

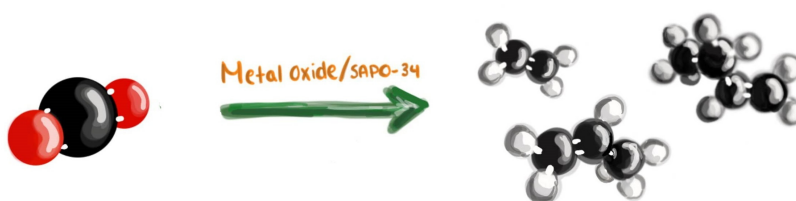
Ninni Maria Unneberg

## CO<sub>2</sub> hydrogenation to light olefins over metal supported SAPO-34

Which metals or metal combinations exhibits the  
best selectivity and conversion?

Bachelor's project in Natural Science with Teacher Education  
Supervisor: Muhammad Mohsin Azim

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Faculty of Natural Sciences  
Department of Chemistry



## Abstract

Direct hydrogenation of carbon dioxide to high value-added chemicals is a promising approach to mitigate the accumulated surplus of carbon dioxide in the atmosphere and at the same time reduce the dependency on fossil fuels by closing the carbon cycle. Various efforts have been made to offer a direct and sustainable route, and bifunctional catalysts of metal oxides on zeotypes show great potential in this respect. Tandem catalysis offers a highly attractive way to couple reactions and make the route thermodynamically favourable. Herein, 14 different metal oxides or metal oxide composites supported on the zeotype SAPO-34 have been compared for the direct conversion of CO<sub>2</sub> to light olefins. Chiefly, they have been discussed in terms of CO<sub>2</sub> conversion and light olefin selectivity. The conversion ranges from 12,6 to 54,6%, while the selectivity ranges from 48 to 90% for the reported catalysts in this project. As a result, zirconium, indium and zinc appears to be common metals among the best performing ones. The results also indicates that the introduction of zinc increases the selectivity in many cases despite often decreasing conversion. In conclusion, the In<sub>2</sub>O<sub>3</sub>-ZrO/SAPO-34 catalyst prepared by Gao *et al.* exhibited the best conversion and selectivity without too many unwanted biproducts such as methane and carbon monoxide. However, the novel Fe<sub>2</sub>O<sub>3</sub>@KO<sub>2</sub>/ZrS/SAPO-34 and Ce-CuZnZr@Zn-SAPO-34 also achieved remarkably high conversion. Still, there are remaining challenges before the process can be applied commercially. For all those reasons including the potential environmental gain, further research should be conducted on the topic.

## Sammendrag på norsk

Direkte hydrogenering av karbondioksid til høyverdige kjemikalier er en lovende strategi for å lukke karbonsyklusen ved å redusere overskuddet av karbondioksid i atmosfæren og samtidig minske avhengigheten av fossile brennstoff. De siste tiårene har det vært et stort insentiv i forskningsmiljøet for å finne en bærekraftig og direkte rute for konverteringen. Bifunksjonelle katalysatorer komponert av metalloksider på zeotyper har vist stort potensiale i denne sammenhengen. Tandemkatalysen har en gunstig termodynamisk effekt. I denne prosjektoppgaven har 14 ulike metalloksider eller metalloksid-kombinasjoner på zeotypen SAPO-34 blitt sammenlignet for den direkte konverteringen av CO<sub>2</sub> til lette olefiner. Hovedsakelig har de forskjellige katalysatorene blitt diskutert med hensyn på CO<sub>2</sub> konvertering og lett olefinselektivitet. Det er blitt rapportert konvertering fra 12,6 til 54,6%, og selektivitet mellom 48 og 90%. Resultatene indikerer at zirconium, indium og sink er komponenter i katalysatorene som utviser best selektivitet og konvertering. I tillegg tyder resultatene på at sink øker selektiviteten for lette olefiner i mange tilfeller, til tross for at konverteringen ser ut til å bli lavere. Alt i alt utviste In<sub>2</sub>O<sub>3</sub>-ZrO/SAPO-34-katalysatoren fremstilt av Gao *et al.* best konvertering og selektivitet uten for mange uønskede biprodukter som metan og karbonmonoksid. Imidlertid oppnådde også Fe<sub>2</sub>O<sub>3</sub>@KO<sub>2</sub>/ZrS/SAPO-34 og Ce-CuZnZr@Zn-SAPO-34 bemerkelsesverdig høy konvertering. Likevel er det utfordringer før prosessen kan tas i bruk kommersielt. Den potensielle miljøgevinsten gjør temaet svært aktuelt for videre forskning.

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## 1. Introduction

Carbon dioxide is recognized as one of the greenhouse gases (GHG) with emissions that contribute most to the greenhouse effect.<sup>1</sup> Climate change and global warming, as a result of increasing concentrations of GHGs in the atmosphere, are regarded as one of the greatest challenges in the 21<sup>st</sup> century.<sup>2</sup> The Intergovernmental Panel on Climate Change (IPCC) and the United Nations Climate Change Conference (COP21, Paris, 2015) have emphasized the importance of limiting the increase in global average temperature to not exceed 2°C to avoid more dangerous consequences.<sup>2</sup> In order to achieve this goal, CO<sub>2</sub>-emissions has to be reduced by at least 50% by 2050.<sup>1</sup> Although CO<sub>2</sub> capture and carbon dioxide storage (CCS) has been of high interest during the last decades, it has not made a significant contribution to solving the climate issues mostly because of technical and economic barriers.<sup>3,4,5</sup>

More recently carbon capture and utilisation (CCU) has gained a lot of attention.<sup>1</sup> Instead of regarding CO<sub>2</sub> as an expensive waste, there has been a shift to regarding it as a potential carbon source. The prospect of recycling carbon dioxide into high-value chemicals, such as fuels and chemical feedstock is an enormous economic and environmental incentive.<sup>6</sup> CCU can reduce emission into the atmosphere, directly by converting CO<sub>2</sub>, and indirectly by reducing waste and replacing fossil fuels with CO<sub>2</sub> as carbon source.<sup>7</sup> Utilisation of CO<sub>2</sub> may contribute to reducing the atmospheric load while also generating a profit.<sup>7</sup> Governments and companies would easier follow suit if CO<sub>2</sub> could be used as a raw material for profitable products.<sup>5</sup> In order for such conversions to be economically feasible, considerable research into novel technologies and sustainable routes of synthesis is urgently required.<sup>8</sup>

