QFL 5835-6: Catálise – Uma Visão Integrada

Atividade 1: Analise do TOF de 5 artigos científicos

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Artigo 1:

ACS Catalysis

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Article

Understanding the Relationship Between Kinetics and Thermodynamics in CO2 Hydrogenation Catalysis

Matthew S Jeletic, Elliott Hulley, Monte L Helm, Michael T. Mock, Aaron M. Appel, Eric S. Wiedner, and John Charles Linehan

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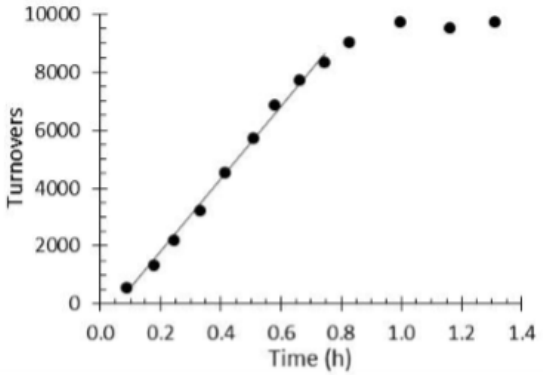

Figure 1. A plot of turnovers (mol $[VkdH]^+[HCO_2]^-$ / mol catalyst) versus time for 0.036 mM $Co(BPE5)_2H$ at 20 atm of 1:1 H_2:CO_2 and 570 mM Vkd in THF-d_8 at 21 °C. The reaction ceases when all of the Vkd has been consumed. The line is the best linear fit and was used to determine the TOF (R_2 = 0.99).

Table 1. Catalytic conversion of CO_2 and H_2 to formate with Verkade's base at 1.8 atm.[a]

Catalyst	Initial Loading (mM)	TOF (h^{-1}) [b]	Turnovers [b]
$Co(dmpe)_2H$	0.28	6400	1900 [c]
$Co(BPE5)_2H$	2.6	540	170
$Co(dmpbz)_2H$	2.6	270	200
$Co(depe)_2H$	25	21	20
$Rh(dmpbz)_2^+$	0.27	3100 [d]	1100
$Rh(depe)_2^+$	0.30	1600 [d]	280
$Rh(dmpe)_2^+$	2.7	90 [d]	55
$Rh(dmpe)_2^+$	2.7	640 [e]	88 [e]

[a] Catalytic conditions; 500μL THF-d_8, 1.8 atm 1:1 CO_2:H_2, 21 °C, 400-430 mM 2,8,9-triisopropyl-2,5,8,9-tetraaza-1-phosphabicyclo[3,3,3] undecane (Verkade's base), typical run time 2 h or less. [b] Uncertainties are 10%. [c] Previously reported. [d] Initial TOF. [e] *tert*-Butylimino-tris(dimethylamino)phosphorane, $pK_a \sim 38$ for $P_4{}^tBuH^+$ in MeCN,[62] was used instead of Verkade's base.

No presente artigo o autor apresenta um gráfico de Turnovers (quantidade de mols formados de $[VkdH]^+[HCO_2]^-$ por mol de catalisador) por tempo de reação, **Figura 1** do artigo, então o autor calcula o TOF a partir da inclinação da reta na parte linear. A **Tabela 1** do artigo apresenta alguns valores de TOF obtidos.

O TOF calculado no gráfico da **Figura 1** a partir da inclinação da reta é de 13000 h^{-1}, o R^2 da reta (0,99) demonstra que o método pode ser considerado um método eficiente na comparação da eficiência dos catalisadores e condições estudadas.

Artigo 2:

Table 1. Catalytic activities of different catalysts for the dehydrogenation of hydrous hydrazine.

