

QFL 5835 - Catálise: uma visão integrada

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Atividade 1

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Artigo 1

Catalytic wet peroxide oxidation of formic acid in wastewater with naturally-occurring iron ore

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TABLE 3
Different experimental conditions of the wet oxidation of formic acid and their observed rate constants

no	Amount of catalyst	[H ₂ O ₂]	[formic acid]	k _{obs} x 10 ⁴ min ⁻¹	TOF s ⁻¹
A1	50 mg	4 M	1.26 M	5.11 (2)	7.12 x 10 ⁻⁸
A2	50 mg	6 M	1.26 M	6.24 (2)	7.12 x 10 ⁻⁸
A3	50 mg	8 M	1.26 M	6.59 (2)	7.12 x 10 ⁻⁸
A4	50 mg	10 M	1.26 M	8.78 (1)	7.12 x 10 ⁻⁸
A5	50 mg	12 M	1.26 M	8.92 (0.2)	7.12 x 10 ⁻⁸
A6	50 mg	15 M	1.26 M	12.00 (3)	7.12 x 10 ⁻⁸
B1	50 mg	4 M	2.52 M	7.35 (6)	2.24 x 10 ⁻⁷
C1	50 mg	4 M	6.3 M	9.87 (2)	5.60 x 10 ⁻⁷
D1	50 mg	4 M	12.6 M	17.3 (3)	1.12 x 10 ⁻⁶
A7	100 mg	4 M	1.26 M	10.00 (1)	3.36 x 10 ⁻⁸
A8	150 mg	4 M	1.26 M	14.31 (2)	2.30 x 10 ⁻⁸
A9	200 mg	4 M	1.26 M	21.75 (3)	1.73 x 10 ⁻⁸

Hydrogen peroxide decomposition and formic acid oxidation test with Fe₂O₃ catalyst

$$\text{TOF} = \frac{\text{Moles formic acid converted}}{\text{Moles of Fe}_2\text{O}_3 \times \text{Time(s)}}$$

Reaction mixtures (10 mL) were prepared according to Table 3, while stirring at 35°C. After the pH was adjusted to 2 with the addition H₂SO₄, the required amounts of formic acid and Fe₂O₃ catalyst (iron ore) were added. Samples were taken at regular intervals and analysed by ATR FTIR.

Turnover frequencies (TOF) were determined by the following equation:

In addition, pseudo first-order rate constants, k_{obs}, were calculated by fitting kinetic data to the first-order equation

(Espenson, 1995) $[A]_t = [A]_0 e^{-k_{obs}t}$ with [A]_t and [A]₀ the absorbance of the indicated species at time t and at t = 0.

Comentário: no artigo foi realizado o estudo cinético da decomposição do peróxido de hidrogênio e do ácido fórmico com diferentes quantidades de catalisador. Valores de k_{obs} foram bem explorados e o TOF calculado segundo a equação mostrada ao lado. Entretanto, a falta de informação do tempo de atividade do catalisador impede o cálculo do TON.

H₂O₂ decomposition with iron ore powder

[H ₂ O ₂]	pH	k _{obs} x 10 ⁵ min ⁻¹	TOF s ⁻¹
2 M	2	1.09 (0.3)	1.97 x 10 ⁻⁹
4 M	2	1.08 (0.4)	3.93 x 10 ⁻⁹
6 M	2	1.06 (0.4)	5.89 x 10 ⁻⁹
9 M	2	1.03 (0.5)	8.85 x 10 ⁻⁹

Artigo 2

Determining Number of Active Sites and TOF for the High-Temperature Water Gas Shift Reaction by Iron Oxide-Based Catalysts

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Table 1. WGS Activity, Number of Sites [$n(^{16}\text{O})$], and Turnover Frequencies (TOFs)^a

catalyst	WGS activity-H ₂ O conversion ($\times 10^{-6}$ mol/s-g)	Ns: $n(^{16}\text{O})$ ($\times 10^{-3}$ mol/g)	density of Ns (^{16}O atoms/nm ²)	TOF ($\times 10^{-3}$ s ⁻¹)
Fe ₂ O ₃	1.2 \pm 0.1	0.9 \pm 0.1	19 \pm 2	1.3 \pm 0.2
Cr ₂ O ₃ -Fe ₂ O ₃	2.0 \pm 0.1	1.7 \pm 0.2	16 \pm 2	1.2 \pm 0.2
CuO-Cr ₂ O ₃ -Fe ₂ O ₃	5.7 \pm 0.3	1.6 \pm 0.2	16 \pm 2	3.5 \pm 0.4

^a10% CO/Ar (10 mL/min), He (30 mL/min), and water vapor (H₂O/CO \sim 1); T = 330°C.

