ChemPubSoc Europe

DOI: 10.1002/cctc.201500995

CHEMCATCHEM
Communications

# Ruthenium Dispersion: A Key Parameter for the Stability of Supported Ruthenium Catalysts during Catalytic Supercritical Water Gasification

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The catalytic supercritical water gasification of isopropanol (450 °C, 30 MPa) over Ru catalysts supported on carbon and metal oxides was performed in a fixed-bed plug flow reactor. The Ru loading was between 1.2 and 2 %. The catalyst stability over a period of 50 h was in the order: Ru/C > Ru/$ZrO_2$ > Ru/$Al_2O_3$ ≈ Ru/$TiO_2$. Considerable coke deposits were found on Ru/$Al_2O_3$ and Ru/$TiO_2$, which suggests that coke formation was responsible for the loss of activity, whereas the coke content was much lower on Ru/C and Ru/$ZrO_2$, which confirms their better coking resistance. Clearly, Ru/C was the most stable catalyst as a loss of only 3 % of its initial activity was measured. The high Ru dispersion of Ru/C and Ru/$ZrO_2$ was beneficial for the improvement of the catalyst stability because of the higher gasification rate versus the coke formation rate.

The production of gaseous biofuels (such as $H_2$ and $CH_4$) from wet biomass (e.g. microalgae, biomass residues) has attracted a lot of attention during the last decade. For this purpose, catalytic supercritical water gasification (CSCWG) is a promising technology. Its main advantage is its capability to process wet biomass (water content > 60 wt %) without the need for a drying step, which allows a high thermal efficiency to be reached (70–77 %).[1] At moderate temperatures (374–500 °C), a catalyst is required to reach a high biomass conversion and a high $CH_4$ or $H_2$ yield. For the production of $CH_4$, supported Ru catalysts are known to be the most suitable catalysts because of the high activity of Ru to decompose the large organic molecules by C–C bond cleavage as well as their high $CH_4$ selectivity because of the ability of Ru to cleave C–O bonds.[2] Only a few catalyst supports are able to preserve their physical structure in the harsh environment of supercritical water ($T >$ 374 °C, $p > 22.1$ MPa). Carbon and some metal oxides such as rutile-$TiO_2$, monoclinic-$ZrO_2$, and $\alpha$-$Al_2O_3$ were reported to be stable.[3–5] In a previous study,[6] we reported that the lifetime of Ru/C catalysts was affected by the decomposition of the reactant (isopropanol) to coke over the carbon surface, whereas Ru leaching and Ru sintering were found to have minor effects on the catalyst deactivation. Zöhrer et al.[7] studied the stability of Ru supported on metal oxides (Ru/$TiO_2$ and Ru/$ZrO_2$) during the CSCWG of glycerol and observed some coke deposits on the spent catalysts. Therefore, coking is a serious issue in the gasification of organic compounds under supercritical conditions. In this work, we compare the stability of Ru catalysts supported on carbon and metal oxides (rutile-$TiO_2$, monoclinic-$ZrO_2$, and $\alpha$-$Al_2O_3$) during the CSCWG of isopropanol (IPA) to evaluate their respective coking resistance. The use of alcohols as model compounds is relevant as they have been reported as intermediate products during the supercritical water gasification of real biomass.[8] Fundamentally, IPA is a good model compound because it is a simple molecule yet it contains C–C, C–H, and C–O bonds as well as primary and secondary carbon atoms. The characteristics of the supported Ru catalysts are listed in Table 1. It seems that a higher BET specific surface area (SSA) favors a higher Ru dispersion. Although the BET SSA of Ru/$ZrO_2$ was significantly smaller than that of Ru/C, its Ru dispersion was still high. This result demonstrates that a relatively small BET SSA of ~20 $m^2 g^{-1}$ is already large enough to achieve highly dispersed Ru nanoparticles by a wet impregnation method.

