催化裂化干气综合利用新流程探讨

——乙烷脱氢与CO_2加氢反应—反应耦合制乙烯

A Study on a New Process for the Comprehensive Utilization of FCC Dry Gas

—The Coupling Reactions of Ethane Dehydrogenation and CO_2 Hydrogenation for the Production of Ethylene

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作者简介

徐龙伢，理学博士，研究员，中共党员，1964年出生于江苏省，1988年硕士毕业分配到中国科学院大连化学物理研究所，1996年晋升研究员，1998年取得博士学位，获1998年中国科学院院长奖学金特别奖、1998年中国科技发展基金会侯祥麟基金奖和1998年辽宁省青年科技一等奖，享受政府特殊津贴。由于他所取得的成果及在国内外的影响，被美国现代科学协会聘请为国际会员，并于1999年应日本政府高薪聘请赴日本北海道大学作访问教授，取得很好的成果后，谢绝日本教授挽留，于2000年6月回国继续从事科研。他以第一排名取得的国际先进水平鉴定成果2项，以第一作者在国内外核心科技刊物上发表论文60余篇，申请专利近30项，授权专利10多项（其中一项获美国、日本、欧洲、澳大利亚等10个国家授权），由他作为主要工作者开发的催化裂化干气制乙苯技术分别在抚顺、大庆和大连石化公司实现了工业化生产，产生了显著的经济效益和社会效益。

导师简介

林励吾，1929年10月14日生于广东汕头，1952年毕业于浙江大学化工系，1952年到中国科学院大连化学物理研究所工作，1965年晋升为副研究员，1978年晋升为研究员，1989年在美国西北大学化学系任访问教授半年，1993年当选为中国科学院院士，现任大连化学物理研究所学术委员会主任、催化国家重点实验室学术委员会主任、催化学报主编。

他在20世纪60年代研制出加氢异构裂化催化剂及工艺，缓解了当时国内航空煤油短缺的严重问题。70年代与石油部合作研制出我国第一代多金属重整催化剂。80年代研制出长链烷烃脱氢催化剂。这些催化剂都在工业生产中发挥着重要作用，取得了重大的经济效益和社会效益。在基础研究方面，他和学生们长期从事金属催化研究，在催化剂制备科学、烃类转化、C_1化学及甲烷转化方面提出了创新性的概念，先后在国内外刊物发表论文200多篇。先后培养博士研究生22名和硕士研究生10名，被评为中国科学院优秀研究生导师。

内 容 提 要

本论文结合催化裂化干气综合利用生产乙烯的应用背景，进行新催化剂、新过程、新流程的开拓性研究，提出的乙烷脱氢与 CO_2 加氢反应一反应耦合制乙烯的新过程，具有很强的创新性及实用意义。其特点是通过 CO_2 与乙烷脱氢中产生的 H_2 和碳耦合反应生成 CO 以提高乙烯产率及消除积炭，从而大大提高乙烷制乙烯的转化率、选择性和催化剂的稳定性。本论文在进行催化剂的研制及开发的同时进行深入的基础研究，从热力学阐明反应耦合的可能性，据此对催化剂组分进行调整以提高耦合反应的效率，从而取得了优化组合的结果；从积炭动力学的结果证明，$CO_2 + C = 2CO$ 的逆歧化反应是使催化剂积炭消除的有效手段；通过动力学试验优化了反应条件，这些基础研究及所取得的结果为催化剂及工艺进一步放大试验奠定了基础。

摘　要

低碳烷烃的活化和利用一直是化学家所重视的课题，本文研究了乙烷脱氢与 CO_2 加氢反应—反应耦合制乙烯新过程及新催化剂，并取得了具有突破性的结果，引起学术界和企业界的兴趣和重视。

乙烯是重要的最基本有机原料。迄今为止，乙烯的来源基本上是依靠石油系原料裂解制得，如传统的高温水蒸气裂解制乙烯的工艺过程是将油田气、炼厂气中的乙烷等低碳烷烃转化为乙烯，过程裂解温度高，耗用大量水蒸气，过程能耗很大，裂解产品组成复杂，分离净化困难，只适合大规模生产。面临石油资源的日益短缺及对乙烯供不应求矛盾的日益尖锐，化学家们一直在寻找生产乙烯的新技术路线，催化工作者进行了大量的研究以期通过催化乙烷脱氢或氧化脱氢的方法从乙烷生产乙烯，但迄今尚没有催化活性和选择性都令人满意的结果。本文通过 CO_2 加氢与乙烷脱氢耦合，研究开发出使乙烷在较低温度下高转化率、高选择性脱氢生成乙烯的新催化剂，有可能为利用炼厂气、油田气中的乙烷生产乙烯提供一条新的技术路线，同时可利用 CO_2 副产合成气或氢气。

