

# The role of metal and support sites on the hydrogenation of acetic acid on Ru-based catalysts

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## Introduction

The use of biomass as raw material for the manufacture of fuels and chemicals creates various challenges for chemical processes. Acetic acid is currently manufactured by three alternative processes: acetaldehyde oxidation, *n*-butane oxidation, and methanol carbonylation. It is, however, an important by-product of the pyrolysis of biomass and together with other oxygenates produced decreases the quality and complicates the handling of the resulting fuels. Their transformation into other chemical products, such as alcohols, aldehydes, and ketones would provide useful outlets into basic and intermediate chemicals. Here, we examine acetic acid conversion, as chemistry prototypical of the transformations required in these processes. Few studies of the hydrogenation of acetic acid have been reported, most of them with emphasis on model transition metal surfaces<sup>1</sup>, and a few on more practical supported catalysts<sup>2</sup>. Only Rachmady and Vannice<sup>3</sup> focused on supported noble metal catalysts and proposed that reaction involves both Pt and support sites. Here, we report the behavior of Ru-based catalysts for the hydrogenation of acetic acid.

## Materials and Methods

Supported Ru (1% Ru) catalysts were prepared by incipient wetness impregnation of Al<sub>2</sub>O<sub>3</sub> (Alcoa, Puralox), ZrO<sub>2</sub>·x(OH)<sub>2</sub>, TiO<sub>2</sub> (Degussa, P25), and SiO<sub>2</sub> (Degussa, Aerolyst 3038) with aqueous solutions of Ru(NO)(NO<sub>3</sub>)<sub>3</sub>·xH<sub>2</sub>O (Aldrich, 56 wt % Ru). Zirconium oxyhydroxide supports were prepared by precipitation from ZrOCl<sub>2</sub> aqueous solutions<sup>4</sup>. Impregnated supports were treated in ambient air at 398 K overnight and then treated in air and reduced in pure flowing H<sub>2</sub> both at 673 K. The extent of reduction measured by temperature-programmed methods showed full reduction at <573 K. Some samples were subsequently treated with cesium acetate to increase the density and strength of basic sites. Acetic acid rates and selectivities were measured by placing samples in a quartz tube, with reactants and products analyzed by on-line mass spectrometry. The effluent stream was also periodically sampled into a gas chromatograph connected to a mass selective detector to identify all reaction products and to allow periodic calibration of the mass spectral signals. Rate measurements were carried out at ambient pressure and 423- 623 K, and a space velocity of 50 moles acetic acid/kg-cat·h. H<sub>2</sub> and acetic acid pressures were varied in the ranges of 0.25-4.0 and 0-24 kPa, respectively, using Ar as an inert internal standard. Separate experiments co-feeding reaction products, such as acetone and acetaldehyde, were also carried out.

## Results and Discussion

Initial experiments were designed to measure the catalytic properties of the pure supports after they were treated at 673 K in flowing air. Obtained results are summarized in Table 1, showing the temperature required to achieve 50 % acetic acid conversion and the selectivities for the principal reaction products (methane and acetone). All supports gave detectable formation rates for acetone, with some methane co-produced predominantly at low

conversions. The most active supports (ZrO<sub>2</sub> and TiO<sub>2</sub>) also catalyzed condensation reactions to form aliphatic and aromatic hydrocarbons and unreactive residues. The presence of basic sites, prevalent on TiO<sub>2</sub> and ZrO<sub>2</sub> supports, gave the highest rates and acetone selectivities, while SiO<sub>2</sub> was the least active among these supports. These results suggest a mechanism involving the formation of surface acetates, whose decomposition leads to the formation of the reaction products<sup>5</sup>.

**Table 1. Acetic acid reaction rates and selectivities on supports used in this study.**

Support	T <sub>50</sub> (K)	S <sub>acetone, max</sub> (T (K), x (%))	S <sub>methane, max</sub> (T (K), x (%))
SiO <sub>2</sub>	>673	not detected	50.1 (633, 5)
Al <sub>2</sub> O <sub>3</sub>	646	28 (673, 80)	20 (548, 15)
TiO <sub>2</sub>	578	30 (608, 80)	18 (523, 10)
ZrO <sub>2</sub>	542	35 (573, 82)	15 (488, 20)

T<sub>50</sub>, temperature required for 50 % conversion; S<sub>max</sub>, maximum selectivities for acetone and methane (T and acetic acid conversion at which achieved)

The presence of Ru on these supports inhibits coke formation (as observed from the carbon balance and the final appearance of the catalyst) and leads to the predominant formation of acetaldehyde, the expected product of acetic acid hydrogenation; ethanol and ethane, the subsequent hydrogenation products, were formed with <1% selectivity. The formation of acetone and of condensation products is also inhibited by Ru, suggesting that H<sub>2</sub> activation on the Ru function and subsequent spillover onto the support scavenges acetate intermediates and prevents their parallel reactions. In order to corroborate the role of support basic sites in this reaction scheme, the concentration of basic sites of the Ru/ZrO<sub>2</sub> catalyst was increased by treating with cesium acetate solutions. The main effect observed was an increase of the selectivity for acetone and direct hydrogenation products (being even observed ethanol and ethane) and a decrease in the hydrogenolysis activity.

**Table 2. Summary of the experiments carried out with the studied catalysts**

Ru catalysts	T <sub>50</sub> (K)	S <sub>acetone, max</sub> (T (K), x (%))	S <sub>methane, max</sub> (T (K), x (%))	S <sub>acetaldehyde, max</sub> (T (K), x (%))
Ru/SiO <sub>2</sub>	673	32 (623, 6)	34 (623, 6)	60 (673, 33)
Ru/Al <sub>2</sub> O <sub>3</sub>	623	40 (673, 10)	14 (523, 8)	80 (523, 8)
Ru/TiO <sub>2</sub>	533	25 (573, 70)	45 (523, 17)	60 (623, 10)
Ru/ZrO <sub>2</sub>	513	30 (523, 40)	12 (523, 40)	68 (673, 10)

These data show the important interplay between metal and support functions in the conversion of acetic acid and related oxygenates to more useful products. Basic sites catalyze acetone formation and the addition of Cs also inhibits methane formation. Taken together with previous studies<sup>3</sup>, these data show that supports can be generally used to modify reaction selectivity on other metals, such as Pt, Pd, and Rh.

## References

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