**Table 1.** Characteristics of the fresh supported Ru catalysts.

| Catalyst | BET SSA [$m^2 g^{-1}$] | $V_{total}$[a] [$cm^3 g^{-1}$] | Ru loading [wt %] | $D_{CO}$[b] | $d_{p,CO}$[c] [nm] |
|---|---|---|---|---|---|
| Ru/$TiO_2$ | 4 | 0.03 | 1.8 | 8 | 16.3 |
| Ru/$ZrO_2$ | 23 | 0.19 | 1.2 | 52 | 1.9 |
| Ru/$Al_2O_3$ | 5 | 0.04 | 1.2 | 6 | 23.3 |
| Ru/C | 653 | 0.70 | 2 | 61 | 1.6 |

[a] Measured at $p/p_0 = 0.99$. [b] Ruthenium dispersion determined by CO pulse chemisorption. [c] Ruthenium particle size calculated according to the formula developed by Borodziński and Bonarowska.[9]

The catalytic performance of the supported Ru catalysts during the CSCWG of 10 wt % isopropanol at 450 °C and 30 MPa over 50 h is shown in Figure 1. To operate at carbon conversions below 100 %, a weight hourly space velocity normalized to one gram of Ru ($WHSV_{gRu}$) was used. For the Ru/C

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Supporting Information and ORCID(s) from the author(s) for this article are available on the WWW under http://dx.doi.org/10.1002/cctc.201500995.

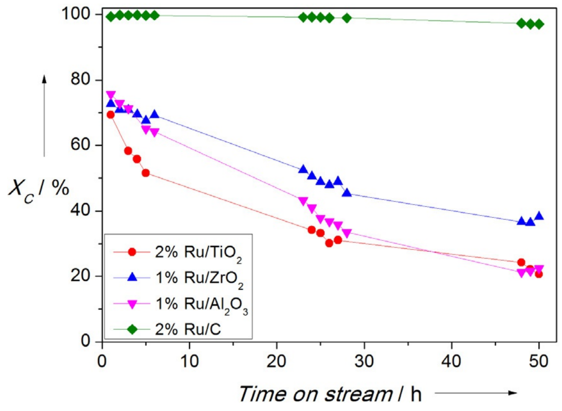

**Figure 1.** CSCWG of 10 wt% isopropanol over Ru catalysts supported on carbon and on metal oxides at 450 °C and 30 MPa for 50 h with $\mathrm{WHSV}_{gRu} = 5202\ g_{Org}\,g_{Ru}^{-1}\,h^{-1}$.

catalyst, this space velocity was still too low to reach incomplete conversion but it was at the limit of our setup. The stability of the catalysts decreased in the order: Ru/C > Ru/ZrO$_2$ > Ru/Al$_2$O$_3$ ≈ Ru/TiO$_2$. Although the initial activity of all the Ru catalysts supported on metal oxides was similar, which depended on the type of metal oxide, the difference of the activity loss was considerable. For instance, Ru/TiO$_2$ and Ru/Al$_2$O$_3$ lost approximately 25 and 14% of their initial activity, respectively, during the first 5 h, whereas Ru/ZrO$_2$ lost only ≈7%. The better stability of Ru/ZrO$_2$ can be related to its higher Ru dispersion, which favored a higher gasification rate compared to the coke formation rate. In contrast, after 50 h the stability of Ru/C remained almost unaffected. Such a good stability can be explained by the high capacity of the small Ru nanoparticles to convert isopropanol fully to gaseous products at such a high $\mathrm{WHSV}_{gRu}$. It is known that a high Ru dispersion is needed to achieve a high activity during the CSCWG of isopropanol.[6]

The gas composition confirms the good catalytic performance of Ru/C as the CH$_4$ concentration was close to the thermodynamic chemical equilibrium (Table 2 and Figure S4).