首先分析乙烷蒸气裂解的热力学，表明裂解乙烷制乙烯的反应温度应超过 1120 K，各副反应进行的可能性比乙烷脱氢制乙烯反应要大得多，尤其是生炭生焦反应的热力学可能性极大。裂解温度超过 1380 K 时，乙烯转化为乙炔的反应在热力学上极为有利，表明裂解乙烷脱氢制乙烯的最佳反应温度为 1120～1380 K。

分析 $C_2H_6 \xrightarrow[-H_2]{k_1} C_2H_4 \xrightarrow[-H_2]{k_4} C_2H_2 \xrightarrow[-H_2]{k_5} C$ 过程的动力学。为提高乙烯产率，反应时间越短越好，反应温度越高越好，综合工艺方面的问题全面考虑，采用的反应温度大约在 850～900℃，反应时间

在0.1～0.5 s左右，保持乙烷转化率在60%左右最合适。

对乙烷氧化脱氢生产乙烯的研究进展进行分析，总结了乙烷在碱(碱土)金属氧化物上的氧化脱氢、乙烷在稀土元素氧化物上的氧化脱氢、乙烷在担载的钒催化剂上的氧化脱氢制乙烯研究的最新进展及反应机理。

提出了乙烷脱氢与CO_2加氢反应—反应耦合高转化率、高选择性制乙烯新反应过程，分析了该过程的特点及优越性：催化剂表面CO_2参与乙烷脱氢反应转化为CO，明显降低传统乙烷水蒸气裂解反应温度(大于50 ℃)，提高乙烷转化率及乙烯选择性，催化剂表面CO_2与焦炭反应生产CO，减少乙烷裂解过程中积焦，延长操作周期。

对乙烷脱氢与CO_2加氢反应—反应耦合制乙烯过程所包括的主要反应进行热力学分析：乙烷裂解制乙烯反应、逆水煤气变换反应、乙烷加氢裂解生成甲烷反应、乙烷与CO_2重整制合成气反应等，总结出乙烷与CO_2反应综合通式：

$$xC_2H_6 + yCO_2 \rightleftharpoons zC_2H_4 + wCO + pCH_4 + qH_2O + rH_2$$

为提高乙烯选择性，还必须抑制甲烷的生成。当然，不同性能的催化剂将使反应朝着不同的反应途径进行，其中，开发研究CO_2与乙烷反应制乙烯的反应催化剂具有一定的难度。由于乙烷与CO_2反应制乙烯需要较高反应温度(780～800 ℃)，反应过程中将发生复杂的副反应，因而其关键是开发新型催化剂，要求催化剂具有很高活性和乙烯选择性，抑制热力学允许的副反应发生。

通过理论分析和实验结果，证明了在催化剂表面乙烷与CO_2反应制乙烯过程主要是由乙烷脱氢与CO_2加氢两个反应耦合而成：

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2, CO_2 + H_2 \rightleftharpoons CO + H_2O$$

即乙烷脱氢生成乙烯和氢气，氢气再与CO_2发生逆变换反应生成CO和水，促使乙烷不断脱氢生成乙烯，提高乙烷转化率和乙烯选

择性。

催化剂表面 CO_2 与乙烷反应制合成气的过程则是重整过程：

$$C_2H_6 + 2CO_2 \rightleftharpoons 4CO + 3H_2$$

由于催化剂性能的差异，乙烷与 CO_2 反应过程不同，反应产物及分布也不同，通过研制不同反应性能的催化剂，控制 CO_2 与乙烷的反应途径。

首先研究了乙烷与 CO_2 重整制合成气反应的 Ni/Si－2 催化剂，所研制的 K－La－Ni/Si－2 催化剂具有很好的反应性能，La_2O_3 和 K_2O 助剂是 Ni/Si－2 催化剂的重要助剂，能明显提高合成气选择性和收率。

