

# 学位論文の要旨

学位論文題目： Catalyst development for carbon neutral liquid fuel production from carbon dioxide（二酸化炭素からのカーボンニュートラル液体燃料製造用触媒の開発）

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In the past decades, severe climate deterioration has been induced by massive emissions of carbon dioxide (CO<sub>2</sub>). Trapping, storing and reutilizing CO<sub>2</sub> emissions from industry is needed urgently to achieve global carbon neutrality. With the development of industrialization, cars, trucks and airplanes, liquid fuel is indispensable in human life. Converting CO<sub>2</sub> into carbon neutral liquid fuel (C<sub>5+</sub> hydrocarbons) is an essential way to relieve rapid consumption of fossil fuels and high demands for carbon-based energy resources at the same time. However, the low CO<sub>2</sub> conversion of photocatalysis and the short chain of the products from electrocatalysis limited their large-scale utilization. Compared to photocatalysis and electrocatalysis, which are still in the development stage, thermocatalytic hydrogenation of CO<sub>2</sub> has been widely studied and commercialized due to the ultra-high efficiency and well controllability of target products.

Generally, thermocatalytic hydrogenation of CO<sub>2</sub> generally occurs via a methanol-mediated route (MeOH route) or a CO<sub>2</sub> modified Fischer-Tropsch synthesis (CO<sub>2</sub>-FTS) mechanism. For the MeOH route, CO<sub>2</sub> is first hydrogenated to methanol (MeOH). The MeOH then is converted to hydrocarbons via some dehydration and/or coupling reactions. Unfortunately, the catalysts for the MeOH route are expensive and the reaction process is complicated. In the case of CO<sub>2</sub>-FTS route, CO<sub>2</sub> is first reduced to carbon monoxide (CO) by reverse water gas shift (RWGS) reaction through two widely recognized mechanisms. The first mechanism is a redox mechanism, in which CO<sub>2</sub> is reduced by catalysts to form CO and the catalysts subsequently be reduced to produce water (H<sub>2</sub>O). The second one is a formate-intermediate mechanism, in which CO<sub>2</sub> reacts

with hydrogen ( $H_2$ ) directly to form formate, followed by further hydrogenation to produce CO and  $H_2O$ . After the RWGS reaction, hydrocarbons can be produced by FTS reaction. Similarly, two possible mechanisms, including direct CO dissociation mechanism and H-assisted CO dissociation mechanism, for the FTS reaction are widely reported. In the direct CO dissociation mechanism, CO is first adsorbed and dissociated to \*C and \*O on catalyst. Then, \*CH<sub>x</sub> intermediate species are formed by the reaction of dissociated surface carbon with adsorbed surface hydrogen atoms. Simultaneously, dissociated \*O is removed by reacting with adsorbed \*H and \*CO to produce  $H_2O$  and  $CO_2$ , respectively. Finally, \*CH<sub>x</sub> intermediate species are further coupled and/or hydrogenated into hydrocarbons. As for the H-assisted CO dissociation mechanism, FTS reaction occurs via the following elementary steps: (1) \*CO reacts with \*H to form formyl (\*HCO) intermediates and subsequently be further hydrogenated to hydroxymethylene (\*HCOH) intermediates; (2) \*HCOH is dissociated to \*OH and \*CH that ultimately form  $H_2O$  and monomers (\*CH<sub>2</sub>), respectively; (3) coupling, hydrogenation and dehydrogenation of \*CH<sub>2</sub> into paraffins and olefins as products.

As a big challenge in  $CO_2$ -FTS, researchers have been struggling in adjusting the products distribution for a high selectivity of target products. However,  $CO_2$  hydrogenation through the  $CO_2$ -FTS route generally exhibits a broad spectrum of products that can be described as an Anderson-Schulz-Flory (ASF) model. The classical ASF model limits the maximum selectivities of hydrocarbons. For example, the selectivities of  $C_2$ - $C_4$  hydrocarbons, gasoline ( $C_5$ - $C_{11}$ ), jet fuel ( $C_8$ - $C_{16}$ ) and diesel ( $C_{10}$ - $C_{20}$ ) are restricted by 58 %, 48 %, 41 % and 40 %, respectively. Therefore, my work focuses on developing novel catalysts to break the limitation of the ASF model and thus increase the yield of carbon neutral liquid fuel.

According to the reaction process of  $CO_2$ -FTS, both RWGS reaction and FTS reaction play important roles in  $CO_2$  hydrogenation. In chapter 1, multi-promoters, including potassium, manganese and titanium, were incorporated into iron catalyst for improving  $CO_2$  hydrogenation and the influences of each promoter were investigated in detail. Besides, the content of each component was optimized to achieve a well-matching tandem catalysis performance between RWGS reaction and FTS reaction.

