

# Catálise: Uma visão integrada

Discente: Bruno Henrique Arpini

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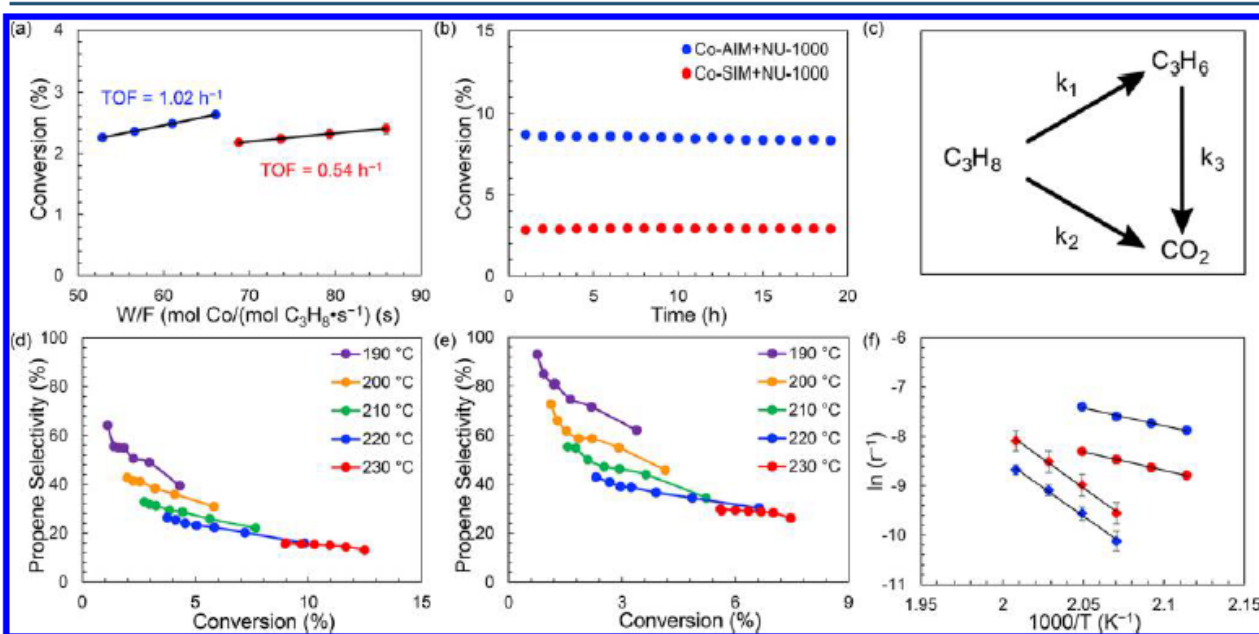
# Metal–Organic Framework Supported Cobalt Catalysts for the Oxidative Dehydrogenation of Propane at Low Temperature

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**Figure 1.** Structural representation of the MOF support, NU-1000, as well as the two preparation methods of Co-based catalysts for propane ODH catalysis.



**Figure 2.** Oxidative dehydrogenation of propane catalyzed by Co-AIM and Co-SIM+NU-1000: (a) determination of the TOF by varying the molar space time ( $W/F$ ) of propane at 230 °C; (b) stability test of Co-AIM and Co-SIM+NU-1000 at 230 °C; (c) possible catalytic pathways involving the propane ODH process; (d, e) selectivity toward propene formation for the propane ODH process catalyzed by Co-SIM+NU-1000 (d) and Co-AIM+NU-1000 (e) with different propane conversions at various temperatures; (f) Arrhenius plots of the propane ODH process (circles) catalyzed by Co-AIM+NU-1000 (blue) and Co-SIM+NU-1000 (red) as well as the propene combustion process (diamonds) catalyzed by these two materials in a similar temperature range.

