# Tandem Catalytic Synthesis of Benzene from $CO_2$ and $H_2$

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**Abstract:** Benzene as an important raw material for production of industrial chemicals, is generally synthesized from petroleum and coal tar. Here, we realized benzene synthesis from greenhouse $CO_2$ and $H_2$ with two connected reactors by a tandem catalysis reaction comprising $CO_2$ methanation and $CH_4$ aromatization. The $Ni/SiO_2$ catalyst loaded in the first reactor was used to convert $CO_2$ to $CH_4$, and the formed $CH_4$ was sequentially converted to benzene on the Mo/HZSM-5 catalyst in the second reactor. This concept will provide a new pathway for the direct synthesis of benzene and $CO_2$ utilization.

**Keywords:** Benzene, $CO_2$, Tandem catalysis.

## 1. Introduction

Utilization of $CO_2$ for production of chemicals and fuels has been moved into spotlights owing to the increasing energy and environmental problems in recent years. $CO_2$ methanation has been investigated by various suitable catalytic systems focusing on group VIII metals supported on various metal oxides.[1]Among these catalysts, Ni-based catalysts are preferred as promising candidates for the $CO_2$ methanation due to relative low price, high intrinsic activity and high selectivity for methane.[1, 2]

As we know, methane can be converted to benzene and hydrogen over HZSM-5 zeolite supported molybdenum catalyst (Mo/HZSM-5) via methane dehydroaromatization (MDA, $6CH_4 \rightarrow C_6H_6 + 9H_2$, $\Delta H_{298K} = 523.018$kJ/mol), which was first reported by Wang.[3] Mo has been demonstrated to exhibit excellent MDA performance, and HZSM-5 structure is one of the most-selective zeolites for benzene formation among the various Mo-doped zeolite structures.[4-6] HZSM-5 as catalyst support for the MDA process, with two-dimensional porous structure and a pore diameter, which are close to the dynamic diameter of a benzene molecule, can effectively ensure the formation of benzene.

In this work, we presented a new benzene synthesis route by coupling a consecutive catalysis reaction comprising $CO_2$ methanation and $CH_4$ aromatization, in which methane produced by $CO_2$ methanation in the first reactor can be directly converted to benzene by the methane dehydroaromatization (MDA) in the second reactor. The two reactions were conducted over $Ni/SiO_2$ and Mo/HZSM-5 catalyst in dual connected reactors, respectively.

## 2. Experimental

### 2.1 Catalyst preparation

$Ni/SiO_2$, as the catalyst of $CO_2$ methanation, was prepared by the incipient wetness impregnation method with commercially available silica gel and an aqueous solution of $Ni(NO_3)_2{\bullet}6H_2O$. Then, the catalyst was dried at 120°C for 12h, and calcined in air at 450°C for 4h.

Mo/HZSM-5, as the catalyst of MDA, was prepared by a method similar to that of $Ni/SiO_2$ with pretreated HZSM-5 ($SiO_2/Al_2O_3=80$, calcined at 500°C for 4h) and the precursor of an ammonium molybdate solution ($(NH_4)_6Mo_7O_{24}{\bullet}4H_2O$), then dried at 120°C for 4h and calcined in air at 500°C for 4h. The Mo metal loading amount was 6% in weight. Finally, the catalyst was pressed, crushed and sorted into size of 20-40 mesh.

### 2.2 Reaction procedure

Both the first-and second-stage reactors were flow type fixed quartz tube with an inner diameter of 9 mm and length of 300mm. The first-stage reactor for $CO_2$ methanation contained $Ni/SiO_2$ catalyst. The second-stage reactor for MDA reaction contained Mo/HZSM-5 catalyst. Reaction conditions were as follows unless otherwise noted. First-stage reaction: $Ni/SiO_2$, 0.4 g; $H_2/CO_2=6$; reaction temperature, 400°C; atmosphere pressure; GHSV, 4500 ml/g/h. Second-stage reaction: Mo/HZSM-5, 0.5 g; reaction temperature, 680, 700 and 750°C; atmosphere pressure.

## 3. Results and discussion

### 3.1 Catalyst characterization

The XRD patterns of HZSM-5 zeolite, Mo impregnated HZSM-5 zeolite (Mo/HZSM-5), and $Ni/SiO_2$

catalyst are presented in Fig.1. Fig.1 (a) exhibits the XRD patterns of fresh Ni/$SiO_2$ catalyst without reduction, where NiO crystalline phase is detected. In Fig.1 (b), compared with the XRD pattern of pure HZSM-5 zeolite, it is difficult to find some obvious changes for the Mo/HZSM-5, because Mo loading amount is relatively low, with fine dispersion of Mo inside zeolite. However, it should be noted that the relative crystallinity of Mo/HZSM-5 catalyst decreases slightly after Mo impregnating. The decreases of peak intensity in the pattern of Mo/HZSM-5 also indicate the entrance of molybdenum oxide into the channels.