研制的 Cr/Si－2 催化剂具有较好的催化乙烷与 CO_2 制乙烯反应的性能，添加 Mn、Ni 氧化物和 K_2O 助剂可抑制乙烷裂解成甲烷反应，提高乙烯选择性；对于乙烷与 CO_2 制乙烯反应，Fe/Si－2 催化剂显示出比 Cr/Si－2 催化剂更好的性能，添加 Mn 氧化物可提高 Fe/Si－2 催化剂活性，K_2O 助剂可同时提高催化剂活性和乙烯选择性，抑制乙烷裂解生成甲烷。所研制的 K－Fe－Mn/Si－2 催化剂，乙烷转化率达 69%、乙烯选择性达 93%、乙烯单程收率达 57%。提高反应原料气中 CO_2/C_2H_6 摩尔比，有利于提高 Cr/Si－2 和 Fe/Si－2 催化剂的乙烷转化率和乙烯选择性。添加水蒸气有利于减少催化剂在反应过程中的积炭。

Cr/Si－2 催化剂和 Fe/Si－2 催化剂上 CO_2 加氢生成 CO 和 H_2O 反应与 CO_2 和乙烷制乙烯反应之间都存在平行关系，具有较高 CO_2 加氢反应性能的催化剂，同样具有较高的乙烷与 CO_2 反应制乙烯的催化活性。通过催化剂 CO_2－TPD、CO_2/H_2－TPSR、CO/H_2－TPSR 及 CO_2/H_2－脉冲反应等研究表明，MnO 和 K_2O 助剂可增强 Fe/Si－2 催化剂对 CO_2 的吸附量和吸附能力，促使 CO_2 加氢转化为 CO 和 H_2O，因而，K－Fe－Mn/Si－2 催化剂表现出很好的催化反应性能。

通过对炼厂干气中稀甲烷和乙烷同时与 CO_2 重整制合成气反应催化剂性能考察，表明 K－La－Ni/Si－2 催化剂表现出较好的稀甲烷和乙烷与 CO_2 重整制合成气反应性能，K_2O 和 La_2O_3 助剂可提高 Ni/Si－2 催化剂甲烷/乙烷和 CO_2 转化率及合成气收率；通过对炼厂干气中乙烷与 CO_2 制乙烯反应催化剂性能考察，表明 K－Fe－Mn/Si－2 催化剂比 K－Cr－Mn－Ni/Si－2 催化剂具有更好的催化活性、乙烯选择性及稳定性，在 100 mL 装置上放大制备 K－Fe－Mn/Si－2 催化剂，达到乙烷转化率 66%、乙烯选择性 93%、乙烯收率 55% 的好结果，催化剂具有耐硫等杂质能力；催化剂合适操作条件：780～800 ℃，0.1～0.7 MPa，800～1200 h^{-1}。

研究了 K－La－Ni/Si－2 和 K－Fe－Mn/Si－2 及 Cr/Si－2 系列催化剂的再生性能，表明 K－La－Ni/Si－2 和 K－Fe－Mn/Si－2 催化剂具有很好的再生性能，而 Cr/Si－2 系列催化剂的再生性能较差；反应过程中 9Fe9Mn/Si－2 催化剂积炭量最低，Mn 对 Fe/Si－2 催化剂表面积炭有明显的抑制作用。根据乙烷与 CO_2 反应过程中催化剂积炭动力学参数的计算，积炭速率方程可表示如下：

9Fe/Si－2 催化剂：

$$dc/dt = 29.7121 \exp(-18073.5/RT)\, p_{CO_2}^{-0.76} p_{C_2H_6}^{1.04}$$

9Fe9Mn/Si－2 催化剂：

$$dc/dt = 0.5824 \exp(-9951.4/RT)\, p_{CO_2}^{-0.05} p_{C_2H_6}^{1.14}$$

研究积炭催化剂的烧炭性能，表明积炭 9Fe9Mn/Si－2 催化剂的起始烧炭温度比 K－Cr－Mn－Ni/Si－2 催化剂低 150～250 ℃，且积炭 9Fe9Mn/Si－2 催化剂于 540 ℃ 可完全烧炭，而 K－Cr－Mn－Ni/Si－2 完全烧炭温度高达 800 ℃；由于 9Fe9Mn/Si－2 催化剂的积炭没有石墨化或石墨化炭较少所致，因而，Fe－Mn/Si－2 系列催化剂具有很好的烧炭能力和再生性能。

