Atividade 1 – Catálise: Uma visão integrada

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Amphiphilic dipyridinium-phosphotungstate as an efficient and recyclable catalyst for triphasic fatty ester epoxidation and oxidative cleavage with hydrogen peroxide†

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Table 1 Optimisation of catalyst synthetic conditions

	Catalyst synthetic conditions			Methyl oleate epoxidation conditions and results[a]					
Entry	$H_2O_2/H_3PW_{12}O_{40}$	$DP^{+2}/H_3PW_{12}O_{40}$	Solvent	Catalyst loading (mol%)	Time (h)	Conversion	Epoxide selectivity	TON	TOF (h^{-1})
1	30 : 1	3 : 2	H_2O[b]	1.1	4	99%	58%	89	22
2	30 : 1	3 : 2	$CHCl_3$	1.1	4	97%	58%	88	22
3	30 : 1	3 : 2	MeOH	1.1	4	98%	84%	88	22
4	200 : 1	3 : 2	MeOH	1.1	4	95%	99%	85	22
5[c]	200 : 1	3 : 2	MeOH	1.1	2	71%	73%	64	32
6	200 : 1	5 : 1	MeOH	1.1	2	24%	96%	22	11
7	200 : 1	1 : 2	MeOH	0.22	4	88%	99%	400	100
8	200 : 1	1 : 2	H_2O*	0.22	4	89%	95%	404	101
9	200 : 1	1 : 2	MeCN	0.22	3	98%	96%	447	149

[a] Conditions for the epoxidation of methyl oleate: 500 mg of methyl oleate (1 eq.), 222 μL of H_2O_2 30% (1.32 eq.). Heated at 60 °C. No solvent. [b] H_2O needed to be heated above 80 °C to dissolve the dipyridinium bromide. [c] 50 mg of H_2WO_4 were added to the epoxidation of methyl oleate.

- Este artigo não disponibilizou nenhum dado cinético, indicando que provavelmente os dados de TOF foram calculados em apenas um tempo.

Esterification of lactic acid over TiO_2–ZrO_2 catalysts

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Neste trabalho os autores apresentaram uma curva cinética contendo apenas dois pontos. o TOF deve ser calculado no trecho linear inicial da cinética. Neste artigo, o TOF foi calculado apenas no ponto específico de 1 hora, como indicado no trecho retirado do próprio artigo. Além disso, como podemos ver na figura 2, para o período de 1 hora algumas curvas como a (c) 75 mol% Ti já começaram a perder a linearidade. Para obter dados mais confiáveis, o grupo poderia ter inserido dados cinéticos antes do período de 1 hora e então considerar a velocidade inicial da reação para os cálculos de TOF.

Based on the *n*-butyl lactate yield data at 1 h and 170 °C (shown in Fig. 2) and the catalyst surface area data (shown in Fig. 4), turnover frequency and acid site density were calculated via the following equations:

$$\text{turnover frequency} = \frac{(\text{moles of } n\text{-butyl lactate formed at } t = 1 \text{ h})}{(1 \text{ h})(\text{moles of catalyst acid sites})} \quad (1)$$

