

Supporting Information for

**Continuous Flow Aerobic Alcohol Oxidation Using a Heterogeneous Ru(OH)_x/Al₂O₃
Catalyst**

David S. Mannel^a, Shannon S. Stahl^{b,}, and Thatcher W. Root^{a,*}*

^aDepartment of Chemical and Biological Engineering

^bDepartment of Chemistry, University of Wisconsin-Madison, Madison Wisconsin, 53706

E-mail: stahl@chem.wisc.edu, thatcher@enr.wisc.edu

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Table of Contents

Figures of Packed Bed Reactor (PBR).....	2
Physical Parameters of PBRs.....	3
Results of ICP-AES Analysis	5
Batch time courses	6
Efforts to achieve on-stream catalyst regeneration.....	7

Figures of Packed Bed Reactor (PBR)

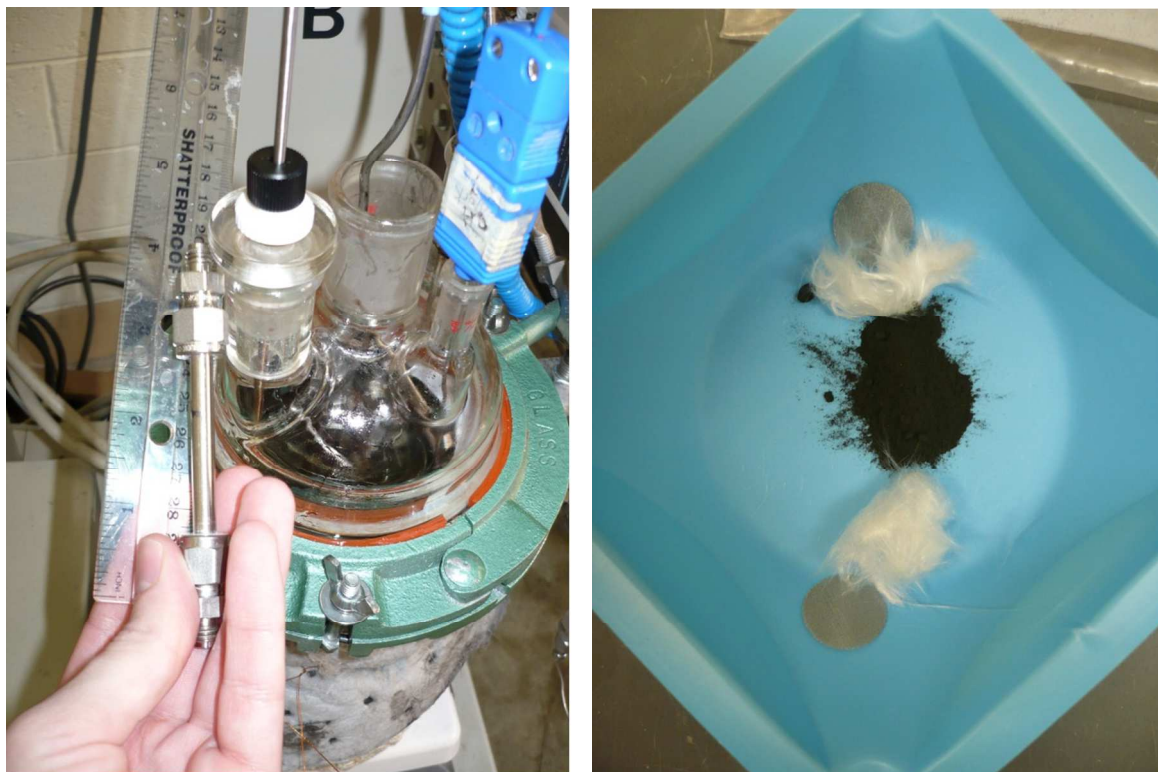


Figure S1: Left: picture of assembled packed bed reactor next to the heating bath.

Right: Ordering and appearance of materials packed inside the reactor tube.

Physical Parameters of PBRs

Table S1: Physical parameters for the PBRs used in this study.

