



Innovative photocatalysts integrated in flow photoreactor systems for direct CO<sub>2</sub> and H<sub>2</sub>O conversion in solar fuels

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### Preliminary report on the photocatalyst candidates: Synthesis conditions and photocatalytic activity evaluation

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# NEFERTITI

NEFERTITI–D3.2–Preliminary report on the photocatalyst candidates:  
Synthesis conditions and photocatalytic activity evaluation

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## 1. Introduction

Ethanol has attracted considerable interest in recent years because of its importance as a chemical raw material and renewable carbon resource.<sup>4-6</sup> Although thermal driven conversion of syngas to ethanol have been applied in industry, the limitation of catalyst development has always been a confronting problem in this field.<sup>7</sup> Moreover, precise control of C-C coupling and the insertion of CO to improve the selectivity of C<sub>2</sub> oxygenates are always difficult in thermodynamic syngas conversion. To meet future demand for increased ethanol production, it is worth exploring more catalyst designs and pathway designs for them.<sup>8</sup> An alternative is the solar driven catalysis that offers a high potential for transforming CO by means of photo-thermal process. The catalyst design strategy is through coupling the excellent catalysts reported in the thermal catalysis with the materials with light absorption properties to improve the photothermal synergy effect. The main catalytic systems we consider for photocatalytic syngas to alcohols are including modified methanol catalysts (Cu-based catalysts), modified FTS catalysts (Fe-based catalysts), noble metal catalysts (Rh-based catalysts) and some novel photocatalysts (Ni@TiO<sub>2-x</sub>).

Olefins are feedstocks for many high value-added chemical products and the “Fischer–Tropsch to olefins” (FTO) process has long offered a way of producing lower olefins directly from syngas which is derived from coal, biomass and natural gas.<sup>9-11</sup> However, application of this technology is still limited by low olefin selectivity and high methane selectivity. Photo-driven reactions toward CO utilization are sustainable routes and can improve olefin selectivity of and solve the problems encountered in the current thermal catalysis by photothermal synergy.<sup>12</sup> Because of the high energy efficiency of this photothermal effect, the catalyst surface temperature can reach 300-500 °C or even higher providing enough energy to drive thermodynamically

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4 West T. Ethanol mediates[J]. *Nature Catalysis*, **2021**, 4(4): 263-263.

5 Farrell A E, Plevin R J, Turner B T, et al. Ethanol can contribute to energy and environmental goals[J]. *Science*, **2006**, 311(5760): 506-508.

6 Luk H T, Mondelli C, Ferré D C, et al. Status and prospects in higher alcohols synthesis from syngas[J]. *Chemical Society Reviews*, **2017**, 46(5): 1358-1426.

7 Spivey J J, Egbeki A. Heterogeneous catalytic synthesis of ethanol from biomass-derived syngas[J]. *Chemical Society Reviews*, **2007**, 36(9): 1514-1528.

8 Grim R G, To A T, Farberow C A, et al. Growing the bioeconomy through catalysis: a review of recent advancements in the production of fuels and chemicals from syngas-derived oxygenates[J]. *ACS Catalysis*, **2019**, 9(5): 4145-4172.

9 Torres Galvis H M, Bitter J H, Khare C B, et al. Supported iron nanoparticles as catalysts for sustainable production of lower olefins[J]. *Science*, **2012**, 335(6070): 835-838.

10 Torres Galvis H M, Bitter J H, Davidian T, et al. Iron particle size effects for direct production of lower olefins from synthesis gas[J]. *Journal of the American Chemical Society*, **2012**, 134(39): 16207-16215.

11 Koeken A C J, Torres Galvis H M, Davidian T, et al. Suppression of carbon deposition in the iron-catalyzed production of lower olefins from synthesis gas[J]. *Angewandte Chemie*, **2012**, 124(29): 7302-7305.

12 Gao W, Gao R, Zhao Y, et al. Photo-driven syngas conversion to lower olefins over oxygen-decorated Fe<sub>3</sub>C<sub>2</sub> catalyst[J]. *Chem*, **2018**, 4(12): 2917-2928.

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unfavorable reactions.<sup>13</sup> Thus, the photoinduced thermal effect that simultaneously exists with photoinduced carriers may be possible to break the Anderson-Schulz-Flory distribution and get a higher o/p.<sup>14</sup> The strategy is to modify the Fe-based catalyst to obtain excellent photothermal catalysts for the light-driven FTO.