Catalyst[a]	Solvent/ medium	T [°C]	Select. H_2 [%]	TOF [h^{-1}]	E_a [kJ mol^{-1}]	Ref.
$Rh_{0.8}Ni_{0.2}$/MXene	aqueous NaOH	50	100	857	38.2	this work
$Rh_{55}Ni_{45}$/Ce(OH)	aqueous NaOH	50	100	395	38.8	[34]
$Rh_{4.4}Ni$/graphene	aqueous NaOH	30	100	28	–	[18]
$Rh_{34}Ni_{66}$@ZIF-8	aqueous NaOH	50	100	140	58.1	[35]
$Pt_{0.6}Ni_{0.4}$/PDA-rGO	aqueous NaOH	50	100	2056	33.39	[36]
$(Ni_3Pt_7)_{0.5}$-$(MnO_x)_{0.5}$/ NPC-900	aqueous NaOH	50	100	706	50.15	[37]
$Ni_{88}Pt_{12}$/MIL-101	aqueous NaOH	50	100	471	40.4	[38]
$Ni_{0.8}Pt_{0.2}$/MIL-101-NH_2	aqueous NaOH	50	100	676	53.2	[11]
Ni_3Pt_7/BNG-1000	aqueous NaOH	30	100	199.4	28.4	[39]
$Ni_{0.9}Pt_{0.05}Rh_{0.05}/La_2O_3$	aqueous NaOH	25	100	45.9	–	[40]
$Ni_{0.9}Pt_{0.1}/Ce_2O_3$	aqueous NaOH	25	100	28.1	42.3	[19]
Ni_6Pt_4-SF	aqueous NaOH	25	100	150	–	[41]
$Pt_{60}Ni_{40}$-CNDs	aqueous NaOH	50	100	170	43.9	[42]
$Ni_{0.58}Pt_{0.42}$/graphene	aqueous NaOH	30	100	434	23.9	[43]
$Ni_{0.9}P_{t0.1}$/MIL-101	aqueous NaOH	30	100	140	48.4	[44]
$Rh_{0.8}Ni_{0.2}$@CeO_x/rGO	aqueous NaOH	30	100	36.4	58	[45]

[a] PDA-rGO: diamine-alkalized reduced graphene oxide, SF: support free, CNDs: carbon nanodots, rGO: reduced graphene oxide.

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CHEMCATCHEM Communications

Highly Dispersed Bimetallic Nanoparticles Supported on Titanium Carbides for Remarkable Hydrogen Release from Hydrous Hydrazine

Tong Liu,*[a] Qingtao Wang,[a] Jingzhi Yuan,[a] Xue Zhao,[a] and Guanhui Gao*[b]

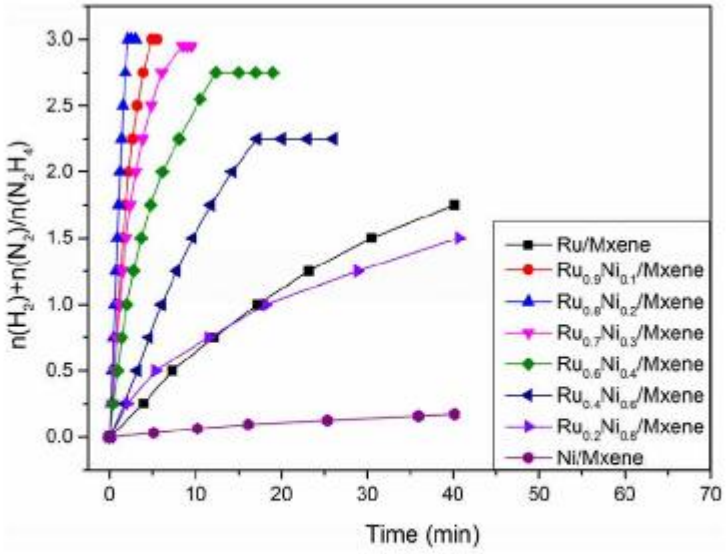

Figure 3. Time-course plots for H_2 generation from the decomposition of $N_2H_4 \cdot H_2O$ with different Rh/Ni molar ratios ($0 \leq x \leq 1$) at 50 °C. Molar ratio of metal/$N_2H_4 \cdot H_2O$ = 0.067.

No artigo eles não especificam como foram realizados os cálculos de TOF, entretanto os autores realizaram um estudo cinético da reação como mostrado na **Figura 3**, o que leva a acreditar que os valores foram tirados a partir desse estudo.

Artigo 3:

ACS Catalysis
Research Article
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Organometallic Preparation of Ni, Pd, and NiPd Nanoparticles for the Design of Supported Nanocatalysts

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Table 4. Catalytic Performance of $FFSiNH_2Ni_xPd_y$ in the Hydrogenation of Cyclohexene[a]

entry	catalyst	TOF[b]	time[c] (min)
1	$FFSiNH_2Ni$	0	nr
2	$FFSiNH_2Ni_9Pd$	0	nr
3	$FFSiNH_2NiPd$	14 000	150
4	$FFSiNH_2NiPd_9$	56 000	25
5	$FFSiNH_2Pd$	37 000	45
6	$NiPd_9$	15 900	150

[a]Reaction conditions: 20 000 mol of cyclohexene per mol of metal, 6 bar of H_2, 75 °C. [b]TOF expressed as $mol_{cyclohexene} \cdot mol_{Ni+Pd}^{-1} \cdot h^{-1}$. [c]Time for complete reaction. nr = no reaction after 12 h.