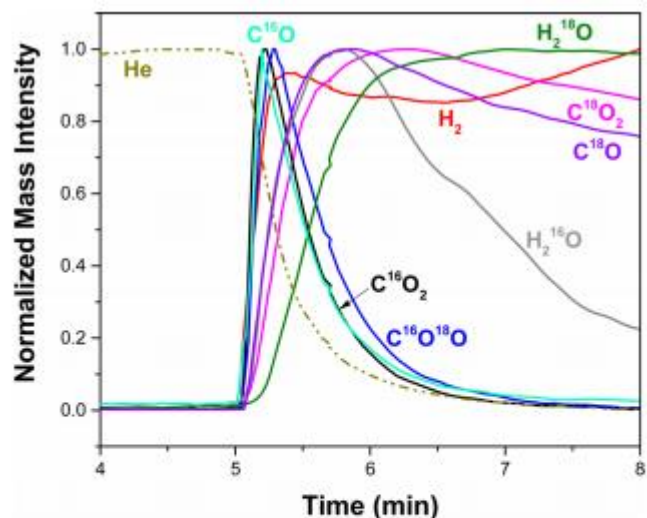


Figure 3. Transient response of He, H₂, C¹⁶O₂, C¹⁶O¹⁸O, C¹⁸O₂, C¹⁶O, C¹⁸O, C¹⁶O, and H₂¹⁶O during isotope switch after inert flush on Cr₂O₃-Fe₂O₃ (T = 330 °C). The MS signals for all products were normalized to the same maximum and minimum intensity for better comparison of their transient behavior. The CO isotope signals are corrected for contribution of CO₂ cracking in the MS because cracking of the dominant CO₂ isotopes in the mass spectrometer significantly contribute to the CO MS signals.

- **Comentário:** o TOF foi calculado pela divisão da conversão de água em T = 330°C, que é o momento do início da conversão, pelo número de sítios ativos. Se considerarmos a parte linear do gráfico da água como o tempo ativo do catalisador, pode-se calcular o TON multiplicando-se o TOF dado por esse intervalo de tempo.

Artigo 3

Metal organic framework-mediated synthesis of highly active and stable Fischer-Tropsch catalysts

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Table 4: Catalytic performance of unpromoted Fe-catalysts after 4 h TOS†.

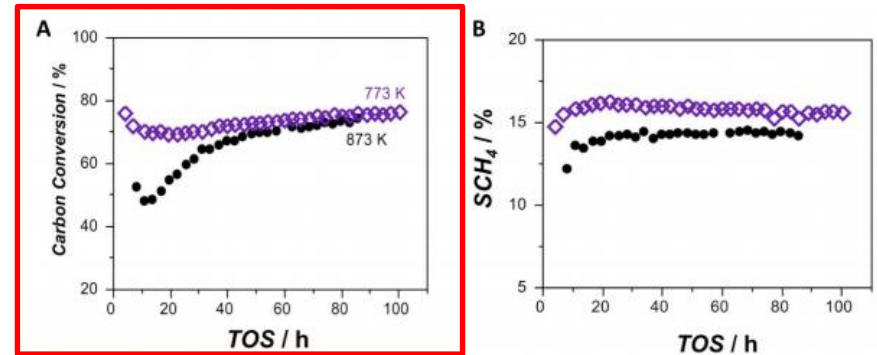
From: Metal organic framework-mediated synthesis of highly active and stable Fischer-Tropsch catalysts