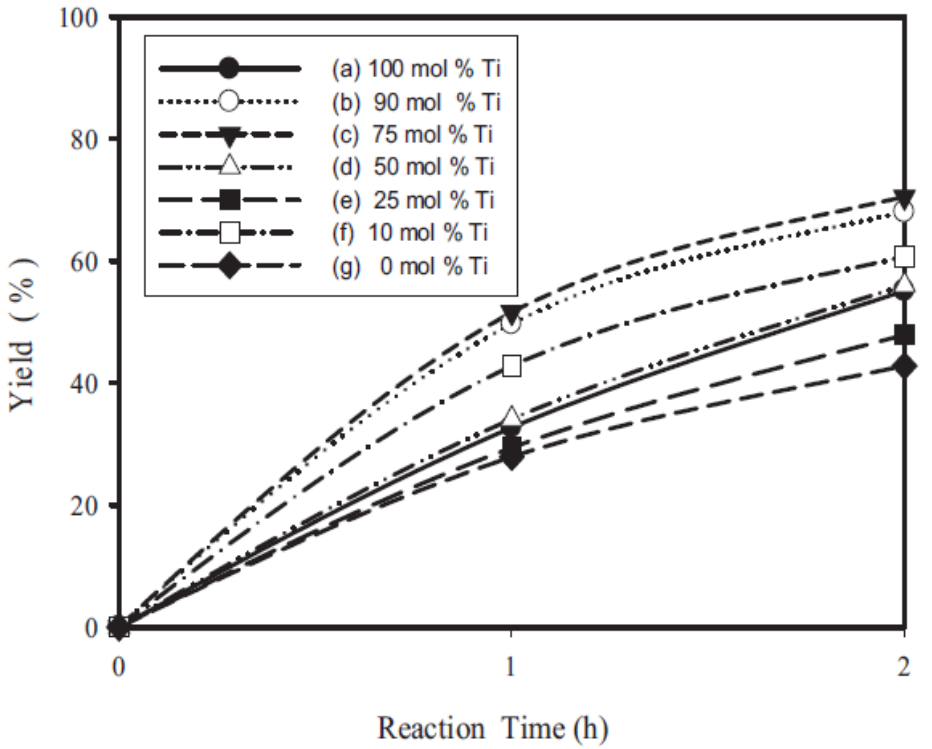

Fig. 2. Influence of reaction time and catalyst composition on *n*-butyl lactate yield at 170 °C, t = 1 h and 2 h.

Exceptionally high turnover frequencies recorded for a new chitosan-based palladium(II) catalyst

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Este artigo não construiu curvas cinéticas para cada uma das entradas da tabela 2, contudo este grupo obteve estes dados com alguns cuidados. Os valores de TON foram calculados utilizando uma quantidade muito pequena de catalisador (5.10^{-3}%mol) durante apenas 5 minutos, de modo a garantir que as medidas seriam realizadas na velocidade inicial da reação. Considero está uma alternativa interessante a construção de curvas cinéticas. Também foram fornecidos os dados de BET e as áreas superficiais respectivas.

Table 1
BET and BJH analyses of results of Chitosan-pyridil-based Pd(II) catalyst.

Surface area (m^2/g)	Single point surface area	0.0688
	BET surface area	0.0284
	BJH adsorption cumulative surface area of pores 17.000–3000.000 Å width	0.001
Pore volume (cm^3/g)	Single point adsorption total pore volume	0.000015
	BJH adsorption cumulative volumes of pores 17.000–3000.000 Å width	0.000024
Pore size (Å)	Adsorption average pore size (4V/A by BET)	20.6525
	BJH adsorption average pore width (4V/A)	708.698

Table 2
Effect of chitosan-pyridil-based Pd(II) catalyst on Suzuki C—C reactions.

Entry	X	Y	Yield (%)	TON	TOF
1	Br	2-OCH_3	91	18200	219277
2	Br	3-OCH_3	95	19000	228916
3	Br	4-OCH_3	>99	20000	240964
4	Br	3-NH_2	85	17000	204819
5	Br	4-NH_2	88	17600	22000
6	Br	3-NO_2	79	15800	190361
7	Br	4-NO_2	82	16400	205000
8	Br	4-CN	84	16800	210000
9	I	2-CH_3	33	6600	82500
10	I	3-CH_3	44	8800	106024
11	I	4-CH_3	69	13800	166265
12	I	4-OCH_3	82	16400	197590
13	I	3-NO_2	73	14600	175904
14	Cl	3-OCH_3	55	11000	137500
15	Cl	4-OCH_3	64	12800	154217
16	Cl	3-NO_2	68	13600	163855
17	Cl	4-CH_3	14	2800	33735
18[a]	Br	4-OCH_3	44	8800	367

Reaction conditions: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, 5×10^{-3} mol% chitosan-pyridil-based Pd(II) catalyst, 50 °C, 5 min (~0.08 h) under MW.
TON: turnover number, yield of product/per mol of Pd.
TOF: turn over frequency, TON/time of reaction (hour).
[a] Conventional heating method: 1.12 mmol aryl halide, 1.87 mmol phenyl boronic acid, 3.75 mmol K_2CO_3, 5×10^{-3} mol% catalyst, 100 °C, 24 h, 6 mL toluene.

Transesterification of sunflower oil on single step sol–gel made Al_2O_3 supported CaO catalysts: Effect of basic strength and basicity on turnover frequency

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Table 1
Total surface areas, average pore sizes, basicity and basic strength of the catalysts.

Catalysts	BET surface area (m^2/g)	BJH adsorption average pore diameter (Å)	Total basicity (μmol CO_2/m^2)	Basic strength (peak temp., °C)
Pure CaO	2.43	52.92	2.48	114
30% CaO/Al_2O_3	33.78	46.54	58.75	165
				394
60% CaO/Al_2O_3	1.58	47.11	7.15	146
85% CaO/Al_2O_3	0.99	60.03	63.23	157
Pure Al_2O_3	264	35.99	6.87	170