Este artigo trata apenas de dados de TOF de uma forma muito sucinta, explicando apenas que os valores encontrados foram advindos da divisão do amontoado total de Cobalto no MOF (considerou todo o metal como disponível) dividido pelo fluxo da mistura de propano e  $O_2$ . Nenhuma curva cinética foi mostrada ou sequer citada, e como pode ser visto na figura ao lado os TOF parecem ser calculados longe do “0” de conversão da reação, dando assim pouca informação sobre o papel do catalisador de fato e, se este valor está mais próximo ou mais afastado do equilíbrio termodinâmico da reação.

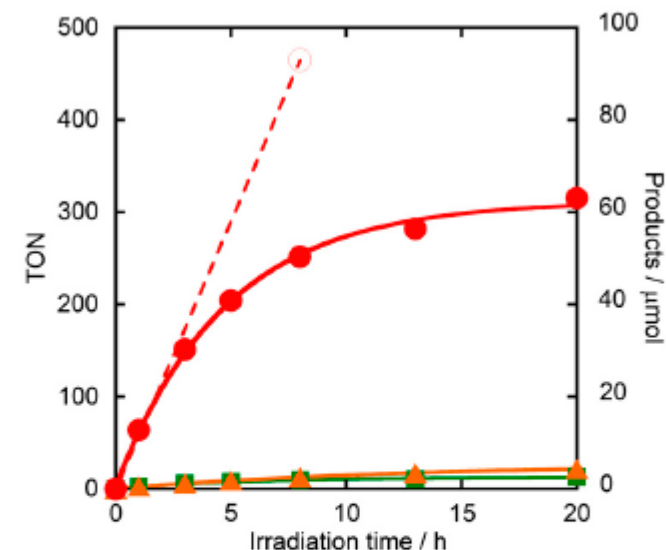
# Photocatalytic CO<sub>2</sub> reduction with high turnover frequency and selectivity of formic acid formation using Ru(II) multinuclear complexes

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In this reaction condition, it is difficult to determine reasonable TON values because too-large amounts of the products—i.e., formic acid and BNA<sub>2</sub>S—should be accumulated in the reaction solution after long irradiation and the products obstruct the photocatalytic reaction (see below). The photon flux determined that the rates of the photocatalytic reactions—i.e., the ordinary light source—even using a 500-W Xe lamp cannot supply enough photon flux for determining maximum TOF values. For obtaining more exact values of TON and TOF, we reduced the concentrations of the photocatalysts in the reaction solutions and used different light sources as follows.



**Fig. 1.** Photocatalytic formation of formic acid (red filled circle), CO (green filled square), and H<sub>2</sub> (orange filled triangle) as a function of irradiation time. The (red dotted line) shows the amount of formic acid generated by photocatalysis, under the assumption that the side reaction effect by BNA<sub>2</sub>S and the effect of the decrease of BNAH can be neglected: A CO<sub>2</sub> saturated DMF-TEOA (4:1 v/v, 4 mL) solution containing BNAH (0.1 M) and (1,1) (0.05 mM) was irradiated by >500-nm light.

Este artigo tratou dos conceitos de TON e TOF de uma forma muito bem condizente e, reconhecendo as limitações do seu sistema, desenvolveram outra metodologia (como visto ao lado) para então obter TON confiáveis o suficiente (abaixando a concentração dos fotocatalisadores) para assim então plotarem em uma curva de TON x Time (h) a curva cinética e obterem o TOF da parte que pareceu ser realmente a inicial. Faltou apenas o cálculo do R<sup>2</sup>.

