

Investigating deactivation and kinetics of levulinic acid hydrogenation on titania supported ruthenium catalysts

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Highlights

- Cause of deactivation - sintering, coking, leaching and ruthenium oxidation state investigated
- Deactivation kinetics higher at lower operating temperatures.
- Leaching and coking not observed. Sintering and changing oxidation state dominant phenomena.
- First order kinetics of levulinic acid hydrogenation upon catalyst stabilization after initial deactivation.

1. Introduction

Successful substitution of traditional industrial commodities derived from non-renewable sources with renewable counterparts has been one of the primary focus in recent years. Lignocellulosic biomass sourced through agricultural and forestry residues, waste streams from paper and pulp mills to produce alternate chemicals can help accomplish this. Among a multitude of chemicals that can be obtained from these sources, γ -valerolactone (GVL), produced via levulinic acid (LA) hydrogenation, can be used as a solvent and fuel additive. The hydrogenation of LA typically takes place under aqueous phase conditions. Recent trends on ruthenium-catalyzed LA hydrogenation have led to a variety of catalytic supports being used¹. Amongst these, TiO₂ has shown promising catalytic activity albeit suffering from deactivation. This work utilizes high operating temperatures ($T > 100^\circ\text{C}$) to investigate stability and LA hydrogenation kinetics upon full deactivation of the catalyst. Slower deactivation kinetics are prevalent at higher operating temperatures. On doubling the ruthenium loading (from 1 to 2 wt.%), the catalytic activity upon stabilization surpasses twice its value (from 10 to 53%). This was attributed to first-order dependence on LA with a deactivated Ru (2 wt.%)/TiO₂ at 100 and 200°C.

2. Methods

Ru/TiO₂ was synthesized using incipient wetness impregnation techniques with RuCl₃ as the metallic precursor. Catalytic activity testing was performed in a packed bed reactor with upflow conditions. The samples at reactor outlet were analyzed using HPLC (Zorbax Phenyl reversed phase 4.6*250mm column) and UV/vis detector. Ruthenium oxidation state was calculated using XPS on fresh and spent catalyst samples, TEM and TGA were used to analyze particle size distribution and coking of the samples, respectively.

3. Results and discussion

Figure 1 shows the drop of catalyst activity over a period of five hours using Ru (1 wt.%)/TiO₂. The deactivation rate is highest for 100°C and decreases with temperature. This is in stark contrast with sintering as the main cause of deactivation since this phenomenon would otherwise be favored at high operating temperatures and high partial pressures of water. On the other hand, evidence of some degree of sintering was observed using TEM for particle size distribution measurements. While TEM results show a 60% decrease in specific surface area of active metal particles, a 90% drop in catalytic activity is observed. In addition, an increase in Ru⁰ content with longer time on stream suggests in-situ reduction and change in the catalytic structure with reaction time. Besides, no ruthenium was detected with ICP analysis of the liquid reaction sample; and no significant differences in the TGA curves of spent catalysts

from different time-on-streams. The catalytic activity of Ru (1 wt.)/TiO₂ at 200°C stabilized to 10% LA conversion on the third day of time-on-stream and showing stable activity of 10% conversion until 270 hours of operation.

To determine the effect of ruthenium loadings on deactivation kinetics, active metal loading was initially doubled (i.e., from 1 to 2 wt.%) and later, total catalyst mass was doubled (i.e., from 100 to 200 mg) while maintaining ruthenium loading at 1wt.%. Both the catalytic beds showed significantly slower deactivation kinetics (0.023-0.025 vs. 0.219 hr⁻¹ with 100 mg 1 wt.% Ru/TiO₂) with an observed LA conversion of 51-53% upon stabilization of catalytic activity after initial deactivation. Similar LA conversions (12 and 51%) were obtained at 100 and 200°C, respectively, with different inlet LA concentrations (1, 2 and 5 wt.%). This indicates a first-order LA dependence for the hydrogenation kinetics.

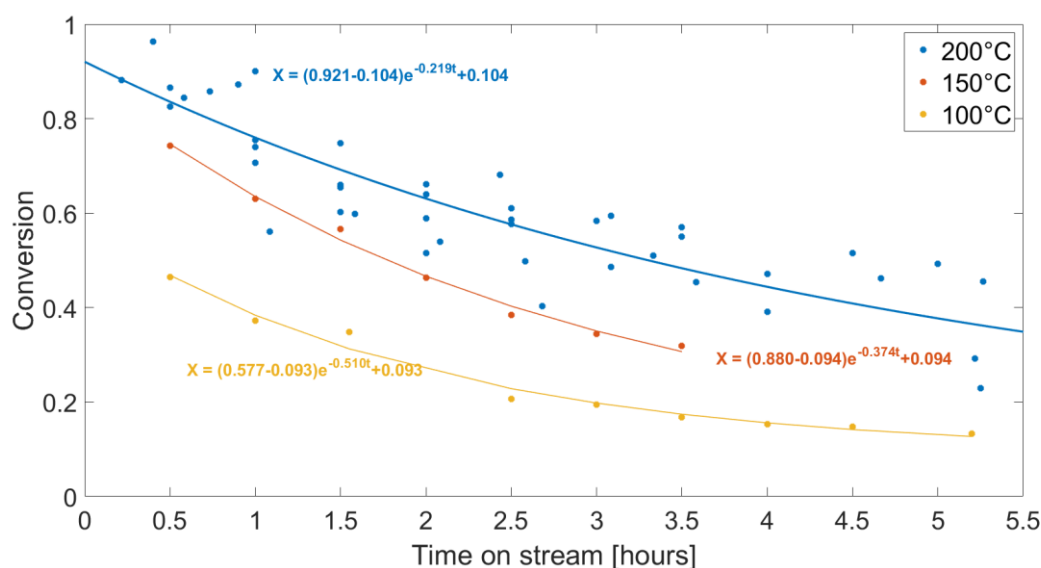


Figure 1. Deactivation of 1 wt.% Ru/TiO₂ (100 mg) at different temperatures with 2 wt.% LA in water. Flowrate - 1 mL/min of 2 wt.% LA and 40 NmL/min H₂.

4. Conclusions

We have shown that at higher operating temperatures (at 200°C), the deactivation rate of titania-supported ruthenium catalysts is slower than that observed at lower temperatures (at 100 and 150°C). Sintering and changes in the ruthenium oxidation state are the primary causes for deactivation in aqueous phase LA hydrogenation. We report a first-order dependence on LA for the aqueous phase hydrogenation kinetics valid from 100 to 200°C. This is applicable for catalysts stabilized after initial deactivation and not at the beginning of the catalyst lifespan. Decoupling the rate of sintering and changing ruthenium oxidation state might be beneficial in optimizing reaction and catalytic parameters for LA hydrogenation.

References

- [1] Abdelrahman, O.; Heyden, A.; Bond, J. Analysis of Kinetics and Reaction Pathways in the Aqueous-Phase Hydrogenation of Levulinic Acid To Form γ -Valerolactone over Ru/C. *ACS Catalysis* 2014, 4, 1171–1181

Keywords

Deactivation, hydrogenation, sintering, kinetics