Reactor	A	B
Mass Ru(OH) _x /Al ₂ O ₃	1.25 g	20.8 g
Mass Ru	29 mg	480 mg
PBR O.D.	¼"	½"
PBR Length	6"	12"
PBR Volume	2.5 mL	28.6 mL
Volume % Solid	20	21
Volume % Liquid	> 75	> 74
Volume % Gas	< 5	< 5
Peripheral Tubing Volume	3.3 mL	13 mL

Liquid and Gas + Liquid RTD curves for the large and the small reactor. RTD curves generated for the other reactor as well as the fit using the nCSTR model are presented in Figures S2-S4.

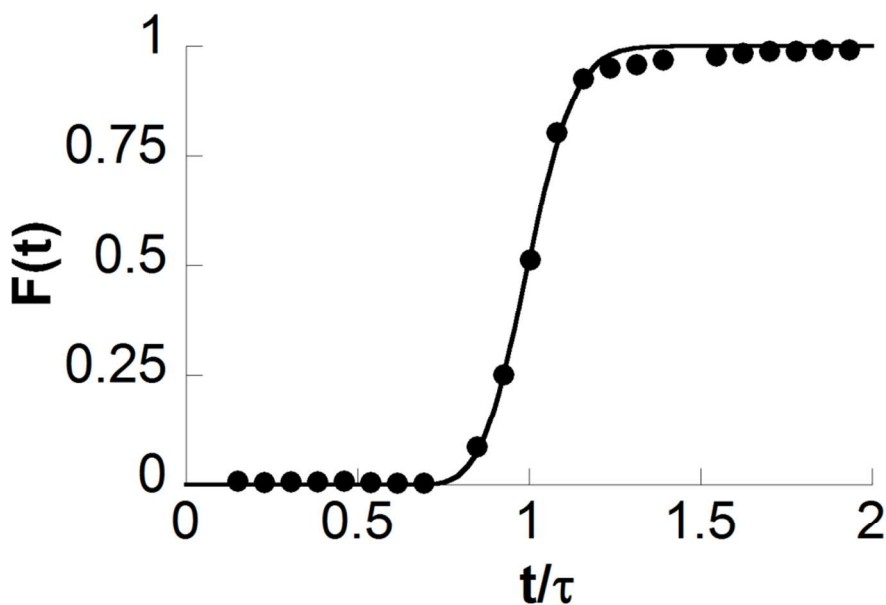


Figure S2: RTD of liquid flow through PBR A. 1.25 g Ru(OH)_x/Al₂O₃, 0.5 mL/min liquid flow of 0.002 to 0.004 M phenanthrene in toluene. nCSTR model fit with $n = 85$ and $\tau = 8.6$ min.

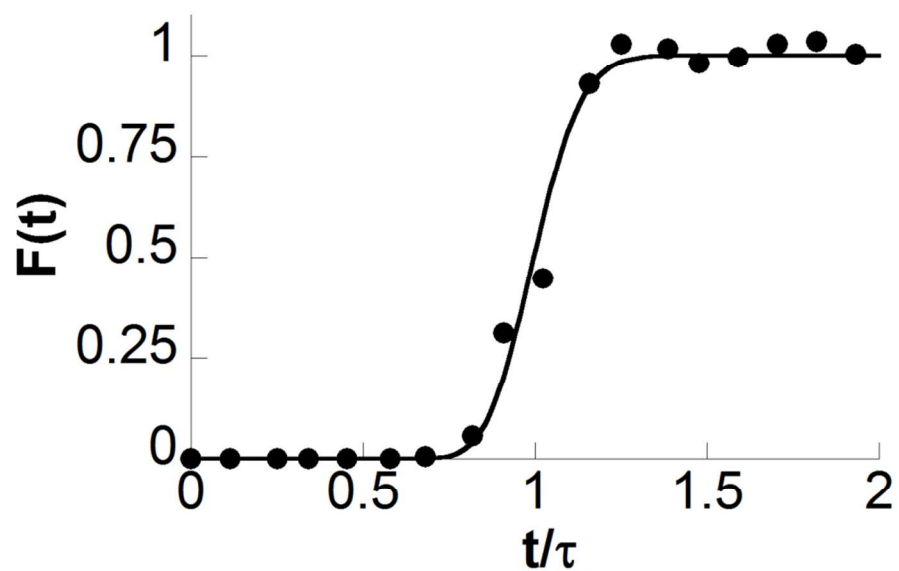


Figure S3: Liquid RTD with gas and liquid flow through PBR A. 1.25 g Ru(OH)_x/Al₂O₃, 0.05 mL/min liquid flow of 0.01 M tetradecane to 0.01 M tetradecane and 0.01 M phenanthrene in toluene and 4 sccm gas flow (8 % O₂ in N₂) at 11 bar and 80 °C. nCSTR model fit with $n = 83$ and $\tau = 44$ min.