Table 1. Photocatalytic properties of the supramolecules and the model system\*

| entry | photocatalyst | reductant              | products/ $\mu\text{mol}^{\dagger}$ |     |                | $\Phi_{\text{HCOOH}}^{\ddagger}$ | TON <sub>HCOOH</sub> <sup>§</sup> | $\Phi_{\text{em}}^{\text{¶}}$ | $\tau_{\text{em}}^{\text{  }}$ ns | $k_q^{\text{**}}$ $10^7 \text{ M}^{-1} \text{ s}^{-1}$ | $\eta_q^{\text{††}}$ % |
|-------|---------------|------------------------|-------------------------------------|-----|----------------|----------------------------------|-----------------------------------|-------------------------------|-----------------------------------|--|------------------------|
|       |               |                        | HCOOH                               | CO  | H <sub>2</sub> |                                  |                                   |                               |                                   |  |                        |
| 1     | (2,1)         | BNAH                   | 30.4                                | 1.8 | 1.8            | 0.041                            | 562                               | 0.085                         | 726                               | 1.97   | 59                     |
| 2     |               | MeO-BNAH <sup>**</sup> | 36.8                                | 2.4 | 1.9            | 0.061                            | 671 (396) <sup>§§</sup>           |                               |                                   | 4.72   | 77                     |
| 3     | (1,1)         | BNAH                   | 26.9                                | 2.8 | 0.9            | 0.038                            | 315                               | 0.083                         | 745                               | 1.64   | 54                     |
| 4     | (1,2)         | BNAH                   | 8.4                                 | 7.5 | 1.0            | 0.030                            | 353                               | 0.089                         | 755                               | 2.33   | 64                     |
| 5     | (1,3)         | BNAH                   | 5.3                                 | 8.1 | 0.7            | 0.017                            | 234                               | 0.082                         | 733                               | 2.82   | 67                     |
| 6     | (1,0)+(0,1)   | BNAH                   | 5.3                                 | 1.9 | 0.5            | –                                | 316                               | 0.087 <sup>¶¶</sup>           | 766 <sup>¶¶</sup>                 | 1.02 <sup>¶¶</sup>                                     | 44 <sup>¶¶</sup>       |

\*A 4-mL CO<sub>2</sub>-saturated dimethylformamide–triethanolamine (DMF–TEOA) (4:1 v/v) solution containing reductant (0.1 M) and complexes was irradiated. The concentrations of all the photocatalysts were 0.3 mM for " $\Phi_{\text{HCOOH}}$ " and "Products" and 0.05 mM for "TON<sub>HCOOH</sub>," except for (2,1), of which concentrations were adjusted to half of the other complexes because (2,1) has two photosensitizer units. Therefore, the concentrations of the photosensitizer units were same in all the photocatalytic systems in the series of the experiments.

<sup>†</sup>Irradiated in the Light Irradiation Condition (LIC) 1 for 5 h (light intensity:  $4.9 \times 10^{-8}$  einstein s<sup>-1</sup>).

<sup>‡</sup>Irradiated in the LIC1 (light intensity:  $4.9 \times 10^{-8}$  einstein s<sup>-1</sup>).

<sup>§</sup>Irradiated in the LIC2 for 20 h. TON<sub>HCOOH</sub><sup>§</sup> were calculated as [produced HCOOH]/[added supramolecule].

<sup>¶</sup>Emission quantum yield of the complexes in DMF–TEOA (4:1 v/v) (Excitation wavelength: 480 nm).

<sup>||</sup>Emission lifetime of the complexes in DMF–TEOA (4:1 v/v) (Excitation wavelength: 456 nm).



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## Synthesis of bis(indolyl)methanes using ammonium niobium oxalate (ANO) as an efficient and recyclable catalyst†

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Este artigo trata de um mesmo catalisador que apresenta diferentes comportamentos em diferentes tipos de sistemas reacionais, porém em momento algum os termos como TON e TOF foram discutidos, para assim entender melhor como a cinética da reação é diferente (ou não). Não se sabe se os valores de conversão estão próximos ao equilíbrio ou não justamente por não ter estes dados, e também a forma em que o catalisador desempenha um papel decisivo para diminuir drasticamente o tempo de reação.