In all the routes that have been proposed for CCU, catalysis plays a fundamental role.<sup>8</sup> Development of new processes, pathways, reactors and catalysts, which are more efficient and selective than the existing ones, is needed.<sup>6</sup> The catalytic hydrogenation and conversion of CO<sub>2</sub> with renewable hydrogen is considered a suitable route into light olefins. These reactions can be achieved with relatively high selectivity.<sup>9</sup> If the hydrogen used in the CO<sub>2</sub> hydrogenation is directly produced from renewable energy sources, this will become a valuable strategy for renewable energy utilization in both chemical industry and power generation.<sup>10,11</sup>

In this matter, thermocatalytic hydrogenation of carbon dioxide into high value-added chemicals is an important process. Among the pursued products are alcohols, alkanes, olefins and aromatics. In particular, light olefins are very important intermediates in the chemical industry.<sup>12</sup> Especially due to their use in polymer production, usually from fossil fuels. Along with the increasing demand for plastic, the need to develop a more sustainable route for this synthesis has become even more pressing.<sup>1</sup>

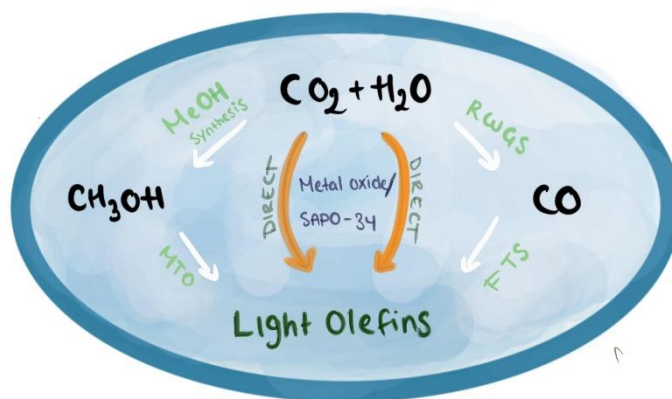
Zeotype-based catalysts have been paid special attention during the last years because of properties like porosity, specific surface area, acidity and interaction with active metals.<sup>1</sup> Bifunctional catalysts combining zeotypes with metals which activate CO<sub>2</sub> can play a significant role for these conversions - especially if a multifunctional catalyst can be used in one single reactor.<sup>13</sup> However, designing such a catalyst is still a challenge. In this bachelor project different metal supports for the zeotype SAPO-34 will be compared. Which metals or metal combinations exhibits the best CO<sub>2</sub> conversion and light olefin selectivity?

## 2. Theory

### 2.1 Conversion of CO<sub>2</sub> to olefins

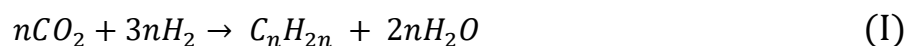
#### 2.1.1 Different routes for conversion

Light olefins are defined as the alkenes C<sub>2</sub>H<sub>4</sub>, C<sub>3</sub>H<sub>6</sub> and C<sub>4</sub>H<sub>8</sub> in this paper, often denounced C<sub>2</sub>=-C<sub>4</sub>=. There are two main routes through which CO<sub>2</sub> can be converted to olefins, as illustrated in Figure 1. The first is the reverse water gas shift (RWGS), where CO<sub>2</sub> is converted to CO, combined with the Fischer-Tropsch synthesis (FTS) where CO is converted to hydrocarbons. The second is the methanol-mediated synthesis where CO<sub>2</sub> is hydrogenated to MeOH and further converted to hydrocarbons.<sup>14</sup> Promoted catalysts can combine steps for a direct CO<sub>2</sub> hydrogenation to olefins.<sup>15</sup> This requires a tandem catalyst which activates CO<sub>2</sub> for hydrogenation, but also synthesizes lower olefins, usually a zeolite, in this study SAPO-34.<sup>16</sup>



**Figure 1:** An illustration of the pathways for direct conversion of CO<sub>2</sub> to light olefins via MeOH-route or RWGS-FTS-route. Inspired by Sharma *et al.*<sup>22</sup>

Total reaction:<sup>9</sup>



Yet there has not been a commercial application for the RWGS-FTS route because of low selectivity to light olefins.<sup>17</sup> Comparatively, the MeOH-route shows more promising results whereas the MTO-process has been successfully commercialized with a C<sub>2</sub>=-C<sub>4</sub>= selectivity of

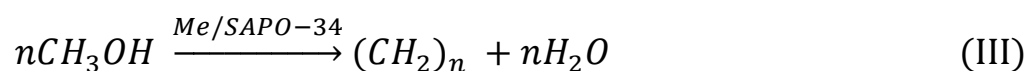
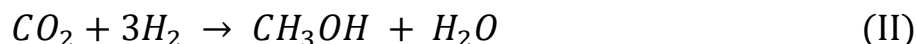


about 80%.<sup>17</sup> Light olefin production can be produced in two reactors: first CO<sub>2</sub> to methanol and then MTO. Alternatively it can be converted directly in a one-pot hydrogenation of CO<sub>2</sub> to olefins where methanol works as an intermediate which is further dehydrated in the same reactor.<sup>1</sup>

### 2.1.2 MeOH-route

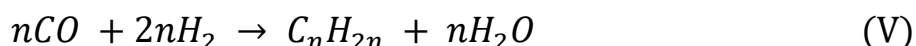
The route is receiving increasing scientific interest for the chemical recycling of CO<sub>2</sub> as it is connected to well established technologies.<sup>8,9</sup> The reaction is thermodynamically favourable at lower temperatures, which in fact limits the conversion due to accumulated heat.<sup>1,18</sup> When methanol is formed, the next step is the MTO-reaction.<sup>19</sup> There are three main steps. First the formation of dimethyl ether (DME); second the initial C-C bond formation; and third the subsequent conversion to higher hydrocarbons through carbenium ion mechanism.<sup>20</sup> It is commonly accepted that the MTO-reaction follows the hydrocarbon pool (HCP) mechanism.<sup>21</sup> Despite extensive study, there has not been achieved a full agreement on the complex pathway and mechanism.<sup>1</sup> Most importantly is the formation of the first C-C bond from MeOH followed by successive formation of higher hydrocarbons.<sup>22</sup>

The two main steps for the MeOH-route are given below:



### 2.1.3 RWGS-FTS-route (CO-based)

CO-based synthesis follows the Anderson-Schulz-Flory (ASF) distribution which limits the possible maximum selectivity.<sup>13</sup> The two main reaction steps are given below:<sup>14,22</sup>



where equation (IV) presents the RWGS reaction and equation (V) presents the FTS reaction, which most commonly is promoted by an iron catalyst at higher temperatures.<sup>22,23</sup>

## 2.2 Catalyst for the conversion

### 2.2.2 Zeotypes

A zeotype is an artificially produced material analogous to zeolites, which are porous materials with a crystal structure containing silica- and alumina-tetrahedra connected through shared oxygens atoms.<sup>24</sup> The structure creates a periodic arrangement of channels and cages where water and metal ions can be adsorbed without altering the structure.<sup>25</sup> These characteristics give rise to several industrial applications. In addition, it is possible to tailor such materials for a distinct application or modify existing ones to achieve for example better selectivity or efficiency.<sup>26</sup>

### 2.2.3 SAPO-34

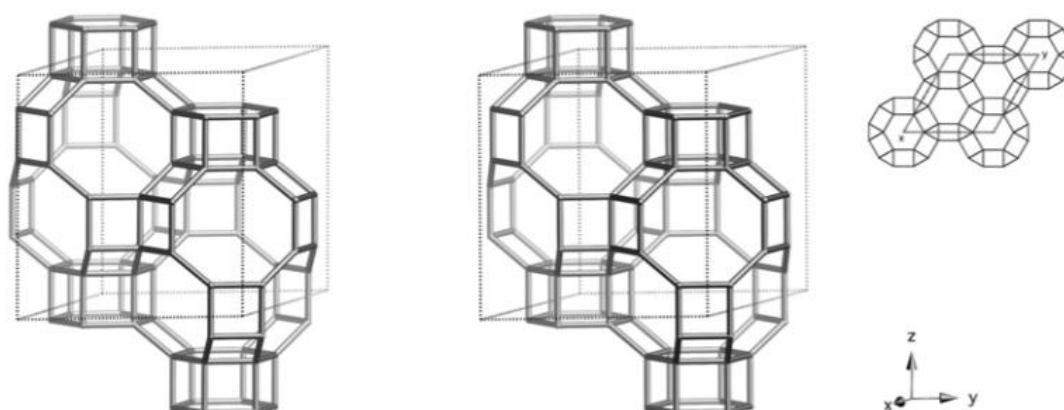


Figure 2: The CHA-framework of the SAPO-34 zeotype.<sup>25</sup>

SAPO-34 is a microporous silicoaluminophosphate (SAPO) molecular sieve with a 3D pore system of relatively small pores. The zeotype, with molecular formula:  $(\text{SiO}_2)_x(\text{Al}_2\text{O}_3)_y(\text{P}_2\text{O}_5)_z$ , consists of corner-sharing tetrahedra of Si, Al and P and has the framework of chabazite (CHA).<sup>25, 27</sup> The CHA framework has eight-membered ring (8MR) pore openings ( $3,8 \text{ \AA} * 3,8 \text{ \AA}$ ) into quite large cavities ( $8,35 \text{ \AA} * 8,35 \text{ \AA} * 8,35 \text{ \AA}$ ).<sup>25</sup> The smaller pore openings facilitates small linear molecules such as methanol and alkenes to diffuse through, and thereby induce a high selectivity.<sup>27</sup> On the other hand, larger intermediates are excluded and mass transport in the catalyst is reduced resulting in a quicker deactivation.<sup>28</sup>

In general, SAPOs are very useful as acidic catalysts.<sup>27, 28</sup> Both HZSM-5 and SAPO-34 has been commercially used for the MTO reaction because of their catalytic performance.<sup>14, 29</sup> SAPO-34 contains Brønsted acid-sites where methanol molecules can be reversibly adsorbed.

Consequently, SAPO-34 has showed molar selectivity towards the synthesis of lighter olefins ( $C_2=C_4$ ) of up to 96%, consistent with the shape selectivity of the 8MR pore openings.<sup>20, 30, 31</sup> The large cavities open up for the HCP pool, while the smaller pore openings only permits the smaller hydrocarbons to escape.<sup>22, 32</sup> The flexibility in the SAPO-system offers possibilities to design them into having desired catalytic properties.<sup>33</sup> Nevertheless, SAPO-34 does not show a strong enough acidity to activate and directly convert  $CO_2$  to light olefins.<sup>1, 19</sup>

#### 2.2.4 Activation of $CO_2$

One way to modify the catalytic properties of a zeotype is to add an active site by introducing metals or metal combinations. SAPO-34 can be modified with metals by incorporation, ion exchange or impregnation.<sup>21, 33</sup> Since  $CO_2$  is a low-energy molecule, the energy barrier for activation is very high.<sup>16, 34</sup> The required catalyst for the hydrogenation must activate both  $CO_2$  and  $H_2$ .<sup>16</sup> The activation process differs between the MeOH-, CO- or  $CH_4$ -based pathways.<sup>23, 35</sup> In short, studies show that  $CO_2$  binds to the active site in a bent configuration where one of C=O-bonds breaks and leaves CO and O adsorbed on the surface ready to react with  $H_2$ . Oxygen binding energy (OBE) is important for high catalytic activity and possibly also product selectivity, especially for the RWGS reaction.<sup>23</sup>

#### 2.2.5 Bifunctional catalyst

Traditionally the conversion via CO or MeOH requires two reactors and two catalysts, and thereby a higher operational cost. It is highly desirable to develop a bifunctional catalyst for direct conversion of  $CO_2$  to light olefins with high selectivity.<sup>36</sup> A direct conversion can alleviate the thermodynamic limitation of regular methanol synthesis by shifting the reaction equilibrium for the MeOH route.<sup>17</sup> Since the MTO process is faster than the hydrogenation of  $CO_2$ , the methanol produced in equation (II) will immediately react further and lead towards higher conversion of  $CO_2$ .<sup>22, 37</sup> On the other hand, the CO-route can achieve higher conversion if the FTS-step is fast enough to overcome the thermodynamic limitation of RWGS.<sup>23</sup>

Furthermore, the coupling (kinetic and thermodynamic) of the tandem reaction in both pathways enable a more efficient conversion to light olefins from  $CO_2$ .<sup>16</sup> A promising approach for such a tandem catalyst is metals or metal oxides over zeotypes.<sup>13</sup> As mentioned, metal oxides can activate  $CO_2$  for hydrogenation and SAPO-34 catalyses both CO and MeOH into hydrocarbons, in particular light olefins. In addition, methanol selectivity is higher and CO selectivity is lower for the tandem process via MeOH than the  $CO_2$  to MeOH reaction alone.