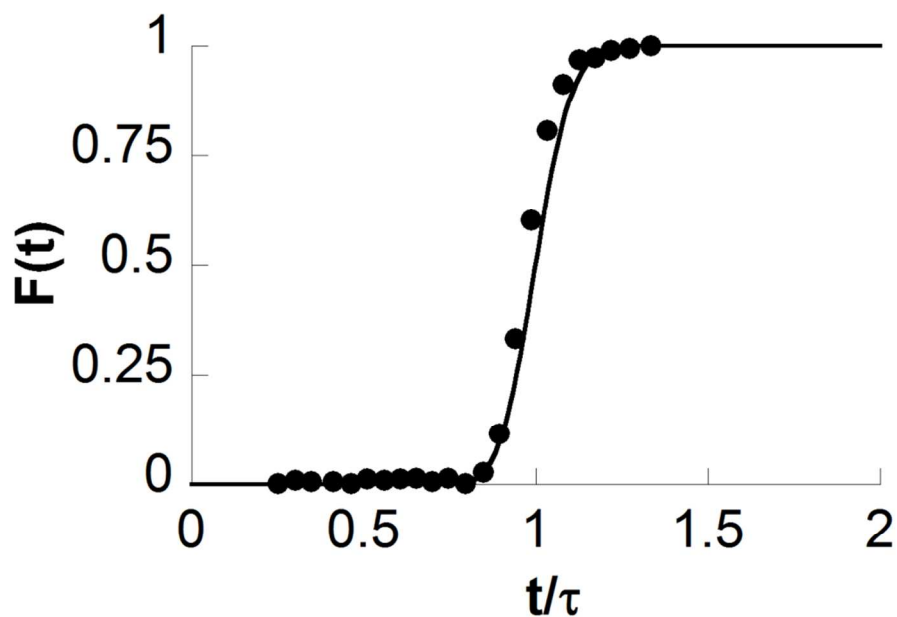


Figure S4. RTD of liquid flow through PBR B. 20.8 g Ru(OH)_x/Al₂O₃, 2 mL/min liquid flow of 0.002 to 0.004 M phenanthrene in toluene. nCSTR model fit with n = 144 and τ = 18 min.

Results of ICP-AES Analysis

Table S2: Ru content of catalysts and solutions from 12 g reaction with 2-thiophene methanol.

Ru(OH) _x /Al ₂ O ₃ Catalyst	Wt. % Ru
Newly Prepared	2.3 ± 0.1
Post-Reaction	2.4 ± 0.1
Indirect post-reaction Ru loss [Ru] in reactor effluent	< 10 ⁻⁵ over 80 h operation 3 ppb