**Table 2** Optimization studies using indole **1a** and aldehyde **2a**, under ultrasound irradiation<sup>a</sup>

| Entry | Catalyst <sup>b</sup> (mol%)                           | Solvent (1.0 mL)                | Conversion to <b>3a</b> <sup>b</sup> (%) |
|-------|--|---------------------------------|--|
| 1     | ANO (5.0)  | Water                           | 4  |
| 2     | ANO (5.0)  | Water                           | 23 <sup>c</sup>                          |
| 3     | ANO (5.0)  | Glycerol                        | 99 <sup>d</sup>                          |
| 4     | ANO (5.0)  | Toluene                         | 1  |
| 5     | ANO (5.0)  | DMSO                            | NR                                       |
| 6     | ANO (5.0)  | DMF                             | 1  |
| 7     | ANO (5.0)  | CH <sub>2</sub> Cl <sub>2</sub> | 2  |
| 8     | ANO (5.0)  | EtOH                            | 49                                       |
| 9     | Nb <sub>2</sub> O <sub>5</sub> (5.0)                   | Glycerol                        | 27                                       |
| 10    | Nb <sub>2</sub> O <sub>5</sub> ·H <sub>2</sub> O (5.0) | Glycerol                        | 32                                       |
| 11    | ANO (3.0)  | Glycerol                        | 92                                       |
| 12    | ANO (10.0)   | Glycerol                        | 95                                       |
| 13    | ANO (15.0)   | Glycerol                        | 97                                       |

<sup>a</sup> Reactions performed with indole **1a** (1.0 mmol), benzaldehyde **2a** (0.6 mmol) and the solvent (1 mL) under ultrasonic irradiation (20 kHz, 60% sonic amplitude) for 3 min. <sup>b</sup> Determined by GC, based on the amount of indole **1a**. <sup>c</sup> The reaction was sonicated for 30 min (final temperature = 50 °C). <sup>d</sup> The final temperature was 110 °C.

**Table 3** Scope and generality of the niobium-catalyzed synthesis of bis(indolyl)methanes **3a–k** using indoles **1a–c** and carbonyl compounds **2a–i**<sup>a</sup>

| Entry | Indole    | Carbonyl compound | Product   | Conventional <sup>b</sup> |                        | Ultrasound <sup>c</sup> |                        |
|-------|-----------|-------------------|-----------|---------------------------|------------------------|-------------------------|------------------------|
|       |           |                   |           | Time (h)                  | Yield <sup>d</sup> (%) | Time (min)              | Yield <sup>d</sup> (%) |
| 1     | <b>1a</b> | <b>2a</b>         | <b>3a</b> | 2.0                       | 97                     | 3                       | 99                     |
| 2     | <b>1a</b> | <b>2b</b>         | <b>3b</b> | 1.0                       | 92                     | 5                       | 92                     |
| 3     | <b>1a</b> | <b>2c</b>         | <b>3c</b> | 3.0                       | 89                     | 8                       | 82                     |
| 4     | <b>1a</b> | <b>2d</b>         | <b>3d</b> | 2.0                       | 99                     | 15                      | 90                     |

## Synthetic Applications of Pd(II)-Catalyzed C–H Carboxylation and Mechanistic Insights: Expedient Routes to Anthranilic Acids, Oxazolinones, and Quinazolinones

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Table 2. *Ortho*-Carboxylation of Anilides via C–H Activation<sup>a,b</sup>

| Entry | Substrate | Product | % Yield         | Entry | Substrate | Product | % Yield           |
|-------|-----------|---------|-----------------|-------|-----------|---------|-------------------|
| 1     |           |         | 60              | 8     |           |         | 98 <sup>c,e</sup> |
| 2     |           |         | 53 <sup>f</sup> | 9     |           |         | 85 <sup>c,e</sup> |
| 3     |           |         | 94              | 10    |           |         | 97 <sup>c,e</sup> |
| 4     |           |         | 70 <sup>d</sup> | 11    |           |         | 88 <sup>c,e</sup> |
| 5     |           |         | 67 <sup>c</sup> | 12    |           |         | 62 <sup>c,f</sup> |
| 6     |           |         | 88 <sup>c</sup> | 13    |           |         | 83 <sup>c,f</sup> |
| 7     |           |         | 53              | 14    |           |         | 69 <sup>d</sup>   |