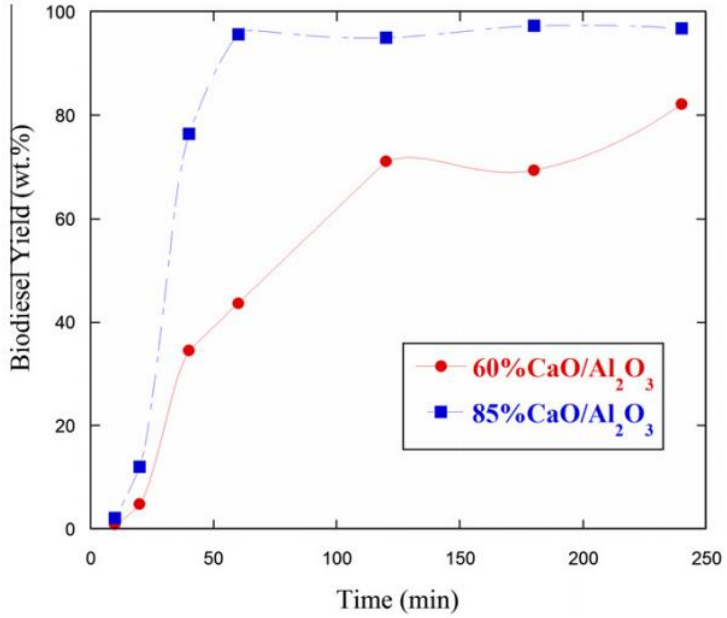

Fig. 1. Biodiesel yield vs. reaction time for 85% and 60% CaO/Al_2O_3 catalysts. Reaction conditions: 6 wt.% catalyst amount, methanol/sunflower oil molar ratio = 9 and the reaction temperature 50 °C.

- Este artigo é um exemplo de como deve ser calculado o TOF. Neste artigo eles indicaram a maneira como os dados foram calculados, faltou apenas a informação do intervalo que foi utilizado nos cálculos. Apresentou os dados de BET e o total de basicidade do catalisadores utilizados, assim como as curvas cinéticas das reações.

Turnover frequency (TOF, s^{-1}) was calculated using the initial reaction rate concept and the total basicity as follows (Ranganathan et al., 2005; Kulkarni and Wachs, 2002):

$$\text{Turnover frequency (TOF, } s^{-1}) = [\text{Initial oil consumption rate}] / [\text{Total basicity}]$$

Bifunctional gold catalysts: Relationship between preparation method and catalytic performance in tandem cellobiose valorization

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- Este artigo explica corretamente como foi calculado o TOF, inclusive especificando qual o intervalo de tempo que foi utilizado. Está informação infelizmente não foi recorrente nos artigos.
- Um item interessante neste artigo é que a dispersão das moléculas foi calculada utilizando fórmulas apropriadas e supondo que as partículas possuem formas cúbicas com uma quantidade variada de átomos na borda.

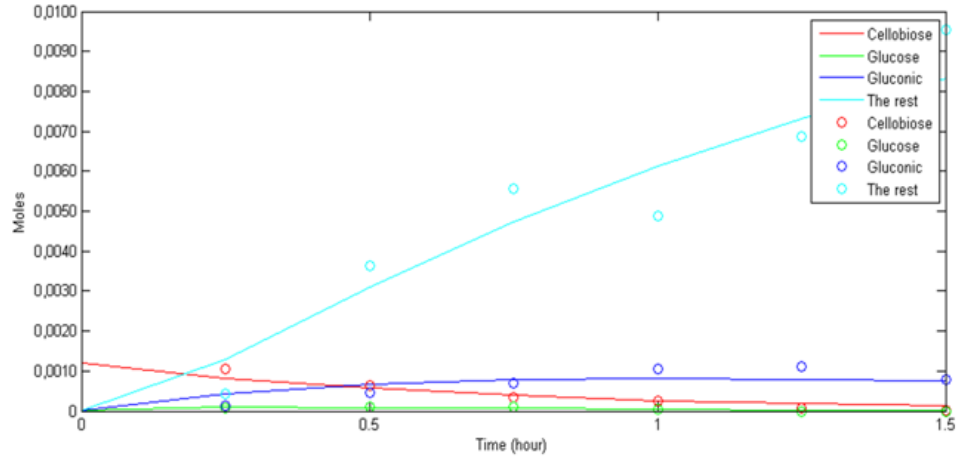

Figure 1s. Correlation between experimentally observed changes in moles of reactants and products with modelled values (lines) obtained for the CR catalyst.

Initial turnover frequency (TOF) was estimated using the cellobiose conversions obtained in the first 15 min of the reaction and the results are gathered in Table 3s in Supporting information, together with the calculated dispersion of gold nanoparticles. The calculated dispersion was used to estimate the amount of gold (in moles) present on the surface of the catalysts which gave TOF values in s^{-1}.