The results showed that the introduction of potassium could improve the RWGS reaction and chain growth capacity by utilizing abundant oxygen vacancy and strong competitive adsorption. With the further addition of manganese, more active carbides sites with benign dispersion were detected owing to the strong interaction between manganese and iron species. When titanium was added, the catalytic performance of the catalyst was improved by stronger CO<sub>2</sub> adsorption capacity and longer resistance time of reactants. Therefore, the well-matching catalysis between RWGS and FTS was achieved on the corresponding K<sub>3</sub>/FeMn<sub>10</sub>Ti<sub>20</sub> catalyst, achieving C<sub>5+</sub> yield as high as 1282.7 g<sub>fuel</sub> kg<sub>cat</sub><sup>-1</sup> h<sup>-1</sup> at a CO<sub>2</sub> conversion of 44.9 % and maintaining a rather low by-products selectivity (9.6 % for CO, 12.8 % for CH<sub>4</sub>).

Recently, the combination of CO<sub>2</sub>-FTS catalysts with solid acidic catalysts, especially zeolites are extensively investigated for optimizing the products selectivity in CO<sub>2</sub> hydrogenation. In chapter 2, a bifunctional catalyst composed of K-Fe/C and ZSM-5 zeolite was developed and it was found to be efficiency in the production of carbon neutral liquid fuel via simply tuning the microenvironment properties of ZSM-5 zeolite. The catalysts were characterized by various methods, such as Brunauer-Emmett-Teller (BET), transmission electron microscopy (TEM), X-ray diffractometer (XRD), temperature programmed desorption (NH<sub>3</sub>-TPD), and X-ray photoelectron spectroscopy (XPS). K-Fe/C catalyst was mainly responsible for the formation of olefins, while ZSM-5 catalyst was mainly responsible for olefin secondary reaction, such as aromatization, isomerization, and cracking reaction. Surface acid properties of ZSM-5 were well regulated through different ion-exchange strategies, in which the strong surface acid properties of ZSM-5 were eliminated with the utilization of K<sup>+</sup>-ion exchange strategy and then it presented a high C<sub>5+</sub> selectivity by suppressing the light saturated hydrocarbons formation.

Herein, two highly efficient catalysts were rationally designed and successfully synthesized for the production of carbon neutral liquid fuel from CO<sub>2</sub> hydrogenation via the CO<sub>2</sub>-FTS route. This work provides new insights into the realization of global carbon neutrality by reutilizing of CO<sub>2</sub>.

## 【審査結果要旨】

(学位申請者 趙 恒)

当学位審査委員会は本論文を詳細に審査し、かつ論文審査会を令和5年1月18日公開で開催し、その発表と質疑応答について審査した。その審査結果を下記のようにまとめる。

二酸化炭素(CO<sub>2</sub>)と水素から低炭素液体炭化水素燃料の製造は常に低温ではCO<sub>2</sub>反応しない、高温なら炭素連鎖成長せず、ガス状炭化水素が過剰に生成し、C5+液体炭化水素の選択性が低いというジレンマに直面している。主に二章から構成される本論文は、この問題を解決するために新規な触媒を開発し、転化率と選択率共に高い触媒を開発した。

第1章で反応シーケンスを詳細に分析し、CO<sub>2</sub>と水素から一酸化炭素を生成するRWGS反応と後継する一酸化炭素のin situ水素化(FT合成)反応の速度バランスを調節し、マンガンおよびカリウム助触媒を添加し、RWGS反応の触媒サイトである鉄酸化物およびFT合成の触媒サイトである鉄炭化物の量を制御することによって、一酸化炭素の副生を大幅に抑制し、C5+液体炭化水素の選択性を大幅に向上させた。同時に表面水酸基豊富な新規チタン酸化物メソ体触媒担体を投入し、上記鉄-マンガン-カリウムの酸化物/炭化物を安定に高分散させ、カリウムの塩基性を増強させることもあって、比較的低温でも高いCO<sub>2</sub>転化活性を実現した。まとめられたK<sub>3</sub>/FeMn<sub>10</sub>Ti<sub>20</sub>触媒では転化率(45%)と選択率(51)が同時に高く、C5+液体炭化水素空時収率は1283g-oil/kg-cat.hと非常に高いレベルまで実現できた。触媒の反応メカニズムも詳細に解析した。

第2章では、上記第一章である直鎖炭化水素を一段でガソリンなどの分岐炭化水素まで合成することを目指し、CO<sub>2</sub>と水素から、新規鉄系触媒と各種酸性ゼオライト触媒の混合触媒を用いて、一段でC5+分岐液体炭化水素に成功した。カリウム修飾ZSM-5ゼオライト触媒およびカリウム-鉄-炭素系触媒からなるハイブリッド触媒を用いると、70%以上の選択率でC5+分岐液体炭化水素を、CO<sub>2</sub>と水素から直接合成できた。各種分光スペクトルを用いて、触媒の反応メカニズムも詳細に解析した。

論文の最初と最後に緒言およびまとめもある。

上記の内容は国際学術専門誌に原著論文2報として掲載された。

当審査委員会は以上を総合的に判断した結果、審査論文は、エネルギー、環境、無機および有機化学合成、触媒化学諸分野において、学術的価値のある知見を与えたと判断し、博士の学位論文として十分な価値を有し、博士の学位を授与するに値する論文であると判定した。