<sup>a</sup> 10 mol % Pd(OAc)<sub>2</sub>, 0.5 equiv of *p*-TsOH·H<sub>2</sub>O, 1 equiv of benzoquinone, 1 atm of CO, HOAc/dioxane (2:1), 60 °C (entries 1, 4–6, 8, 10, and 11) or 80 °C (entries 2, 3, 7, 9, and 12–14), 18 h (entries 3–6 and 14), 24 h (entries 1, 2, and 7–11), or 36 h (entries 12 and 13), Hi-Vac valve Schlenk tube. <sup>b</sup> Isolated yields. <sup>c</sup> Dioxane was used as a solvent. <sup>d</sup> HOAc/toluene (2:1) was used as a solvent. <sup>e</sup> 0.5 equiv of NaOAc was used as an additive. <sup>f</sup> 15 mol % Pd(OTf)<sub>2</sub>(MeCN)<sub>4</sub> was used.

Este artigo apesar de se tratar de um artigo muito bem escrito e detalhado não demonstrou dados cinéticos de forma correta, mesmo tratando de catálise e tempo de reação muito longos, foram escolhidas apenas 3 diferentes tempos de reação (18, 24 e 36 horas) mas não mostrando onde de fato o TON permanece praticamente constante, e portanto não mostrando se de fato estes tempos de reação relativamente “grandes” são necessários. Ao menos o TON poderia ser calculado facilmente, pois têm-se 10 mol% de catalisador e rendimentos observados.

# Trivalent Titanium Salen Complex: Thermally Robust and Highly Active Catalyst for Copolymerization of CO<sub>2</sub> and Cyclohexene Oxide

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The copolymerization results of CO<sub>2</sub> and CHO are listed in Table 1 using (Salen)Ti(III)Cl (complex 1) as catalyst and [PPN]X as cocatalyst, and corresponding results from (Salalen)Ti(IV)Cl (complex 2) were also shown for comparison. As we have previously reported, (Salalen)Ti(IV)Cl required a high pressure of 4.0 MPa for the most favorable activity, and thus, all the experiments were carried out under 4.0 MPa. First, the reaction was carried out in the presence of [PPN]Cl (1 equiv), with CHO (1000 equiv) at 70 °C for 6 h (Table 1, entry 1), a TOF of 84 h<sup>-1</sup> was obtained (Table 1, entry 1). The copolymer was obtained in almost completely alternating structure, and no production of cyclohexene carbonate was detected. The catalytic activity increased steadily with the temperature (Table 1, entries 1–5), and the TOF reached 230 h<sup>-1</sup> at 90 °C; it was notable that (Salen)Ti(III)Cl produced a copolymer with a TOF of 557 h<sup>-1</sup> at 120 °C and still no cyclic byproduct and ether unites were observed. It was more than 10 times higher than the maximal TOF of (Salalen)Ti(IV)Cl, and close to that of (Salen)Cr(III)X, which was the most active metal salen binary catalyst for CO<sub>2</sub>/CHO copolymerization.<sup>13</sup>