O TOF do artigo é expressado em $mol_{cyclohexene} \cdot mol_{Ni+Pd}^{-1} \cdot h^{-1}$ e o cálculo é feito a partir velocidade iniciais de reação, a **Tabela 4** do artigo mostra alguns valores de TOF obtidos.

No final do artigo no estudo de reciclagem o TOF foi calculado a partir da inclinação da reta do turnover vs. tempo, em baixas conversões (<20%).

O Cálculo do TOF é confiável, pois as medidas são feitas nos inícios das reações usando as velocidade iniciais.

Artigo 4:

Contents lists available at ScienceDirect

Journal of Catalysis

journal homepage: www.elsevier.com/locate/jcat

Xantphos doped Rh/POPs-PPh_3 catalyst for highly selective long-chain olefins hydroformylation: Chemical and DFT insights into Rh location and the roles of Xantphos and PPh_3

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Table 3
Hydroformylation of different long-chain olefins on Xantphos doped Rh/POPs-PPh_3 catalyst.[a]

Olefins	Conv. (%)	Aldehydes Sel. (%)	Alkane Sel. (%)	Iso-alkenes Sel. (%)	l/b ratio
1-Hexene	34	88	2	10	87:13
1-Heptene	28	88	3	9	89:11
1-Octene	42	87	3	10	90:10
1-Dodecene	54	87	2	11	89:11

[a] Reaction conditions: 0.0515 g of catalyst (Rh loading at 0.15 wt%), S/C = 5000, CO: H_2 = 1:1 (1.0 MPa initial pressure), 2.0 g of toluene, 100 °C for 5 h.

O Autor no texto diz que o TOF das reações está entre 300 e 500 h^{-1}, entretanto não detalha como o cálculo foi realizado, mostrando apenas os resultados apresentados na **Tabela 3**, dificultando comparações dos resultados de novos trabalhos.

Artigo 5:

Macromolecules

Article

Cite This: *Macromolecules* XXXX, XXX, XXX−XXX

Highly Active Organic Lewis Pairs for the Copolymerization of Epoxides with Cyclic Anhydrides: Metal-Free Access to Well-Defined Aliphatic Polyesters

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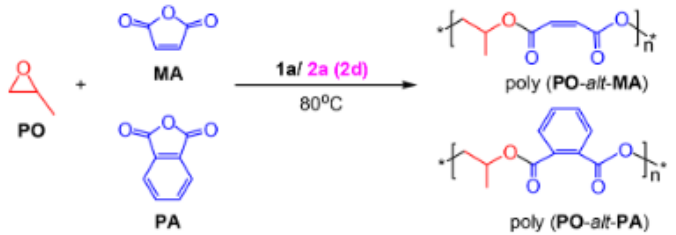
Table 3. Copolymerization of PO with MA (and PA) Catalyzed by 1a with Various LBs at 80 °C[a]



entry	anhyd.	LB	time (h)	conv. (%)[b]	TOF (h^{-1})[b]	M_n (kDa)[c]	$Đ$[c]
1	MA	2a	0.5	21	42	1.3	1.27
2[d]	MA	2a	0.5	7	14	–	–
3	MA	2d	0.5	51	102	2.8	1.29
4[d]	MA	2d	0.5	8	16	0.7	1.17
5	PA	2d	0.3	91	303	20.0	1.12
6[d]	PA	2d	0.3	5	15	–	–

[a]Reaction conditions: [PO]:[MA (PA)]:[1a]:[2a(2d)] = 350:100:1:1, 80 °C; for MA, 2.0 mol % maleic acid for entries 1−4. [b]Conv. (%) is the conversion of the cyclic anhydride, determined by ^{1}H NMR spectroscopy, see Table 1; TOF = (moles of anhydride consumed)/(moles of LB). [c]Determined by gel permeation chromatography in THF, calibrated with polystyrene standards. [d]Without TEB (1a).

Os TOFs nesse artigo foram calculados a partir das conversões finais das reações, inclusive a que teve conversão de 91%, o que faz esses valores não serem confiáveis para futuras comparações. Teria sido mais apropriado realizar um estudo cinético e fazer o cálculo com as velocidade iniciais das reações.