Since SAPO-34 does not show evident CO<sub>2</sub> conversion alone, it is reasonable to deduce that the reaction coupling is a driving mechanism. Thermodynamically the coupling is favourable since the hydrogenation of CO<sub>2</sub> is unfavourable while the MTO is favourable.<sup>16</sup>

### 2.3 Definition of parameters

The main parameters used to compare the different metal oxides or metal oxide combinations are CO<sub>2</sub> conversion and product selectivity, calculated as given below.

$$CO_2 \text{ conversion} = \frac{C_{product}}{C_{total}} * 100\%$$

$$Light \text{ olefin selectivity} = \frac{C_{light \text{ olefins}}}{C_{product}} * 100\%$$

## 3 Results and discussion

### 3.1 Literature and credibility

Generally, there is not a lot of literature on tandem catalysis for the direct conversion of CO<sub>2</sub> to light olefins. Even though there are a few research groups trying to achieve better selectivity and conversion, there are no apparent conflicts of interest or competition biases. Admittedly, this may be because no very efficient catalytic system has made a breakthrough, though the reaction coupling are thermodynamically favourable.<sup>12</sup> Among researchers, the methanol-based route is significantly more popular. Thus, there is noticeable more literature on this pathway than the CO-based.<sup>13</sup> The results are experimental and under realistic conditions, but not yet tested on a bigger industrial scale. When unspecified: conversion refers to conversion of CO<sub>2</sub>; selectivity refers to the selectivity of light olefins; and metal or metal combination abbreviations refers to the metal oxides supported on SAPO-34.

## 3.2 Results from different metal and metal combinations

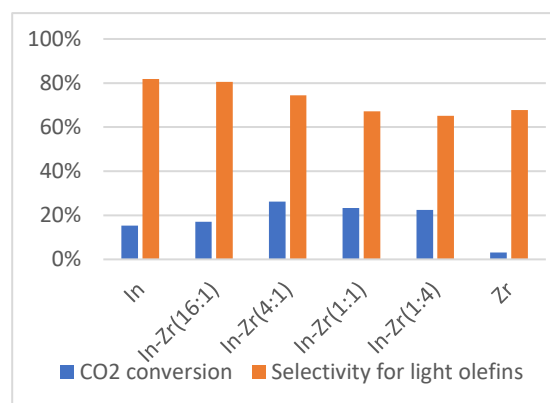
### ***In<sub>2</sub>O<sub>3</sub>/SAPO-34***

Numpilai *et al.* studied the effect of mass ratio of  $\text{In}_2\text{O}_3$  admixed with SAPO-34. The catalyst was prepared by precipitation from  $\text{In}(\text{NO}_3)_3$ . The final product dried overnight and calcined to obtain nano oxide particles. At optimal reaction conditions, the  $\text{CO}_2$  conversion was 34,6% and the light olefin selectivity was about 71%. The authors concluded that the interplay of active sites on both parts of the tandem catalyst are key factors for the catalytic behaviour.<sup>17</sup>

### ***In<sub>2</sub>O<sub>3</sub>-ZrO/SAPO-34***

Firstly, Gao *et al.* demonstrated that an In-Zr/SAPO-34 gave a selectivity of 80-90% and a  $\text{CO}_2$  conversion of ~20% with a catalytic stability of 50h run without apparent decay.<sup>12</sup> Later, the same group reported a  $\text{CO}_2$  conversion of more than 35% and a light olefin selectivity of 80% with an In-Zr composite oxide combined with SAPO-34. In-Zr oxides and SAPO-34 were pressed, crushed and sieved into different granule sizes of 250-400  $\mu\text{m}$ . Further, they were mixed together by vessel shaking (G) or in a mortar (M). Granule stacking gave the best selectivity for light olefins. The incorporation of Zr into  $\text{In}_2\text{O}_3$  improved the catalytic stability and lead to a slightly higher  $\text{CO}_2$  conversion. However, the selectivity decreased slightly from that of pure  $\text{In}_2\text{O}_3$ /SAPO-34.<sup>38</sup> Modifying the  $\text{In}_2\text{O}_3$  surface to increase the stability of intermediates in the  $\text{CH}_3\text{OH}$  formation suppressed the RWGS route and had a significant impact on the product distribution.<sup>22, 38</sup>

Additionally, Dang *et al.* presented a series of In-Zr/SAPO-34 catalysts with different atomic ratios of In:Zr. The results are illustrated in Figure 3. Similarly, they reported a  $\text{C}_2^-$ - $\text{C}_4^-$ -selectivity in the range of 65-80% and the  $\text{CO}_2$  conversion ranges from 15-27%. The mixed metal oxide catalyst was prepared by incorporating Zr into  $\text{In}_2\text{O}_3$ . Moreover, it was discovered that both  $\text{CO}_2$  and reaction intermediates were adsorbed stronger on the oxygen vacancy sites in vicinity of the dopant than in pure  $\text{In}_2\text{O}_3$ . As a result the ratio 4:1 for In:Zr was found ideal.<sup>36</sup> Introducing zirconium increased methanol selectivity for the  $\text{CO}_2$  conversion, and thereby made the MeOH-route more favourable from the CO-route. Even though the incorporation of Zr increased the formation of hydrocarbons, the selectivity for olefins decreased due to smaller pore sizes and greater average distances between the zeolite and metal-oxide.<sup>22, 36</sup>



**Figure 2:** The effect of atomic ratio of In:Zr in the Zr- $\text{In}_2\text{O}_3$ /SAPO-34 catalyst reported by Dang *et al.*<sup>36</sup>