## 2. Objective

The main objective of this stage is focused on developing catalytic systems for syngas conversion into alcohols in traditional thermal catalytic system and then couple them with light-absorbing materials to be applied in light-driven syngas conversion to light alkenes or alcohols. Then the performance of the constructed catalytic systems will be evaluated to select the best photocatalyst. Once determined the suitable photocatalysts, various characterization methods will be combined to elaborate the structure-activity relationship in detail and propose theoretical models for the simulation of the catalyst.

## 3. Methodology

### 3.1. Synthesis of photocatalysts

For olefin synthesis, the Fe-based catalysts (Fe-Zn-x Na) were synthesized by co-precipitation method.  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  aqueous solution (1M) and  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$  aqueous solution (1M) were mixed in a constant pressure funnel. Another funnel was filled with  $\text{Na}_2\text{CO}_3$  aqueous solution (2M). Then both solutions were dipped into a three-necked flask, which was kept 80 °C in a bath. The mixture was continuously stirred at pH around 9.0. After aged at that temperature for 5 hours, the turbid liquid was filtrated and washed with various amount of deionized water. After drying at 60 °C, the orange powder was calcinated in muffle furnace at 350 °C for 4 hours.

For the synthesis of alcohols, the nanodiamond@graphene (ND@G) hybrid carbon support was prepared by annealing fresh nanodiamond powders at 1100 °C (heating rate 5 °C·min<sup>-1</sup>) for 4 h under flowing Ar gas (80 mL·min<sup>-1</sup>). When it finished and cooled to room temperature, the final powder, ND@G, was collected for further use. The Rh-based catalyst uses the traditional wet chemical impregnation method to load Rh metals and other additive metals (Mn, Li, Fe) onto the ND@G support. 0.5 g ND@G was dispersed into 5 mL DI water with 2 wt %  $\text{Rh}(\text{NO}_3)_3$ , 1 wt%  $\text{Mn}(\text{NO}_3)_2$  and 0.75 wt%  $\text{Li}(\text{NO}_3)_2$  and 0.75 wt%  $\text{Fe}(\text{NO}_3)_3$ , and the mixture was ultrasonically

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13 Ren J, Ouyang S, Xu H, et al. Targeting activation of CO<sub>2</sub> and H<sub>2</sub> over Ru-loaded ultrathin layered double hydroxides to achieve efficient photothermal CO<sub>2</sub> methanation in flow-type system[J]. *Advanced Energy Materials*, **2017**, 7(5): 1601657.

14 Torres Galvis H M, de Jong K P. Catalysts for production of lower olefins from synthesis gas: a review[J]. *ACS catalysis*, **2013**, 3(9): 2130-2149.

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treated for 45 min to obtain a homogeneous suspension, then dried at 60 °C for further use.

The Synthesis of Ni@TiO<sub>2-x</sub>: Ni(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O (0.006 mol), HCl (0.25 mL), TiCl<sub>4</sub> (0.25 mL), and urea (0.1 mol) were dissolved into deionised water (100 mL) under vigorous stirring for 24 h at 95 °C; The resulting solid was centrifuged washed thoroughly and dried at 60 °C overnight; Afterwards, NiTi-LDHs nanoplates were calcinated under air with the heating rate of 2 °C /min in the muffle furnace to obtain the mixed oxide NiTi-MMO (the mixture of NiO and TiO<sub>2</sub>). Subsequently, the as-obtained NiTi-MMO mixed oxides were reduced under 10% H<sub>2</sub>/Ar with a flow rate of 60 mL/min and a heating rate of 2 °C /min for 4 h at different temperature, such as 300, 350, 400, 450, 500, 550, and 600 °C, which were denoted as TiO<sub>2-x</sub>/Ni-300, TiO<sub>2-x</sub>/Ni-350, TiO<sub>2-x</sub>/Ni-400, TiO<sub>2-x</sub>/Ni-450, TiO<sub>2-x</sub>/Ni-500, TiO<sub>2-x</sub>/Ni-550, and TiO<sub>2-x</sub>/Ni-600, respectively.