研究了 K－Fe－Mn/Si－2 催化剂表面乙烷与 CO_2 制乙烯反应的两步(耦合)反应：

$$C_2H_6 \rightleftharpoons C_2H_4 + H_2,\ CO_2 + H_2 \rightleftharpoons CO + H_2O$$

的动力学，通过计算求得乙烷脱氢反应(一级反应)动力学方程的参数：

$$K_1^0 = 4.05 \times 10^{14},\ E_1^0 = 232.2\ \text{kJ/mol}$$

CO_2 加氢反应(二级反应)动力学方程的参数：

$$K_2^0 = 1.10 \times 10^5,\ E_2^0 = 39.1\ \text{kJ/mol}$$

催化剂表面 CO_2 与乙烷制乙烯反应的速率常数指前因子比乙烷裂解速率常数指前因子大 32 倍，反应活化能 E_1^0 比乙烷裂解反应活化能 E^0 降低 27.2 kJ/mol，CO_2 与乙烷制乙烯反应的速率比乙烷裂解制乙烯反应的速率大 700 倍；催化剂表面 CO_2 加氢反应活化能 E_2^0 比 CO_2 存在下乙烷耦合脱氢制乙烯反应活化能 E_1^0 小 193.3 kJ/mol，反应速率常数指前因子更小(2.718×10^{-10}倍)，两个反应速率常数基本是同一个数量级。反应初期，CO_2 存在下乙烷裂解脱氢制乙烯反应速率为最大值，随反应时间延长，反应速率逐渐降低并趋于稳定，CO_2 加氢反应速率在反应初期趋于 0，随反应时间增加和达到稳定状态。

总之，本文通过研究开发出乙烷脱氢与 CO_2 加氢反应—反应耦合制乙烯新过程及新催化剂，研究催化裂化干气中稀乙烷与 CO_2 反应制乙烯的新流程，以期结合催化裂化干气中稀乙烯与苯烷基化制乙苯技术，为利用炼厂气(油田气)中乙烷生产乙烯或氢气提供新技术，达到催化裂化干气的催化转化和综合利用。

ABSTRACT

Activation and utilization of lower alkanes have attracted great attention of the catalytic researchers. In this dissertation, new catalysts and the associated reaction process for the production of ethylene via the coupling reaction of ethane dehydrogenation with CO_2 hydrogenation have been studied, and results with breakthrough significance have been obtained, which have gained attention and interest of the academic and industrial circles.

Ethylene is an important basic organic raw material. Up to now, ethylene is produced mainly by high temperature steam cracking of lower alkanes from oil field gas or refinery tail gas. In these steam-cracking processes high cracking temperature and large amount of steam have to be employed, and lead to high energy consumption. Furthermore, the cracking products are quite complicated, which are difficult to separate. These processes usually can only be utilized in mass production scales. Due to the increasing shortage of petroleum resources in one hand and an increasing demand for ethylene on the other hand, researchers are seeking new routes for the production of ethylene. Many researches have been carried out by the catalytic chemists for the production of ethylene by the dehydrogenation or oxidative dehydrogenation of ethane. However, no satisfactory results with regard to activities and selectivities of catalysts have been obtained so far. In this dissertation, novel catalysts with high activities and selectivities have been studied and developed, which can yield ethylene by coupling reaction of ethane dehydrogenation with CO_2 hydrogenation, and under a comparatively lower

temperature. This may possibly open up a new route for the production of ethylene by utilizing the ethane from oil fields and refineries. Furthermore, syn-gas can be obtained as a by-product from this new process.

Thermodynamic analysis of the steam-cracking reactions of ethane was first carried out, which indicated that the temperature needed for the cracking of ethane to ethylene should exceed 1120K. Moreover, the tendency to undergo various side reactions is far greater than the cracking of ethane to ethylene, and this is especially true for the coke-formation reactions. When the cracking temperature is higher than 1380K, conversion of ethane to acetylene is very favorable thermodynamically. Thus, it is concluded that the optimum temperature range for the cracking of ethane to ethylene is 1120～1380K.