### ***In<sub>2</sub>O<sub>3</sub>-ZnZrO<sub>x</sub>/SAPO-34***

Further Dang *et al.* later reported a light olefin selectivity as high as 85%, but with a lower CO<sub>2</sub> conversion of 17%.<sup>39</sup> The composite catalyst of In<sub>2</sub>O<sub>3</sub> supported on ZnZrO<sub>x</sub> was prepared by mechanically mixing with different crystal sized SAPO-34. As a result, CO<sub>2</sub> conversion of 17% and light olefin selectivity of 85% was achieved with larger pore size. On the other hand, pore structure and crystal size did not appear to influence the reaction equilibrium. The 1:1 mass ratio of metal oxide and zeolite gave the relatively best light olefin yield without increasing CO selectivity. Both CO<sub>2</sub> conversion and CO selectivity increased with higher content of In<sub>2</sub>O<sub>3</sub>/ZrO<sub>2</sub> due to decreasing pore size and subsequently shorter diffusion path from the surface to the acid sites.<sup>22, 39</sup>

### ***ZnZrO/SAPO-34***

Li *et al.* prepared a tandem catalyst by dispersing solid ZnZrO particles on Zn-modified SAPO-34 surface. The light olefin selectivity for the reaction was as high as 80%, but the CO<sub>2</sub> conversion was not higher than 12,6%. Compared to the hydrogenation of CO<sub>2</sub> on pure Zn-ZrO<sub>2</sub> catalyst the CO selectivity could be significantly suppressed and the methanol selectivity much higher. This indicates that the overall reaction is not a sum of the two partial reactions, but rather a coupling reaction which only is observed when the two components in the catalyst are in proximate contact. In addition, the tandem catalyst showed resistance when exposed to thermal and sulphur treatments, and this stability shows promising potential for industrial use.<sup>16</sup>

Wang *et al.* found that physically blended ZnO-ZrO<sub>2</sub> with SAPO-34 exhibited the best catalytic performance with a 70% selectivity for light olefins. The CO selectivity of 41% was significantly suppressed to 27% by electronic property tuning of the metal sites by H<sub>2</sub> reduction treatment. Hence, the study illustrated that hydrogen-reduced ZnO-ZrO<sub>2</sub>/SAPO-34 composite catalyst enhanced CO<sub>2</sub> conversion, selectivity for light olefins and reduced CO selectivity.<sup>34</sup>

### ***Cu-CeO<sub>2</sub>/SAPO-34***

Sedighi *et al.* has developed a CuCe/SAPO-34 hybrid catalyst for the direct conversion of olefins from CO<sub>2</sub>. The crystalline catalyst was synthesized by physically coating process. The outside surface of SAPO-34 powder was covered with Cu/CeO<sub>2</sub>. Response surface methodology (RSM) was used to find the optimal reaction conditions. Subsequently the CO<sub>2</sub> conversion of 15,23% and light olefin selectivity of 63,10% was obtained. The highest experimentally obtained olefin selectivity was 71,18%.<sup>37</sup>

### **(Ce-)CuZnZr@(Zn-)SAPO-34**

Chen *et al.* achieved a light olefin selectivity of 72% and a CO<sub>2</sub> conversion of 19,6% with the bifunctional core-shell catalyst of CZZ@Zn-SAPO-34 prepared by physical mixing. The modification of SAPO-34 with zinc reduced the acidity which subsequently led to a lower concentration of intermediate methanol and restrained secondary hydrogenation of olefins.<sup>40</sup>

Liu *et al.* modified CZZ/SAPO-34 with rare earth metals by the co-precipitation method. The samples modified by Y<sub>2</sub>O<sub>3</sub>, La<sub>2</sub>O<sub>3</sub> and Ce<sub>2</sub>O<sub>3</sub> showed good dispersion and higher specific surface area. Whereas the CO<sub>2</sub> conversion was 54-56% and the light olefin selectivity was 51% for the Ce-modified catalyst.<sup>41</sup> More interestingly, the CO<sub>2</sub> conversion was drastically higher than the regular CZZ/SAPO-34.

### **ZnGa<sub>2</sub>O<sub>4</sub>/SAPO-34 and ZnAl<sub>2</sub>O<sub>4</sub>/SAPO-34**

Liu *et al.* prepared a bifunctional catalyst where co-precipitated and spinel structured Zn-Ga mixed oxides was mortar-mixed with SAPO-34. The results were a light olefin selectivity of 86% and a CO<sub>2</sub> conversion of 13%. CO and CH<sub>4</sub> selectivity were 46% and 1%, respectively.<sup>42</sup> Later, the same group reported on the direct conversion of both CO and CO<sub>2</sub> over the tandem catalyst composed of SAPO-34 and different spinel binary metal oxide containing Mg, Al, Ga and Zn. The most promising appears to be the ones containing zinc. The ZnGa<sub>2</sub>O<sub>4</sub>/SAPO-34 and ZnAl<sub>2</sub>O<sub>4</sub>/SAPO-34 catalyst gave a CO<sub>2</sub> conversion of 13 and 15% and a light olefin selectivity of 86 and 87%, respectively.<sup>43</sup>

In comparison with gallium, aluminium increases alkane rather than alkene selectivity. Oxygen vacancies at the surface are responsible for the activation of CO<sub>2</sub> and chemisorption. Changes in Zn/Al ratios lead to changes in the Brønsted acid site densities and subsequently product selectivity.<sup>42, 43</sup> Yet the selectivity here was calculated on a molar carbon basis when excluding CO from the syngas. Therefore it is important to keep in mind that the presence of other reactants may have influenced the results when comparing catalysts.<sup>43</sup>

### **Fe<sub>2</sub>O<sub>3</sub>@KO<sub>2</sub>/ZrS/SAPO-34**

Ramirez *et al.* reported a CO<sub>2</sub> conversion of nearly 50% with a light olefin selectivity of 40-45%, which in terms of conversion outperform conventional bifunctional zeolite-based catalyst systems. These results were achieved with a novel coated ZrS/SAPO-34 catalyst which was prepared by incipient wetness impregnation and combined with Fe<sub>2</sub>O<sub>3</sub>@KO<sub>2</sub>. The authors propose an alternative reaction pathway for the direct conversion from CO<sub>2</sub> to light olefins with

the multifunctional catalyst  $\text{Fe}_2\text{O}_3@KO_2/\text{ZrS}/\text{SAPO-34}$ . The first two steps are the traditional RWGS- and FTS-reaction on the iron catalyst, while the third is the conversion of CO to light olefins on SAPO-34. Lastly, the cracking of heavier hydrocarbons to light olefins on the acid sites of ZrS which are boosted by water from the RWGS reaction. Particularly ZrS allows the cracking of heavier hydrocarbons produced on the iron catalyst. In addition to reporting a light olefin yield of 19,4% - which is the highest reported according to the authors - the selectivity for the undesired bi-products methane and CO is low.<sup>13</sup>

### 3.3 Comparison summary

**Table 1:** Reaction conditions, catalytic performance in terms of conversion and product selectivity for different bifunctional MeO/SAPO-34 catalysts for the direct conversion of  $\text{CO}_2$  to light olefins. The selectivity for methane and lower olefins is calculated from all hydrocarbons, while CO selectivity is based on total carbon from  $\text{CO}_2$  feed.