Batch time courses

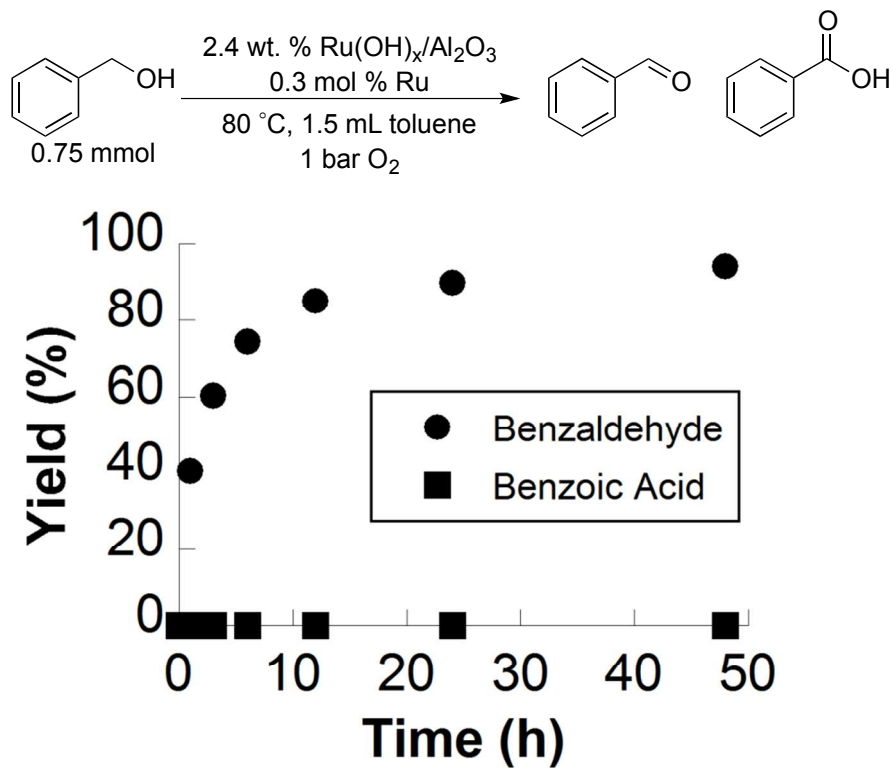


Figure S5. Yield vs. time of benzaldehyde and benzoic acid from reaction of benzyl alcohol with 0.3 mol % Ru.

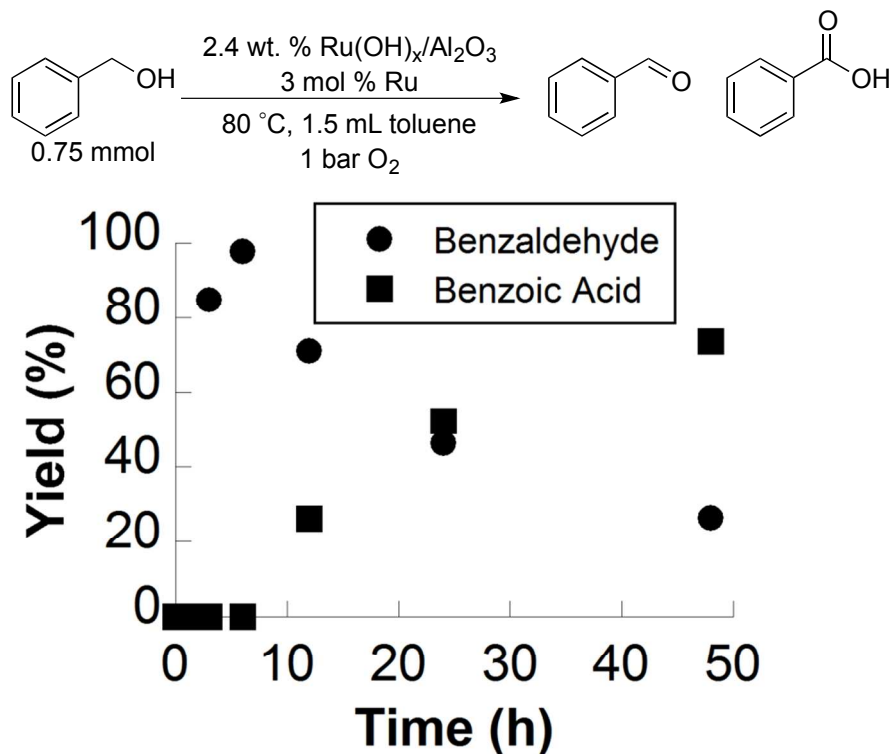


Figure S6. Yield vs. time of benzaldehyde and benzoic acid from reaction of benzyl alcohol with 3 mol % Ru.

Efforts to achieve on-stream catalyst regeneration

Benzoic acid is presumed to arise from the hydration of benzaldehyde to form the hemiacetal. To decrease the rate of benzaldehyde hydration we looked at solvents with higher water solubilities to decrease the activity of the water. The initial rate of benzyl alcohol oxidation was compared under different amounts of added water to the reaction rate with no added water (rate₀) (Figure S7). Non-polar solvents (toluene, ethyl acetate) show very rapid decrease in rate with added water, while more polar solvents (acetonitrile, DMSO) show more stable activity with increasing concentrations of water.