Sample	<i>d</i> (nm)	GHSV ^a cm ³ g ⁻¹ min ⁻¹	X (%)	FTY (10 ⁻⁴ mol g ⁻¹ Fe s ⁻¹)	TOF _{apparent} (s ⁻¹)	α	References
25-Fe@C	3.3	1,000	59	4.9	0.11	0.43	This work
27-Fe@C	2.6	1,000	60	4.4	0.07	0.44	This work
31-Fe@C	2.8	1,000	70	4.4	0.07	0.42	This work
38-Fe@C	3.6	1,000	72	3.8	0.08	0.40	This work
1-Fe/CNF ⁴¹	2.1	100	10	1.4	0.08	0.30	11
5-Fe/CNF	3.2	100	11	0.2	0.02	0.34	11
20-Fe/CNF	6.9	100	10	0.06	0.01	0.44	11
20-Fe/O-CNT	8	833	27	1.4	ND	0.45	36

ND, Not determined; Carbon conversion (X, %), activity per gram of Fe (FTY), apparent turnover frequency (TOF, per mol Fe present) and chain growth probability (α). For comparison, the catalytic performance of some reference catalysts, as reported in open literature, is also included: Fe supported on carbon nano-fibres, prepared by incipient wetness impregnation (X-Fe/CNF, X: wt% of Fe), and Fe supported on oxidized carbon nano-tubes (20-Fe/O-CNT, where Fe loading is 20 wt%). †FTS experiments were carried out at 613 K, 20 bar, and H₂/CO=1.

^aGHSV is expressed as cm³ g⁻¹ min⁻¹ to directly compare our experimental conditions with the ones described in 26, since the catalyst bed density is unknown.

- **Comentário:** o TOF foi calculado segundo a fórmula apresentada, na qual o Fe time yield (FTY) se dá pelo nCO convertido por grama de Fe por segundo. Assim o TOF aparente foi calculado considerando os dados de dispersão do ferro no catalisador. Foi considerada a conversão no t = 10h, ou seja, no início da reação (como devido).



Supplementary Figure 10 FTS performance of Fe@C obtained from the pyrolysis of Basolite F-300 at 773 and 873 K. Carbon conversion (A) and selectivity to methane (B) as a function of time on stream (TOS).

$$FTY = \frac{X_{CO} F_{in,CO} (1 - S_{CO_2})}{w_{Fe}}$$

$$TOF = \frac{FTY \cdot M_{Fe}}{D \cdot \epsilon}$$

Artigo 4

Pore size effects in high-temperature Fischer–Tropsch synthesis over supported iron catalysts



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Table 6

Catalytic performance of iron catalysts supported on silicas with different pore sizes (flowence high-throughput unit, H₂/CO = 2.1, GHSV = 16,200 ml g⁻¹ h⁻¹, 300 °C, 20 bar, time on stream, 60 h).

Catalysts	X _{CO} (%)	Iron time yield (10 ⁻³ S ⁻¹)	CO ₂ selectivity (%C mol)	CH selectivity (%C mol)				Olefin/paraffin C ₂ -C ₄
				CH ₄	C ₂ -C ₄	C ₂ -C ₄ paraffins	C ₃	
10FeSi2.8	0	0	-	-	-	-	-	-
10FeSi5.2	19.4	6.5	7.8	16.9	12.1	19.2	41.6	0.63
10FeSi7.2	23.2	8.7	8.3	16.5	11.8	19.0	41.7	0.62
10FeSi7.7	25.7	9.6	9.3	17.1	11.7	16.7	42.3	0.69
10FeSi9.2	15.4	5.2	6.9	19.6	12.8	17.3	40.8	0.74
10FeSi17.5	28.5	9.6	10.6	13.6	15.2	11.0	47.1	1.38
10FeSi50	33.8	11.4	12.2	13.6	13.7	11.5	47.2	1.19

- **Comentário:** o TOF foi calculado pela razão do χ_{CO} convertido por mol de sítios de ferro na superfície por segundo. Foi considerada a conversão após 60 horas de reação e que, segundo os autores, é o tempo que leva para que o catalisador atinja uma performance catalítica estável.

Artigo 5

Isolated Metal Active Site Concentration and Stability Control Catalytic CO₂ Reduction Selectivity

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Strong correlations were observed between the catalytic reverse water gas shift turn over frequency (TOF) and the fraction of Rh_{iso} sites and between catalytic methanation TOF and the fraction of Rh_{NP} sites.