Catalyst	T [K]	P [MPa]	$\text{CO}_2$ Conversion [%]	$\text{Sel}_{\text{C}_2-\text{C}_4^=}$ [%]	$\text{Sel}_{\text{CO}}$ [%]	$\text{Sel}_{\text{CH}_4}$ [%]	Ref.
Zr- $\text{In}_2\text{O}_3$ /SAPO-34	673	1.5	20	~90	85	1.7	12
Zr- $\text{In}_2\text{O}_3$ /SAPO-34-M	673	3	35.5	80	80	4	38
$\text{In}_2\text{O}_3$ - $\text{ZrO}_2$ /SAPO-34	653	3	26.2	74.5	63.9	2.5	36
$\text{In}_2\text{O}_3$ - $\text{ZnZrO}_4$ /SAPO-34	653	3	17.0	85.0	54.0	1	39
$\text{In}_2\text{O}_3$ /SAPO-34	633	2.5	34.6	70.4	74	1-4	17
Cu-Ce $\text{O}_2$ /SAPO-34	669	2	13.2	61.8	57.1	3.2	37
CuZnZr@Zn-SAPO-34	673	2	19.6	60.5	58.6	14.6	40
Ce-CuZnZr@Zn-SAPO-34	673	3	54.6	51.1	13	13.9	41
Zn- $\text{ZrO}_2$ /Zn-SAPO-34	653	2	12.6	80.0	47	3	16
(Red)ZnO- $\text{ZrO}_2$ /SAPO-34	653	3	~17	70	41	~5	34
Zn- $\text{Ga}_2\text{O}_4$ /SAPO-34	643	3	13.0	86	46	1.0	42
Zn- $\text{Ga}_2\text{O}_4$ /SAPO-34	673	3	13	86	46	1.0	43
ZnAl $_2$ O $_4$ /SAPO-34	673	3	15	87	49	0.7	43
$\text{Fe}_2\text{O}_3@KO_2/\text{ZrS}/\text{SAPO-34}$	648	3	49	48	13	~6	13

The bifunctional metal supported catalysts with reaction temperature and pressure,  $\text{CO}_2$  conversion and product selectivity for  $\text{C}_2^=-\text{C}_4^=$ , CO and  $\text{CH}_4$  are presented in Table 1.



## Metals for CO<sub>2</sub> conversion

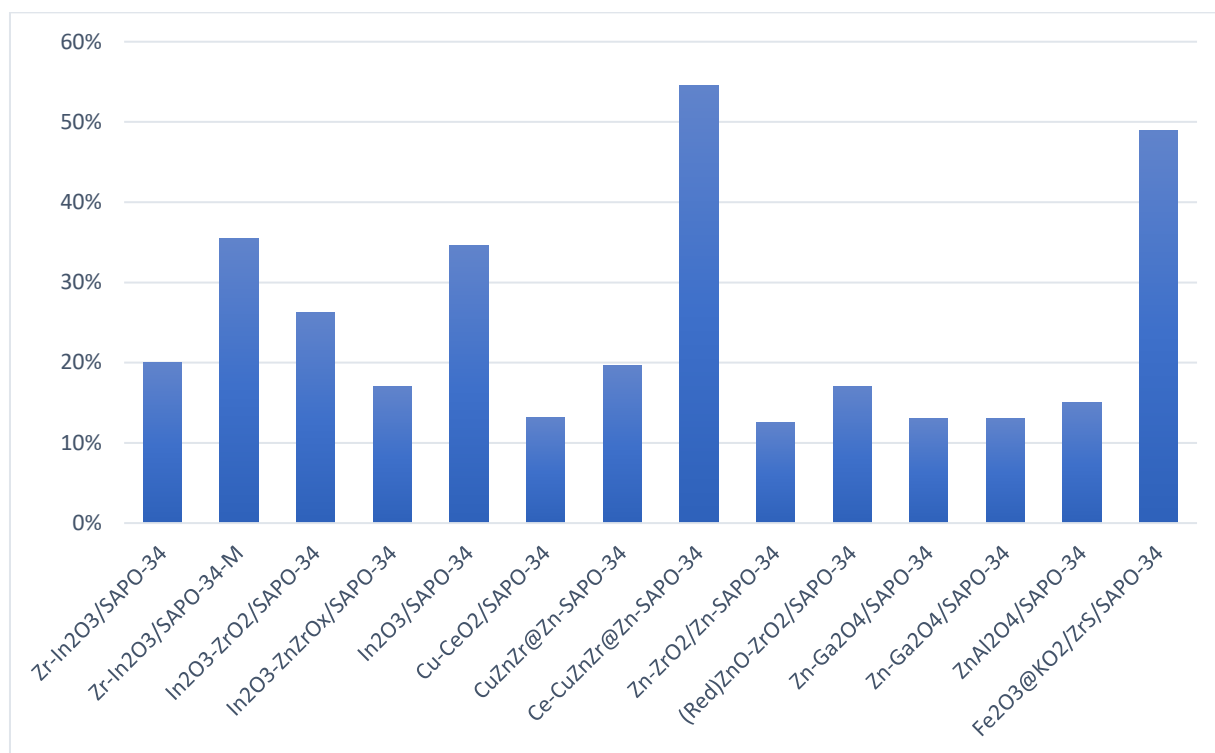
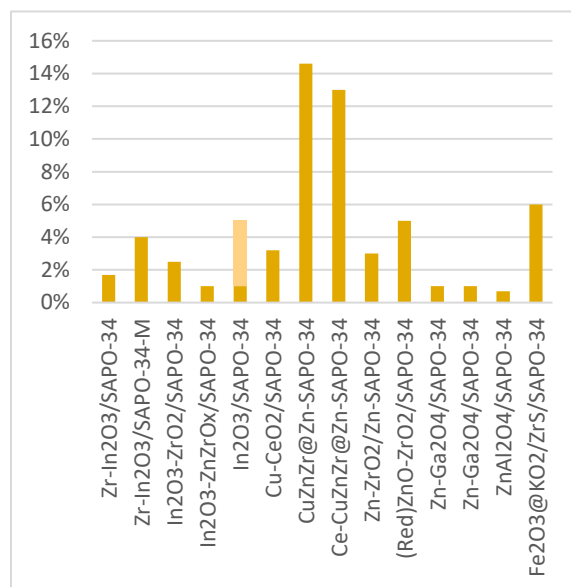


Figure 3: CO<sub>2</sub> conversion for different metal oxide combinations supported on SAPO-34. Data from Table 1.