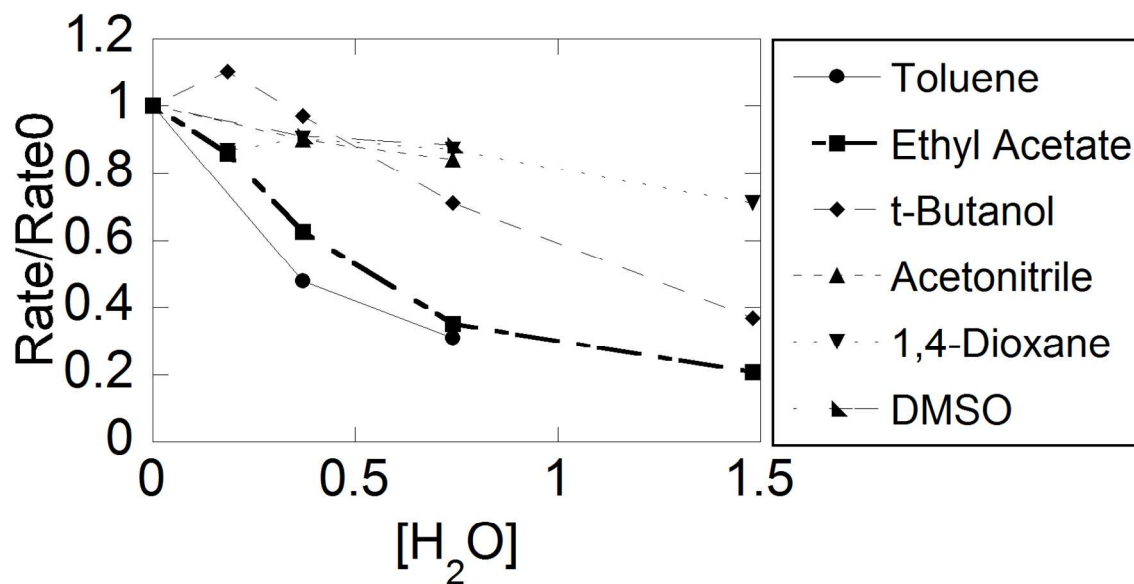


Figure S7. Water poisoning effect on initial rate in various solvents. 0.15 M benzyl alcohol, 3.3 mol % Ru as Ru(OH)_x/Al₂O₃, 60 °C, 1 bar O₂, 1.5 mL solvent. Rates determined from disappearance of benzyl alcohol at short times using GC. Rate₀ is rate with no added water.

In addition to the water poisoning of various solvents, there is a change in base rate (rate₀) for different solvents under standard reaction conditions (Figure S8). Dimethyl carbonate (DMC) was chosen for additional screening as a polar aprotic solvent with initial rates similar to toluene.

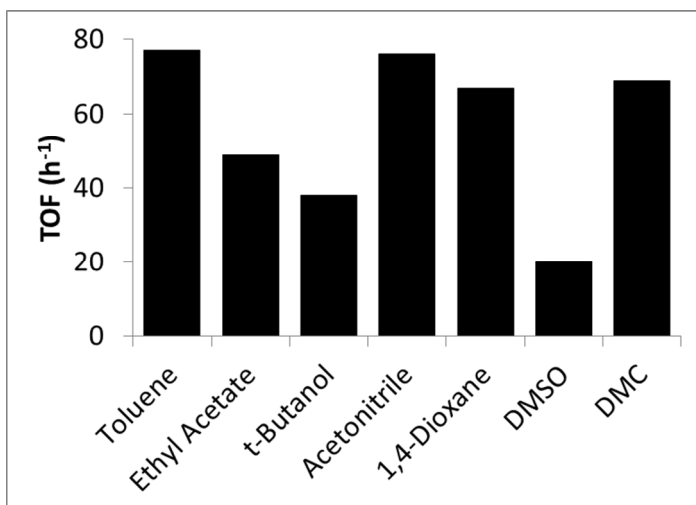


Figure S8. TOF of benzyl alcohol in various solvents. 0.15 M benzyl alcohol, 3.3 mol % Ru as Ru(OH)_x/Al₂O₃, 60 °C, 1 bar O₂, 1.5 mL solvent. Rates determined from disappearance of benzyl alcohol at short times using GC.