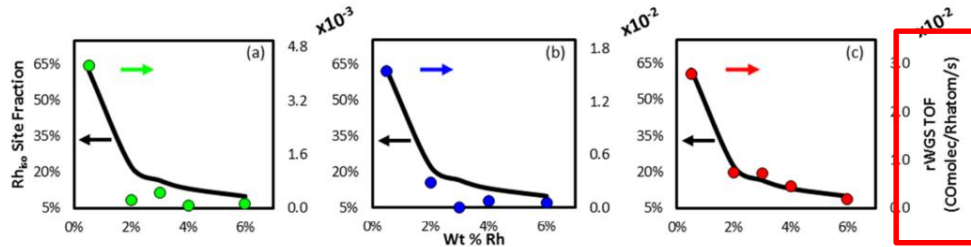


Figure 3. Rh_{iso} site fraction and r-WGS TOF plotted as a function of wt % Rh at (a) 1CO₂:4H₂, (b) 3CO₂:H₂, and (c) 10CO₂:H₂ feed ratios. The left axes are Rh_{iso} site fractions, which are displayed in the plots as a black line connecting the measured values for graphical clarity. The green, blue, and red data points correspond to measured r-WGS TOF and are quantified in the right axis of each plot.

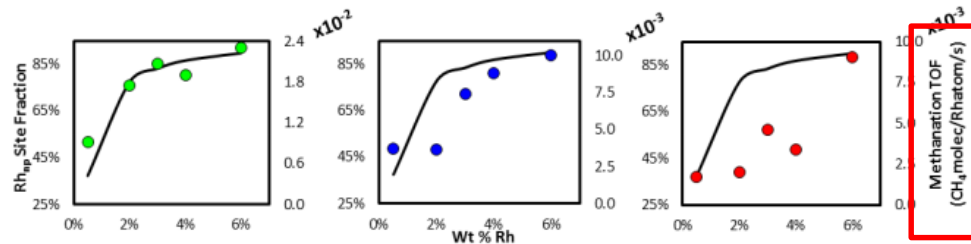


Figure S6. a) Rh_{NP} site fraction and methanation TOF plotted as a function of Wt % Rh at a) 1CO₂:4H₂ b) 3CO₂:H₂, c) 10 CO₂:H₂ feed ratios. The left axes are Rh_{NP} site fractions, which are displayed in the plots as a black lines connecting the measured values for graphical clarity. The green, blue, and red data points correspond to measured methanation TOF and are quantified in the right axis of each plot.

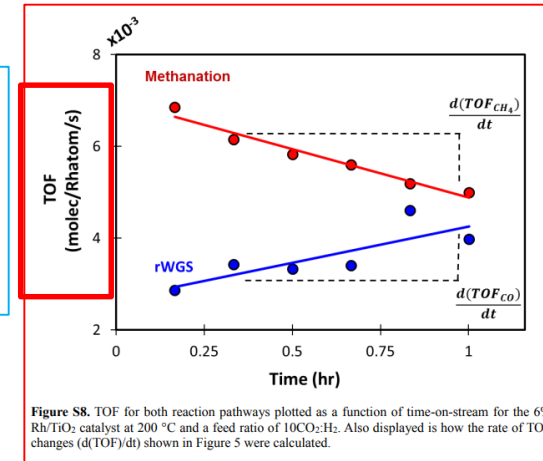


Figure S8. TOF for both reaction pathways plotted as a function of time-on-stream for the 6% Rh/TiO₂ catalyst at 200 °C and a feed ratio of 10CO₂:H₂. Also displayed is how the rate of TOF changes (d(TOF)/dt) shown in Figure 5 were calculated.

- Comentário:** para o objetivo do artigo foram calculados diferentes TOF's usando a conversão de CO por sítios totais, por sítios de Rh *single-atom* e por sítios de nanopartículas de Rh em diferentes momentos da reação, pois há desintegração das NP's em *single-atoms*. Dessa forma pode-se criar os dados de TOF para cada reação competitiva (metanação e RWGS) em cada tipo de sítio (NP e SA), podendo-se gerar também o gráfico de dTOF/dT para cada reação. O estudo foi bem completo em relação aos TOF's, justamente por ser fundamental para o objetivo do artigo.