmospheres of pure water and of carbon compounds affects isoelectricity in significant quantities. The presence of carbon-containing compounds prevents the adsorption of hydroxyl ions on the ZrO₂ surface. H₂-TPR results show that the tetragonal and monoclinic phases of ZrO₂ samples have different H₂ reduction properties. O₂-TPD results show that the ZrO₂ catalyst calcined at 1400 °C and used in gasification of formaldehyde with SCW lost its oxygen desorption properties at high temperatures (600 °C).

The distribution of gas and liquid products of formaldehyde in SCW in the presence of ZrO₂ catalysts varies according to the method of preparation of the ZrO₂ catalyst, the phase composition, the reactant concentration, the reaction temperature, the amount of catalyst and the residence time of the reactants. The highest percentage of hydrogen was obtained in the presence of 0.5 g ZrO₂ catalyst calcined at 500 °C and 10% (wt.) formaldehyde concentration at 400 °C for 30 minutes, which is approximately 64%.

4. Conclusions

As a result of testing the catalytic activities in the gasification of formaldehyde under 673 K temperature and 22.1 MPa pressure in SCW atmosphere, the tetragonal phase turned into monoclinic phase. ZrO₂ produced by calcining ZrO₂ produced by SJ at 1400 °C has a monoclinic phase and its phase composition has not changed with the reaction. Testing the catalytic activities in the gasification of formaldehyde in SCW atmosphere at a temperature of 673 K and a pressure of 22.1 MPa revealed high hydrogen formation in both commercial and ZrO₂-SJ-500 catalysts phases, indicating that monoclinic phase composition is both stable and active.

References

- [1] T. Witoon, J. Chalorntham, P. Dumrongbunditkul, M. Chareonpanich, J. Limtrakul, CO₂ hydrogenation to methanol over Cu/ZrO₂ catalysts: Effects of zirconia phases, *Chem. Eng. J.* 293 (2016) 327–336.
- [2] F.C.F. Marcos, J.M. Assaf, R. Giudici, E.M. Assaf, Surface interaction of CO₂/H₂ mixture on mesoporous ZrO₂: Effect of crystalline polymorph phases, *Appl. Surf. Sci.* 496 (2019) 143671.
- [3] D.A. Ward, E.I. Ko, Synthesis and structural transformation of zirconia aerogels, *Chem. Mater.* 5 (1993) 956–969.
- [4] A. Ates, Activity and stability of TiO₂ samples with different phase compositions in the decomposition of formaldehyde in SCW, *Int. J. Hydrogen Energy.* 46 (2021) 1842–1856. doi:10.1016/j.ijhydene.2020.10.072.
- [5] A. Ates, H. Hatipoglu, Evaluation of Stability and Catalytic Activity in Supercritical Water of Zinc Oxide Samples Prepared by the Sol-Gel Method, *J. Inorg. Organomet. Polym. Mater.* 31 (2066) 4581–4593. doi:10.1007/s10904-021-02066-2.

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