The Synthesis of CuCo-LDHs: Cu(NO<sub>3</sub>)<sub>2</sub>·3H<sub>2</sub>O, Co(NO<sub>3</sub>)<sub>2</sub>·6H<sub>2</sub>O, and Al(NO<sub>3</sub>)<sub>3</sub>·9H<sub>2</sub>O were dissolved in deionized water with [Cu<sup>2+</sup>]+[Co<sup>2+</sup>]+[Al<sup>3+</sup>] = 1.0 M and [Cu<sup>2+</sup>]+[Co<sup>2+</sup>]/[Al<sup>3+</sup>] = 2 M. NaOH and Na<sub>2</sub>CO<sub>3</sub> were dissolved in deionized water with [NaOH] = 1.5 M and [Na<sub>2</sub>CO<sub>3</sub>] = 2[Al<sup>3+</sup>]. The two solutions were simultaneously added into deionized water keeping pH = 9.5 ± 0.1 under vigorous stirring. As the precipitation was completed, the slurry was aged at 60 °C for 12 h, and then filtered, washed with distilled water until pH = 7, and dried at 60 °C for 12 h. And then the prepared catalyst was calcined at 500 °C for 3 h in air. And then the calcined catalyst was reduced at 450 °C for 3 h in hydrogen.

The Synthesis of Fe<sub>5</sub>C<sub>2</sub>/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub>: A solution of metal nitrates [(Cu(NO<sub>3</sub>)<sub>2</sub> (0.6 mol/L), Zn(NO<sub>3</sub>)<sub>2</sub> (0.3 mol/L), Al(NO<sub>3</sub>)<sub>3</sub> (0.1 mol/L)] and a solution of Na<sub>2</sub>CO<sub>3</sub> (1 mol/L) as a precipitant were pumped (at constant flow rate of 5 ml/min) into a stirred and heated glass reactor with a starting volume of 200 mL of demineralized water. The coprecipitation was stopped when 40 mL of metal nitrate solution had been added. The pH was kept at 9.0. After aging for 1 h, the precipitates were filtered and washed three times with 150 mL of demineralized water each, and then dried overnight at 80 °C, calcined at 300 °C under air for 3 h, resulting in the oxide precursor. 10 wt% Fe was impregnated on the oxide precursor and dried overnight at 80 °C, calcined at 300 °C under air for 3 h, then carbonized with syngas at 340 °C for 5 h to get Fe<sub>5</sub>C<sub>2</sub>/Cu-ZnO-Al<sub>2</sub>O<sub>3</sub> for further used.

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## 3.2. Catalytic Tests

Photo-driven CO hydrogenation reactions were carried out in a stainless-steel reactor (volume, ~50 mL) with a quartz window on the top of the reactor. The photo-driven reaction was performed in a gas (vapor)-solid heterogeneous reaction mode. Typically, 200 mg of solid catalyst was spread as a very thin layer (<1 mm) onto round-shaped quartz glassware with an area of 14 cm<sup>2</sup>. Before the catalytic test, the catalyst was activated in situ with H<sub>2</sub>/Ar (10:90) at 400 °C for 2~4 hr. After cooling to room temperature, the two globe valves were closed to keep the gas in the reactor before the sample was taken out in a glovebox. The activated catalysts were transferred to stainless-steel reactor in a glovebox. After evacuation of the reaction system, syngas (CO/H<sub>2</sub>/Ar = 47:47:6, 0.5 MPa) were injected. The light source was a 300 W Xe lamp ( $\lambda = 320\text{--}1100$  nm) to drive the photo-driven CO conversion. The tip of thermometer was maintained in intimate contact with the sample.

## 4. Results

Through the catalytic evaluation of the constructed catalysts, it was found that the main products for light-driven syngas conversion were CO<sub>2</sub> and CH<sub>4</sub> (Table 1). Moreover, it was found that the distribution of alcohol can be related to the RhMn/CeO<sub>2-x</sub> catalyst, which is mainly due to two factors: (a) The partially reduced support or promoter may provide metal cation or oxygen vacancies, which interact with the oxygen end of a carbon monoxide molecule adsorbed on the rhodium surface to facilitate its dissociation or insertion. (b) The generation of oxygen vacancies can change the band gap structure of the catalysts and increase the light absorption performance.

However, compared with the catalytic performance on fixed bed for RhMn/CeO<sub>2-x</sub> (Table 1, line 7), the distribution of alcohol could reach 12.9% (driven by heat). Thus, after evaluating the conditions, pressure and temperature lead to a performance difference. Next experiments will be focused in combining it with black materials with good light absorption properties (NDG<sup>15</sup>, black TiO<sub>2-x</sub><sup>16</sup>, etc.) to improve the photothermal conversion effect, and continue to optimize the catalytic performance by changing the evaluation conditions.