**Table 2.** Summary of results after 50 h of CSCWG of 10 wt% isopropanol at 450 °C and 30 MPa with $\mathrm{WHSV}_{gRu} = 5202\ g_{Org}\,g_{Ru}^{-1}\,h^{-1}$.

| Catalyst | $X_C$[a] [%] | $GE_C$[b] [%] | CH$_4$ [vol%] | CO$_2$ [vol%] | H$_2$ [vol%] | CO [vol%] |
|---|---|---|---|---|---|---|
| Ru/TiO$_2$ | 21 | 13 | 46 | 19 | 35 | 0 |
| Ru/ZrO$_2$ | 38 | 25 | 48 | 21 | 31 | 0 |
| Ru/Al$_2$O$_3$ | 22 | 20 | 44 | 18 | 39 | 0 |
| Ru/C | 97 | 81 | 65 | 21 | 14 | 0 |

[a] $X_C = (1-(\text{mol } C_{Liq,out}/\text{mol } C_{Feed})) \times 100\%$. [b] $GE_C = \text{total mol } C_{Gas}/\text{total mol } C_{Feed} \times 100\%$.

The low CH$_4$ and high H$_2$ concentrations for the Ru catalysts supported on metal oxides revealed that the methanation reaction was less favored, probably because of a decreased rate of C–O bond cleavage. As no CO was detected, it seems that the water gas shift reaction was still favored at a low total carbon conversion ($X_C$).

Interestingly, the carbon gasification efficiency (GE$_C$) values were lower than the $X_C$ values, which indicates carbon accumulation in the reactor. Hence, coke deposition from the decomposition of isopropanol on the catalyst support surface seems to take place for the tested Ru catalysts. According to the GE$_C$ and $X_C$ values for Ru/Al$_2$O$_3$, no coking occurred. As a result of its small BET SSA, it is likely that the coke deposits were more difficult to quantify. Notably, GE$_C$ was calculated from the gas flow rate, and some inaccuracies caused by gas accumulation in the setup might occur.

The temperature-programmed oxidation (TPO) results of the fresh and spent Ru catalysts supported on metal oxides confirm that coke formation occurred during the CSCWG of isopropanol as CO$_2$ peaks were observed with the spent catalysts (Figure 2). The higher peak intensity for Ru/TiO$_2$ and Ru/Al$_2$O$_3$ in comparison to Ru/ZrO$_2$ confirms the better coking resistance of the latter. The different CO$_2$ peaks are likely related to the oxidation of carbonaceous species located on the Ru surface and the catalyst support.

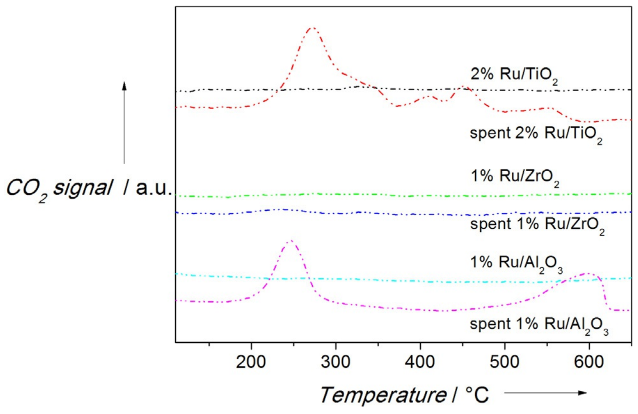

**Figure 2.** TPO of the fresh and spent Ru catalysts supported on metal oxides.

As the coke deposits cannot be characterized by TPO for the Ru/C catalyst because of the combustion of the carbon support itself, Ru/C was characterized by N$_2$ physisorption. The physical structure of the Ru/C was well preserved after 50 h on-stream (Table 3). Although a small fraction of the mesopore volume was lost, likely caused by coke deposits, the total pore volume remained high. This observation suggests that the amount of coke inside the pores is low. In previous work,[6] we

**Table 3.** Physical data for fresh and spent Ru/C.

| Catalyst | BET SSA [m$^2$g$^{-1}$] | $V_{total}$[a] [cm$^3$g$^{-1}$] | $V_{mesopore}$[b] [cm$^3$g$^{-1}$] | $V_{micropore}$ [cm$^3$g$^{-1}$] |
|---|---|---|---|---|
| Ru/C | 653 | 0.70 | 0.58 | 0.12 |
| spent Ru/C | 670 | 0.66 | 0.53 | 0.13 |

[a] Measured at $p/p_0 = 0.99$. [b] Calculated with the t-plot method.

reported that if a 0.5 % Ru/C catalyst was fully deactivated ($X_C = 10\%$) during the CSCWG of isopropanol (450 °C, 30 MPa), the pore volume was reduced drastically by the coke deposits.