We studied in-situ catalyst regeneration and prevention of catalyst activity loss using various bases. Screening various inorganic and organic bases as reaction additives in batch (Table S3) was done in batch reactions to determine how bases affected the overall reaction rate and yield. Li₂CO₃, Na₂CO₃, NaH₂PO₄, and LiOH did not detrimentally impact the reaction prompting investigation into their effect on catalyst stability.

Table S3: Effect of added base on reaction yield in dimethyl carbonate.^a

Entry	Base Identity	Yield (%) at 30 min	Yield (%) at 120 min
1	None ^b	66	100
2	None	38	97
3	Li₂CO₃	33	98
4	Na₂CO₃	42	98
5	NaHCO ₃	20	95
6	KHCO ₃	23	96
7	LiOAc	44	29
8	NaOAc	8	45
9	KOAc	5	12

10	NaH₂PO₄	41	97
11	Na ₂ HPO ₄	35	98
12	Na ₃ PO ₄	26	98
13	Et ₃ N	16	72
14	KOtBu	0	19
15	NaOMe	5	42
16	LiOH	39	95
17	NaOH	20	56
18	KOH	0	18

^aYields from GC using an internal standard. 0.15 M substrate in 1.5 mL dimethyl carbonate, 0.05 M tetradecane, 2.3 wt. % Ru(OH)_x/Al₂O₃ (3.3 mol % Ru), 1 bar O₂, 80 °C, 1 equivalent base to substrate. ^btoluene.

Determination of impact these four bases (runs 3, 4, 10, 16) had on retention of catalyst activity was done using batch reuse experiments. Each catalyst was recovered, rinsed, and re-evaluated for activity with fresh substrate and dimethyl carbonate without additional base. Initial rates (r_k) were compared to the initial rate of the deactivated DMC-only sample (r_2), and the difference in rates for used catalysts was scaled by the difference between the fresh and deactivated catalyst (eq (S1)). With this scaling positive numbers denote the base improved catalyst stability and by how much, while negative numbers denote that the base had a negative impact on catalyst stability. A $F(r)$ value of 1.0 would indicate complete retention of fresh catalyst activity.

$$F(r) = \frac{r_k - r_2}{r_0 - r_2} \quad (\text{S1})$$

The four best bases from initial screening were compared for catalyst stability (Figure S9). NaH₂PO₄ shows additional loss of activity, while the other three show a small improvement or no change.

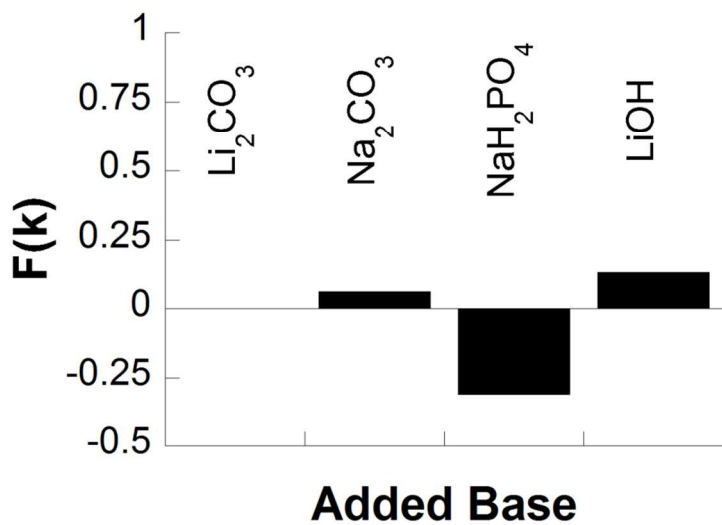


Figure S9: Fractional activity retained after 33 turnovers with different bases. 0.15 M substrate in 1.5 mL dimethyl carbonate, 0.05 M tetradecane, 2.3 wt. % $\text{Ru}(\text{OH})_x/\text{Al}_2\text{O}_3$ (3.3 mol % Ru), 1 bar O_2 , 80 °C, 1 equivalent base to substrate.