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15 Chen X, Peng M, Cai X, et al. Regulating coordination number in atomically dispersed Pt species on defect-rich graphene for n-butane dehydrogenation reaction[J]. *Nature communications*, **2021**, 12(1): 1-9.

16 Tan H, Zhao Z, Niu M, et al. A facile and versatile method for preparation of colored TiO<sub>2</sub> with enhanced solar-driven photocatalytic activity[J]. *Nanoscale*, **2014**, 6(17): 10216-10223.



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Table 1. Photo-activity evaluation and optimization for alcohols.

Catalyst	T (h)	CO Conv./%	CO <sub>2</sub> selectivity/%	Hydrocarbon selectivity/%				
				CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5</sub> +	Alcohol	o/p <sup>c</sup>
TiO <sub>2-x</sub> /Ni-450 <sup>a</sup>	1	4.6	2.1	39.5	37.7	3.8	0	0.23
RhMn/ND@G	1	16.6	29.4	54	12.6	1	0	0.1
RhMnLiFe/ND@G	1	13.2	37.8	19.8	6.7	2.5	0	0.21
	2	52.7	45	43.7	4.68	0	0	0.06
Rh-CeO <sub>2</sub> /ND@G	1	24.4	23.6	28.5	6.5	0.6	0.1	0.13
RhMn/CeO <sub>2-x</sub>	2	4.9	46.59	2.59	1.9	1.5	1.1	2.4
	flow <sup>b</sup>	8.0	44.2	28.8	12.8	1.62	12.9	-
CuCo-LDHs	1	3.86	4.55	18.4	34	16.7	-	1.79
Fe <sub>5</sub> C <sub>2</sub> /CuZnAl <sup>d</sup>	1	27.44	37.09	12.01	17.83	4.67	-	0.08

Reaction condition: H<sub>2</sub>:CO = 1, 0.5 MPa, Xe Lamp (320~1200 nm)

a: the mass of TiO<sub>2-x</sub>/Ni-450 =100 mg, others are 200 mg.

b: fixed bed, H<sub>2</sub>:CO = 1, 320 °C, 3 Mpa, 12000 mL gcat<sup>-1</sup> h<sup>-1</sup>. The data is collected at 2 h

c: o/p=olefin/paraffin

d: the reaction pressure is 0.15 MPa

Higher o/p (olefins/ paraffins) results were obtained by photocatalytic conversion of syngas to light olefins over Fe-based catalysts, which could reach up to 4.3 ratio (Table 2). However, this ratio was even higher under thermocatalytic conditions. In order to increase the ratio obtained under photocatalytic conditions, the reaction will be further optimized by changing the evaluation conditions, such as pressure, ratio of H<sub>2</sub> and CO...

Table 2. Photo-activity evaluation and optimization for lower olefins

Catalyst	P (MPa)	T (h)	CO Conv./%	CO <sub>2</sub> Selectivity/%	Hydrocarbon selectivity/%			
					CH <sub>4</sub>	C <sub>2</sub> -C <sub>4</sub>	C <sub>5</sub> +	o/p
FeZnNa <sup>a</sup>	0.5	5	49.2	38.6	37.4	8.7	2.4	4.3
FeZnNa <sup>b</sup>	2	40	63	22.5	8.6	22.6	46.3	7.4

a: Light driven: batch, The data is collected after 5 h.

b: thermally driven: catalyst (20 mg), 60000 mL gcat<sup>-1</sup> h<sup>-1</sup>, 340 °C. Pretreated with H<sub>2</sub>/N<sub>2</sub> (5%) at 300 °C for 4 h. The data is collected at 40 h.



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## 5. Conclusions

Among the different photocatalyst that have been synthesized, together with the photocatalytic evaluation of them, the catalytic system with alcohol distribution ( $\text{RhMn/CeO}_{2-x}$ ) and high o/p catalyst system (FeZnNa) have been preliminarily obtained. Next steps will be focused in optimizing the photocatalytic performance for syngas to alkenes or alcohols by adjusting the evaluation conditions and the electronic structure of these catalysts to further precise regulation of product distribution.