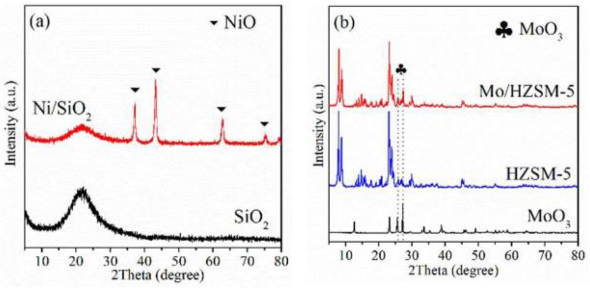


Figure 1. XRD patterns of catalysts: (a) Ni/$SiO_2$; (b) HZSM-5 and Mo/HZSM-5 (HZSM-5) peaks were not marked)

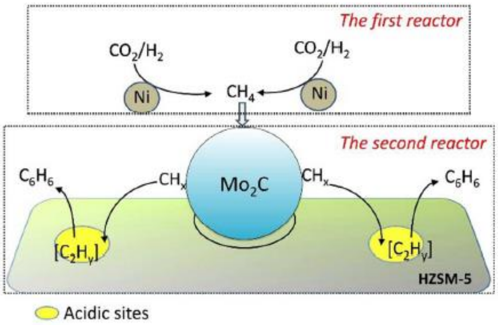
## 3.2 Catalytic performance of dual connected reactors

Table 1. The reaction results of two connected reactors

| Reaction temp(°C) | | $CO_2$ conv.% | Benzene formation rate (μmol/g/min) | Gas Selectivity (C-mol %) | | |
|---|---|---|---|---|---|---|
| First stage | Second stage | | | $CH_4$ | CO | $C_2$ |
| 400 | 680 | 92 | 0.18 | 94.5 | 4.3 | 1.2 |
| 400 | 700 | 92 | 0.53 | 93.7 | 4.9 | 1.4 |
| 400 | 750 | 92 | 0.68 | 92.8 | 5.1 | 2.1 |

The catalytic reaction results of $CO_2$ to benzene (Table 1) clearly demonstrate that benzene can be formed by the two connected reactors. For the case of tandem catalytic reaction from $CO_2$ to benzene in dual reactors, it can be found from Table 1 that increasing the temperature of the second reactor enhanced benzene formation rate since the reaction is endothermic. The reaction products contain liquid target product (benzene), some gas products ($CH_4$, CO, $C_2H_6$ and $C_2H_4$), and few solid carbon depositions. Totally, the formation rate of benzene reaches 0.68 μmol/g/min at 750°C with $CH_4$ selectivity of 92.8%, CO selectivity of 5.1%, $C_2$ selectivity of 2.1%. In consideration of calculated carbon balance, about $1.7\times10^{-1}$% $CO_2$ was converted into benzene at 750°C with a $CO_2$ conversion of 92%.

Scheme 1 provides the reaction mechanism of this tandem catalysis. In details, $CH_4$ was first produced by $CO_2$ methanation over the Ni active sites in the first reactor. Second, $CH_4$ quickly contacted the catalyst sufrace of Mo/HZSM-5 under the driving of gas flow, and was dehydrogenated on the active Mo carbide ($Mo_2C$) to form the surface carbon species CHx ($0<x<3$). Then, the active CHx and a coupled $C_2$ species ($C_2H_y$), as the primary intermediate products, were oligomerized and dehydrocylized to form $C_6H_6$ on the acidic sites of HZSM-5.[7]



**Scheme 1.** A scheme of the reaction mechanism of $CO_2$ and $H_2$ with the two connected reactors

## 4. Conclusions

Through the present work, the tandem catalysis reaction system employing two connected reactors can be applied to synthesize benzene directly. In the first reactor, the Ni/$SiO_2$ catalyst was used to convert $CO_2$ to $CH_4$, and the formed $CH_4$ was sequentially converted to benzene on the Mo/HZSM-5 catalyst in the second reactor. Meanwhile, the formation rate of benzene varied with the changing of reaction temperature in the second reactor. The idea demonstrated in this report provides a new direction for the direct synthesis of benzene from $CO_2$.

## References

1. P. F. Zhu, Q. J. Chen, Y. Yoneyama and N. Tsubaki, *RSC Adv.*, 2014, **4**, 64617-64624.
2. W. Cai, Q. Zhong and Y. X. Zhao, *Catal. Commun.*, 2013, **39**, 30-34.
3. L. S. Wang, L. X. Tao, G. F. Xu and Y. D. Xu, *Catal. Lett.*, 1993, **21**, 35-41.
4. Y. D. Xu and L. W. Lin, *Appl. Catal., A*, 1999, **188**, 53-67.
5. J. H. Lunsfod, *Catal. Today*, 2000, **63**, 165-174.
6. Y. D. Xu, X. H. Bao and L. W. Lin, *J. Catal.*, 2003, **216**, 386-395.
7. H. T. Ma, R. Kojima, S. Kikuchi and M. Ichikawa, *Catal. Lett.*, 2005, **104**, 63-66.