Generally the incorporation of metals in SAPO-34 increased the acid site concentration.<sup>44</sup> The introduction of metals in SAPO-34 for the MTO-reaction has been thoroughly studied compared to that of the direct conversion from CO<sub>2</sub>. Despite this, there is no reason that the findings for the MTO-reaction does not apply for the direct conversion as well. With this as a bias, metal incorporation adjusted the micropore size and acidity and improved catalyst lifetime and light olefin selectivity.<sup>45</sup>

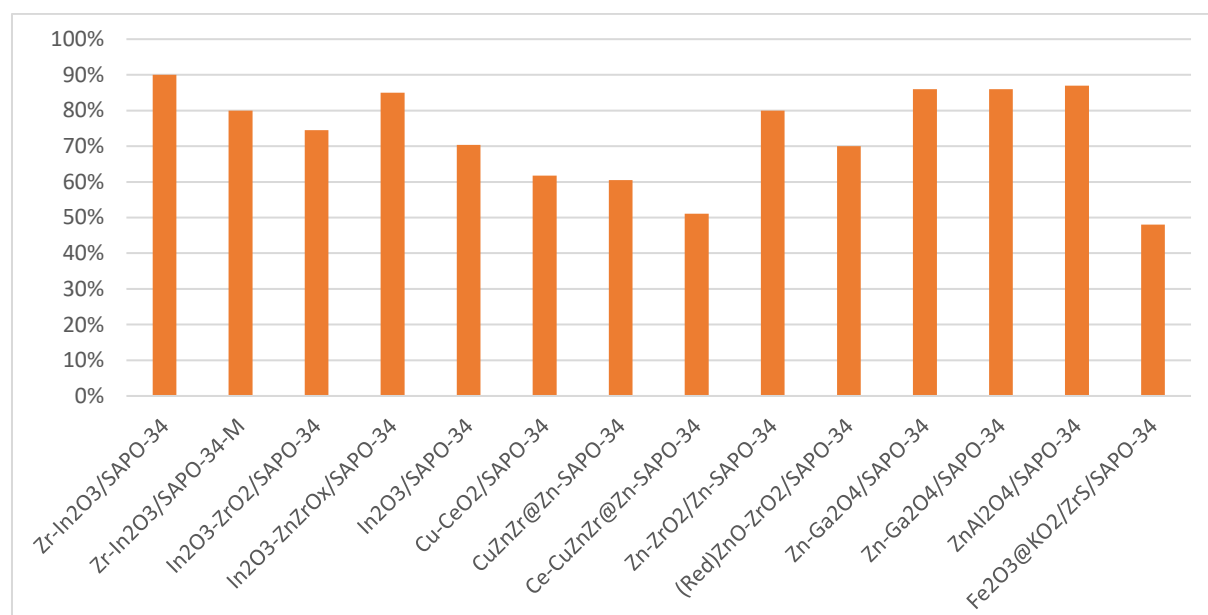
Firstly, it is the metal indium and the Zr-In, Ce-Cu-Zn-Zr and Fe-K-Zr-S metal combinations which gave the highest CO<sub>2</sub> conversions. Among these In-Zr and In achieves lower conversion than the other two, but on the other hand significantly higher selectivity. Following this, it is natural to conclude that zirconium is good for CO<sub>2</sub> conversion. Dang *et al.* demonstrated that a given amount of zirconium can create more oxygen vacancy sites, stabilize intermediates, and prevent sintering of active particles. This is subsequently leading to enhanced catalytic activity and stability at a relatively high temperature.<sup>36</sup> Likewise indium can be a good metal.

Secondly, Ce-Cu-Zn-Zr and Fe-K-Zr-S stands out with significantly higher CO<sub>2</sub> conversions of 54,6 and 49%, respectively. The results indicate promising outlooks for the mentioned catalysts. However, the light olefin selectivity is the lowest among all the discussed catalysts in this paper. Subsequently, methane and other biproducts have higher selectivity, illustrated for methane in Figure 4. Methane is a very powerful greenhouse gas and an unwanted biproduct.



**Figure 4:** Methane selectivity for the compared tandem catalysts. Data from Table 1.

### Metals for light olefin selectivity



**Figure 4:** Light olefin selectivity for different metal oxide combinations supported on SAPO-34. Data from Table 1.

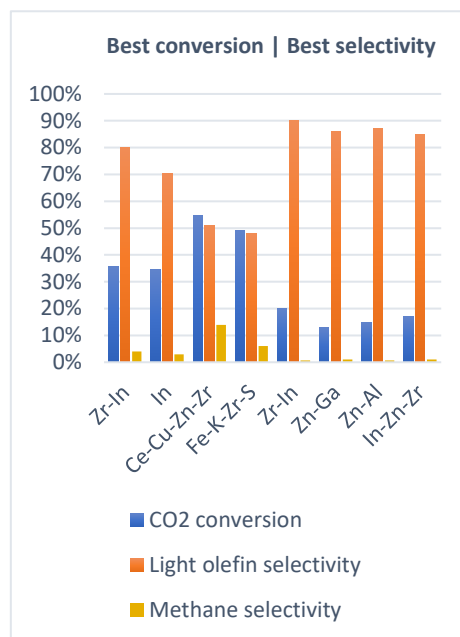
On the other hand, the Zr-In, Zn-Ga, Zn-Al, and Zn-Zr-In combinations achieved the highest light olefin selectivity ranging from 85-90% among all hydrocarbon products. From this it can be deduced that introducing zinc in the catalyst can influence the selectivity positively. The -Zn-O- domains have been found to be responsible for activating H<sub>2</sub> and generating H<sup>\*</sup>-species that again binds with activated CO<sub>2</sub>.<sup>22, 43</sup> Particularly the best performing ones have very low

selectivity for unwanted biproducts. Correspondingly the methane selectivity among these four catalysts ranges as low as 0,7-1%.