| entry           | catalyst | cocatalyst | CHO/catalyst/<br>cocatalyst | T (°C) | t (h) | yield (%) <sup>b</sup> | carbonate linkage (%) <sup>c</sup> | PCHC/CHC <sup>b</sup> | TOF <sup>d</sup> (h <sup>-1</sup> ) | M <sub>n</sub> <sup>e</sup> | M <sub>w</sub> /M <sub>n</sub> |
|-----------------|----------|------------|-----------------------------|--------|-------|------------------------|------------------------------------|-----------------------|-------------------------------------|-----------------------------|--------------------------------|
| 1               | 1        | [PPN]Cl    | 1000/1/1                    | 70     | 6     | 50.1                   | 99                                 | >99/1                 | 84                                  | 7400                        | 1.08                           |
| 2               | 1        | [PPN]Cl    | 1000/1/1                    | 80     | 2     | 32.2                   | 99                                 | >99/1                 | 161                                 | 6300                        | 1.09                           |
| 3               | 1        | [PPN]Cl    | 1000/1/1                    | 90     | 2     | 46.0                   | 99                                 | >99/1                 | 230                                 | 5800                        | 1.11                           |
| 4               | 1        | [PPN]Cl    | 1000/1/1                    | 120    | 1     | 57.7                   | 99                                 | >99/1                 | 577                                 | 4200                        | 1.06                           |
| 5               | 1        | [PPN]Cl    | 2000/1/1                    | 120    | 3     | 29.9                   | 99                                 | >99/1                 | 200                                 | 2700                        | 1.09                           |
| 6               | 1        | [PPN]Cl    | 2000/1/2                    | 120    | 1     | 25.1                   | 99                                 | 94/6                  | 502                                 | 2400                        | 1.08                           |
| 7               | 1        | [PPN]Cl    | 2000/1/10                   | 120    | 1     | 56.3                   | ND                                 | 10/90                 | 1126                                | ND                          | ND                             |
| 8               | 1        | [PPN]Cl    | 2000/1/20                   | 120    | 1     | 79.5                   | ND                                 | 0/100                 | 1590                                | ND                          | ND                             |
| 9               | 1        | [PPN]Br    | 1000/1/1                    | 90     | 3     | 34.5                   | 99                                 | 64/36                 | 115                                 | 2400                        | 1.10                           |
| 10 <sup>f</sup> | 1        | [PPN][DNP] | 1000/1/1                    | 90     | 3     | 43.5                   | 99                                 | >99/1                 | 145                                 | 4500                        | 1.08                           |
| 11              | 1        | [PPN][DNP] | 1000/1/1                    | 120    | 1     | 39.6                   | 99                                 | >99/1                 | 396                                 | 3600                        | 1.07                           |
| 12 <sup>g</sup> | 2        | [PPN]Cl    | 500/1/1                     | 70     | 10    | 44.4                   | 98                                 | 98/2                  | 22                                  | 4200                        | 1.09                           |
| 13 <sup>g</sup> | 2        | [PPN]Cl    | 500/1/1                     | 90     | 8     | 66.0                   | 98                                 | 86/14                 | 41                                  | 4200                        | 1.11                           |
| 14 <sup>g</sup> | 2        | [PPN][DNP] | 500/1/1                     | 70     | 12.5  | 38.2                   | 98                                 | 86/14                 | 15                                  | 4200                        | 1.10                           |

<sup>a</sup>Reaction conditions: neat CHO, CO<sub>2</sub> pressure = 4.0 MPa. <sup>b</sup>Obtained from the normalized integrals of the methylene resonances in <sup>1</sup>H NMR spectra, where PCHC carbonate, ether, and CHC was 4.65, 3.45, and 4.63 ppm (*cis*-CHC).<sup>14</sup> <sup>c</sup>Carbonate linkage content = (carbonate linkages in copolymer)/(carbonate and ether linkages in copolymer). <sup>d</sup>TOF = turnover frequency of CHO to PCHC per hour. <sup>e</sup>Determined by GPC in CH<sub>2</sub>Cl<sub>2</sub> solution using polystyrene standards. <sup>f</sup>With bis(triphenylphosphino)iminium 2,4-dinitrophenolate ([PPN][DNP]) as cocatalyst. <sup>g</sup>According to ref 8.

Neste artigo (2015) os autores mostraram a relação de quantidade em equivalente, algo não muito comum para artigos mais recentes. Os cálculos dos TOFs não foram explicados de maneira nítida, não esclarecendo em que momento foi retirada uma alíquota para o cálculo ou se foi calculado apenas ao final do tempo de reação com a conversão obtida e o total de catalisador adicionado.