After analyzing the kinetics of the sequential reactions $C_2H_6 \rightarrow C_2H_4 \rightarrow C_2H_2 \rightarrow C$, it was found that in order to increase the ethylene yield, the reaction time should be the shorter the better, while the temperature will be the higher the better. Combining considerations of reaction performance, adequate conditions are: reaction temperature of approximately 850～900℃, reaction time of ca. 0.1～0.5 sec, and an ethane conversion of ca. 60%.

Based on analysis of researches in the oxidative dehydrogenation of ethane to ethylene, as well as on summarizing of the newest developments and mechanism of ethane oxidative dehydrogenation over catalysts of alkaline metal (or alkaline earth metal) oxides, rare earth oxides and supported vanadium, a new reaction process for the oxidative dehydrogenation of ethane to ethylene with high conversion and high selectivity has been proposed. The features and advantages of the new process are as follows: CO_2 participates in the dehydrogena-

tion of ethane, and itself is converted to CO. In this way the ethane conversion temperature is apparently reduced (more than 50℃) with respect to that of the conventional steam cracking process. Furthermore, the ethane conversion and selectivity to ethylene can be increased. Since CO_2 can react with the coke deposit on the surface of the catalyst to form CO, coke formation can be reduced, so that the catalyst life can be prolonged.

The main reactions for the dehydrogenation of ethane with CO_2 to ethylene have been deduced to be consisted of: the cracking of ethane to ethylene; the reverse water-gas shift reaction; the hydrocracking reaction of ethane to methane; the reforming reaction of ethane and CO_2 to form syn-gas. After analyzing all these possibilities, an over-all reaction scheme for the reaction of ethane with CO_2 has been proposed as follows: $xC_2H_6 + yCO_2 \Leftrightarrow zC_2H_4 + wCO + pCH_4 + qH_2O + rH_2$. It can be seen from this reaction scheme that in order to increase the selectivity to ethylene, the formation of methane must be suppressed. Naturally, different catalysts will yield different results, and the development of an efficient catalyst for the dehydrogenation of ethane with CO_2 to ethylene is a difficult task. Since this reaction has to be carried out at rather high temperatures (700 ~ 800℃), complicated side reactions will unavoidably be occurred. Therefore, in order to obtain high conversion and high selectivity to ethylene from this process, the key problem is to develop a catalyst, which can suppress the thermodynamically favorable side reactions.

From theoretical analysis and experimental results, it has been verified that the ethane dehydrogenation to ethylene with CO_2 mainly consist two coupling reactions: $C_2H_6 \Leftrightarrow C_2H_4 + H_2$ and $CO_2 + H_2 \Leftrightarrow CO + H_2O$. That is to say, ethane first dehydrogenates to form ethy-

lene and hydrogen, and then hydrogen reacts with CO_2 according to the reverse water-gas shift reaction to form CO and water, thus resulting in a continual dehydrogenation of ethane to ethylene, and enhancing the conversion of ethane and the selectivity to ethylene. As for the reforming of ethane and CO_2 to produce syn-gas, the reaction is: $C_2H_6 + 2CO_2 \Leftrightarrow 4CO + 3H_2$.

Different catalysts will lead to different reactions between ethane and CO_2, and this in turn will result in different products. Therefore, by investigating different catalyst systems, it is possible to control the reaction paths of ethane with CO_2.

Ni/Si－2 catalyst for the reforming of ethane and CO_2 was first studied. It was found that the catalyst of K－La－Ni/Si－2 showed very good catalytic reactivity. Both La_2O_3 and K_2O are essential promoters, and can enhance remarkably the selectivity and yield of syngas.

The Cr/Si－2 catalyst was found to possess good reactivity for the oxidative formation of ethylene from ethane and CO_2. Moreover, addition of Mn and minor amount of nickel oxide could improve the reactivity of the catalyst. Addition of K_2O showed a special effect for the suppression of methane formation. Fe/Si－2 exhibited better reactivity than the Cr/Si－2 catalyst for ethylene formation. Adding Mn to the iron catalyst could enhance its activity, while incorporation of K_2O could simultaneously increase the activity and selectivity to ethylene, as well as suppress methane formation. Thus, the catalyst of K－Fe－Mn/Si－2 can give an ethane conversion of 69%, ethylene selectivity of 93%, and the ethylene yield can be as high as 57%. It was also found that increasing the CO_2/C_2H_6 ratio of the feed gas could increase the ethane conversions and ethylene selectivities of the Cr/Si－2 and Fe/Si－2 catalysts. Besides, addition of

steam to the feed gas could diminish coke formation during the reaction process.