In this study, we showed that a higher Ru dispersion led to a better stability of supported Ru catalysts during the continuous CSCWG of isopropanol. For the catalysts that have a high Ru dispersion (Ru/C and Ru/$ZrO_2$), a lower amount of coke deposits was found, which suggests a better coking resistance. As a result of its higher Ru dispersion in comparison to the catalysts supported on the metal oxides, Ru/C exhibited the best overall catalytic performance (stability, activity, and $CH_4$ selectivity). Hence, Ru/C appears to be the most suitable catalyst for CSCWG.

## Experimental Section

Rutile-$TiO_2$ (pellets, Norpro Saint Gobain SA), monoclinic-$ZrO_2$ (pellets, Norpro Saint Gobain SA), $\alpha$-$Al_2O_3$ (pellets, Alfa Aesar), and carbon (granular, DESOTEC) were sieved to a size fraction of 0.3–0.8 mm. The supported Ru catalysts were prepared by wet impregnation with $Ru(NO)(NO_3)_3$ in a water solution for 6 h followed by solvent evaporation in a rotary evaporator. The materials were washed with pure water during filtration. The Ru loss during washing was quantified by inductively coupled plasma optical emission spectroscopy (ICP-OES; Liberty 110, Varian). After drying at 60 °C overnight in a vacuum oven, Ru/C was reduced under flowing $H_2$/Ar (10:90, 20 mL min$^{-1}$) at 450 °C for 4 h. The Ru catalysts supported on metal oxides were calcined at 450 °C for 4 h. The BET SSA and the pore volume were measured by $N_2$ physisorption by using an Autosorb-1 (Quantachrome Instruments). CO pulse chemisorption was performed by using a fully automated instrument (TPD/R/O 1100, Thermo Scientific) for the measurements of the Ru dispersion ($D_{CO}$) and the Ru nanoparticles size ($d_{p,CO}$) according to a procedure described elsewhere.[6] TPO was performed by using a NETZSCH STA 449 C thermobalance coupled to an FTIR detector (Bruker). The samples (50 mg) were measured from RT to 650 °C with a ramp of 10 °C min$^{-1}$ under a flow of $O_2$/Ar (20:80, 20 mL min$^{-1}$). The catalysts were tested in a fixed-bed plug flow reactor described in detail elsewhere.[6] Isopropanol was purchased from VWR BDH Prolabo (99.8 %). The feed rate was kept at 3 g min$^{-1}$. The amount of Ru/C catalyst in the reactor was ≈0.17–0.28 g. The $WHSV_{gRu}$ was 5202 $g_{Org}\,g_{Ru}^{-1}\,h^{-1}$ for each experiment. The gas phase was analyzed offline by GC (HP 6890) with a thermal conductivity detector. Liquid samples were collected regularly manually and the total organic carbon (TOC) was measured by using a TOC analyzer (Vario TOC cube, Elementar). The observed activity is defined as the total carbon conversion ($X_c$) from the feed to the reactor effluent. The carbon gasification efficiency ($GE_C$) is the relationship between the total amount of carbon in the gas phase and the total amount of carbon in the feed.

## Acknowledgements

*This work was financially supported within the scope of the SunCHem project by the Competence Center Energy and Mobility (CCEM-CH) and Swisselectric Research (Switzerland). The authors would like to thank Alexander Wokaun for the fruitful discussions.*

**Keywords:** alcohols · carbon · ruthenium · supercritical fluids · supported catalysts

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Received: September 8, 2015
Revised: October 27, 2015