### *Metals for conversion and selectivity*

In comparison, the catalysts containing indium, zinc and/or zirconium appears to give the best results for CO<sub>2</sub> conversion and light olefin selectivity. The best catalysts for conversion and selectivity are presented on the left and right in Figure 5, respectively. Comparing the biproducts, the ones with highest selectivity also have the lowest methane selectivity. On the contrary, the CO<sub>2</sub> conversion is 20% or below. Among the ones with highest conversion, the In and Zr-In catalyst have lower methane and higher olefin selectivity than the other two. However, the novel catalysts Ce-CZZ@Zn-SAPO-34 and Fe<sub>2</sub>O<sub>3</sub>@KO<sub>2</sub>/ZrS/SAPO-34 achieve the highest yields for light olefins and should be more thoroughly studied.

Overall, the introduction of indium, zinc and zirconium appears to be good for conversion and selectivity. Although, it appears that a trade-off must be made between the two parameters. On one hand the goal is to convert as much CO<sub>2</sub> as possible, while on the other hand, it may be better to have unconverted reactants that can be used again than unwanted products. In that case, the Ce-Cu-Zn-Zr and Fe-K-Zr-S are less interesting due to the lower light olefin selectivity. In conclusion, the In-Zr and In supported on SAPO-34 exhibits the best conversion and selectivity. Chiefly the introduction of zinc appears to elevate the selectivity, but often lower conversion.



**Figure 5:** The four best performing catalysts in terms of conversion to the left and selectivity to the right compared in regards of CO<sub>2</sub> conversion and selectivity for light olefins and CH<sub>4</sub>. Data from Table 1.

Admittedly, when the highest yields are under 30%, the question if this is a promising outlook for CO<sub>2</sub> conversion must be raised. Still, there is ongoing progress for finding a metal combination which achieves high olefin selectivity and higher CO<sub>2</sub> conversion. Personally, I find the gain of designing such a catalyst big enough for further research on the topic necessary.

## *Other impact factors*

All the discussed catalysts have exhibited the best catalytic activity in the temperature range of 643-673K. Although it has an impact, the 30-degree variance is not significant. Similarly, the pressure ranges from 2-3 MPa. The trend for most catalysts appears to be that the selectivity for light olefins is proportional to increasing pressure. Higher pressure and temperature require more energy and a higher cost. Thus, the increase in selectivity must be compared to the increase in economic and energy cost. Space velocity has not been given focus in this paper, but the trend appears to be like the pressure trend. Also, the mass ratios play a critical role. There are differences in methodology, which of course has an impact. The control of oxygen vacancies and the integration manner are crucial for the reaction.<sup>38</sup> All the mentioned conditions are important for the conversion, but out of the scope of this project.

### *3.4 Challenges for industrial application*

Undoubtedly, the main obstacle for the direct conversion is the difference in optimal temperature. Zeotypes are not active for the necessary C-C coupling in a lower temperature range where several metal oxides show excellent activity for methanol synthesis. On the other hand, the RWGS favours higher temperatures similar to the methanol synthesis.<sup>22, 42</sup> Numerous catalysts has been widely investigated for both routes. The MeOH shows remarkably higher selectivity for light olefins, while the CO-based usually achieves higher CO<sub>2</sub> conversion.<sup>13, 37</sup>

Another challenge is mitigating the undesired side reactions, mainly the formation of CO and methane. Alternations which decreased methane selectivity were reported, but often at the expense of lower CO<sub>2</sub> conversion.<sup>39</sup> The iron containing ZrS/SAPO-34 catalyst is interesting for further research with exceptionally high conversion, and only a slightly higher methane selectivity than most of the compared catalysts. Furthermore, deactivation is a challenge. Water formation can cause deactivation of both metal oxide and zeotype, but also prevents coke deposition and pore blockage in SAPO-34.<sup>21, 22, 46</sup> The metal modification prolongs the catalyst lifetime, and several of the discussed catalysts show little to no deactivation even after 150h on stream.<sup>38</sup> The production of SAPO-34 for MTO catalysis usually requires OSDA which is both expensive and environmentally unfriendly.<sup>27, 28</sup>

## 4 Conclusion

Generally, the MeOH route is more popular among researchers due to higher selectivity for light olefins in the direct conversion from CO<sub>2</sub>. Conversely, the CO-route often achieves higher conversion than the MeOH-route. The tandem catalyst suppresses the RWGS by converting intermediates into lower olefins and shifting the equilibrium. In this bachelor project 14 different metal or metal combinations supported on SAPO-34 have been compared and discussed in terms of conversion and selectivity. It was found that zinc is important for hydrogen activation which subsequently led to higher selectivity. In addition zinc, indium and zirconium were components in many of the best performing catalysts for both conversion and selectivity. Gao *et al.* prepared a catalyst with the combination of indium and zirconium and achieved a selectivity as high as 90% and a conversion of approximately 20% with low selectivity for unwanted biproducts. Furthermore, the Ce-CZZ and FeK/ZrS catalysts exhibited remarkably high conversion of CO<sub>2</sub>. Although, the amount of unwanted biproducts were significantly higher than of the In-Zr catalyst.

Overall, introducing metals appears to prolong the catalyst lifetime and enhance catalytic activity. There are numerous other factors that influence the reaction such as temperature, pressure, mass ratios, preparation and integration methods, but their effect is out of the scope of this project. Although the direct conversion is a very promising route, there are many obstacles to overcome before the catalysts designed for this reaction can be used in the industry. Some of the current limitations include different optimal temperatures for the reaction steps, deactivation and unwanted biproducts. However, the carbon footprint and cost of both conversion and catalyst production must be taken into consideration, in addition to the environmental impact of biproducts.

Nevertheless, a double environmental gain can be obtained if one is able to successfully design a bifunctional catalyst that can achieve both high CO<sub>2</sub> conversion and high light olefin selectivity. For this to happen, future research is needed. As the MTO-process is successfully industrialized, it is probably the CO<sub>2</sub> to methanol-step which requires further study. All the reported studies show little to no methanol product. From this it can be deduced that all methanol is converted. If one can find a metal or metal combination oxide which could increase the synthesis of methanol at a temperature which is optimal for the MTO reaction, then the direct conversion can be applied on an industrial scale and make a CCU breakthrough.

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