It was observed that the reaction of CO_2 hydrogenation to CO and H_2O and the reaction of ethane with CO_2 to produce ethylene showed a parallel relation on the Cr/Si－2 and Fe/Si－2 catalysts. That is, catalysts which have high CO_2 hydrogenation reactivities also showed high activity for the formation of ethylene from ethane and CO_2. Characterization of Fe/Si－2 catalyst system by CO_2－TPD, CO_2/H_2－TPSR, CO/H_2－TPSR and pulse reaction of CO_2/H_2 have showed that the promoters MnO and K_2O can improve the capacity and ability of the catalyst for CO_2 adsorption, accelerate the conversion of CO_2 to CO and H_2O, and remarkably enhance the activity and selectivity of the K－Fe－Mn/Si－2 catalyst.

Furthermore, from investigations of the reforming reactions of CO_2 with methane and ethane present in the FCC off-gas of refineries, it has been found that the K－La－Ni/Si－2 catalyst showed very good reactivity for the production of syn-gas. Addition of K_2O and La_2O_3 promoters to the Ni/Si－2 catalyst can increase CO_2 conversion and syn-gas yield. On the other hand, the K－Fe－Mn/Si－2 catalyst showed better activity, selectivity and stability than the K－Cr－Mn－Ni/Si－2 for the reaction of ethane and CO_2 to ethylene. The K－Fe－Mn/Si－2 catalyst prepared in scale-up conditions was tested in a reaction unit of 100 ml reacting volume, and gave an ethane conversion of 66%, an ethylene selectivity of 93%, and an ethylene yield of 55%. This catalyst also showed very good tolerance for sulfur and other poisonous impurities. The adequate operation conditions for this catalyst are: 780～800 ℃, 0.1～0.7 MPa, 800～1200h^{-1}.

K－La－Ni/Si－2 can also be used as a catalyst for the reform-

ing of ethane/methane and CO_2 to syn-gas, and possesses very good regeneration properties. The regenerated K－Fe－Mn/Si－2 catalyst could also recover its original reactivity for oxidative dehydrogenation of ethane by CO_2, while the Cr/Si－2 catalyst showed inferior regeneration properties. By investigating the behavior of the coke－deposition over these catalysts, it is found that the amount of coke deposited on the K－Fe－Mn/Si－2 catalyst is much lower than all others and that MnO can inhibit the coking on Fe/Si－2 catalyst during the reaction of CO_2 and C_2H_6. With the study of the coke－deposition under different reaction condition, the kinetic parameters and the equation of the coking of the Fe/Si－2 and the Fe－Mn/Si－2 catalysts are obtained as following:

for Fe/Si－2 catalyst:

$$dc/dt = 29.7121\exp(-18073.5/RT)\, p_{CO_2}^{-0.76} p_{C_2H_6}^{1.04}$$

for Fe－Mn/Si－2 catalyst:

$$dc/dt = 0.5824\ \exp(-9951.4/RT)\, p_{CO_2}^{-0.05} p_{C_2H_6}^{1.14}$$

Another information is that the Decoking Temperature of the carbon-deposited Fe－Mn/Si－2 catalyst is 150～250℃ lower than that of the K－Cr－Mn－Ni/Si－2 catalyst. Generally, the coke deposited over the Fe－Mn/Si－2 catalyst can decoked completely at 540℃, while for the K－Cr－Mn－Ni/Si－2 catalyst about 800℃ is needed.

The kinetics of the two-step coupling reactions of $C_2H_6 \Leftrightarrow C_2H_4 + H_2$ and $CO_2 + H_2 \Leftrightarrow CO + H_2O$ have been investigated over the K－Fe－Mn/Si－2 catalyst. Kinetic parameters of the first order reaction of oxidative dehydrogenation of ethane have been calculated to be: $K_1^0 = 4.05 \times 10^{14}$, and $E_1^0 = 232.2$ kJ/mol. Also, the parameters for the second order reaction of CO_2 hydrogenation have been found