

Ru/C as a catalyst for supercritical water gasification of isopropanol for methane production

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Introduction

Catalytic supercritical water gasification (CSCWG) is a promising technology to convert efficiently wet biomass (e.g. microalgae, biomass residues) to biomethane. Although Ru/C catalysts were reported to have good catalytic performances [1], there is still a necessity to assess some relevant parameters related to the catalyst design for the catalyst optimization. Hence, in this work we studied the Ru dispersion effect and the effect of the solvent (water vs acetone) used during the catalyst preparation by carrying out CSCWG with isopropanol as an organic model compound.

Materials and Methods

The Ru/C catalysts were prepared by wet impregnation with $\text{RuCl}_3 \cdot x\text{H}_2\text{O}$ in either water (Ru/C_w) or in acetone (Ru/C_a) during 24 hours followed by solvent evaporation in a rotary evaporator. After the impregnation the samples were washed with pure water, dried overnight in an oven at 90 °C and reduced with H_2 at 450 °C for 4 hours. The samples were characterized by CO pulse chemisorption, N_2 -physisorption and XPS. The catalytic performance were assessed by a fixed-bed plug flow reactor at 450 °C and 30 MPa with 10 wt. % isopropanol in water.

Results and Discussion

The characteristics of the Ru/C catalysts are listed in Table 1.

Table 1. Properties of the Ru/C catalysts.

Catalyst	$V_{\text{mesop.}}$ [cm ³ /g]	$V_{\text{microp.}}$ [cm ³ /g]	Ru loading [wt. %]	Dispersion [%]	Particle size [nm]*
0.5 % Ru/C _w	0.75	0.13	0.58	12	7.5
2 % Ru/C _w	0.73	0.11	2.32	8	11.3
2 % Ru/C _a	0.54	0.11	2.09	11.2	8.1

* Determined by CO pulse chemisorption.

Figure 1 (a) shows the catalytic performance of the 2 % Ru/C_a catalyst at relatively low $\text{WHSV}_{\text{gRu}} = 1228 \text{ g}_{\text{Org}}/(\text{g}_{\text{Ru}} \cdot \text{h})$. The catalyst was able to gasify efficiently 10 wt. % isopropanol over a period of 96 hours with a gas composition close to the thermodynamic chemical equilibrium. This result demonstrates the good capability of Ru for C-O bond cleavage enhancing the methanation reaction. The similarity between the observed activity (X_C) and the carbon gasification efficiency (GE_C) proves that the carbon contained in the feed is fully

converted to gases. In **Figure 1 (b)** a relevant effect of the Ru dispersion was found where the 0.5 % Ru/C_w exhibited a higher activity than the 2 % Ru/C_w. The catalyst prepared with acetone (2 % Ru/C_a) was ca. four times more active than the catalyst prepared with water (2 % Ru/C_w) after 6 hours of CSCWG. The detection of residual chloride (0.28 at%) on the 2 % Ru/C_w by XPS, coming from the ruthenium salt precursor (RuCl_3), suggested to be responsible for the lower observed activity. In fact, it has been reported [2] that water enhances the anchoring of residual Cl^- on the carbon support during the catalyst preparation. It is well known [3] that residual Cl^- negatively affects the catalytic performances of Ru. Furthermore, the lower dispersion value for the 2 % Ru/C_w compared to the 2 % Ru/C_a may be explained by the presence of residual Cl^- . Actually, Cl^- was reported [3, 4] to reduce the CO adsorption capacity by poisoning the Ru surface.

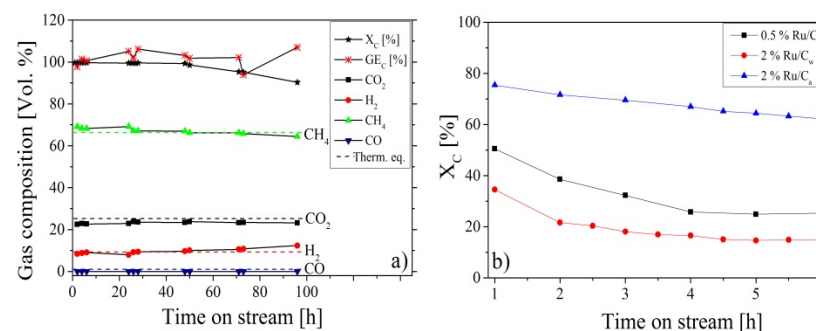


Figure 1. (a) Catalytic performance of the 2 % Ru/C_a catalyst determined with 10 wt. % isopropanol at 450 °C and 30 MPa with $\text{WHSV}_{\text{gRu}} = 1228 \text{ g}_{\text{Org}}/\text{g}_{\text{Ru}} \cdot \text{h}$. (b) Assessment of the Ru dispersion effect and the solvent effect at 450 °C and 30 MPa with $\text{WHSV}_{\text{gRu}} = 5202 \text{ g}_{\text{Org}}/\text{g}_{\text{Ru}} \cdot \text{h}$.

Significance

The Ru dispersion is a key parameter to optimize in order to achieve high catalytic performances. The presence of residual Cl^- on the catalyst coming from the salt precursor (RuCl_3) during the catalyst preparation reduced significantly the catalytic activity.

References

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