第26卷 第6期 催 化 学 报 2005年6月
Vol. 26 No. 6 Chinese Journal of Catalysis June 2005

Article ID: 0253-9837(2005)06-0455-03 **Communication:** 455～457

Carbon Exchange between Methane and Carbon Dioxide over Rh/H-BEA

QIAN Linping, CAO Yong, YUE Bin, REN Yu, CHEN Bailing, HE Heyong
(*Department of Chemistry, Shanghai Key Laboratory of Molecular Catalysis and Innovative Materials, Fudan University, Shanghai 200433, China*)

Key words: rhodium, H-BEA zeolite, supported catalyst, carbon dioxide, carbon exchange, methane, ^{13}C MAS NMR
CLC number: O643 **Document code:** A

The conversion of methane and carbon dioxide into useful products is a challenging subject in the field of C_1 chemistry. The catalytic dry reforming of CH_4 with CO_2 at high temperatures (generally > 1073 K) yields syngas with a low H_2/CO ratio[1], which can be used as the feedstock for Fischer-Tropsch synthesis. A large number of catalysts have been tested and it has been shown that most group Ⅷ metals are resistant to deactivation of the catalysts by the formation of coke. In particular, rhodium catalysts exhibit superior activity and high stability[2～4]. On the other hand, the reforming reaction has to be carried out at high temperatures because this reaction is not thermodynamically favourable at low temperatures. In order to find efficient routes for the transformation of syngas to oxygenates and higher hydrocarbons at low temperatures, research has been carried out on the direct conversion of methane and carbon dioxide into valuable products[5～8]. For example, Huang *et al*[5,6] reported that the activity for the methane and carbon dioxide reaction under mild conditions over Cu-Co-based catalysts is considerable, and they used a two-step method to carry out the conversion of methane and carbon dioxide into acetic acid at 523 K, in which a periodic operation is required to overcome the thermodynamic constraint. However, relatively less attention has been paid to the mechanism of the activation of CH_4 and CO_2 under mild conditions.

Supported rhodium catalysts are active for the activation of methane at low temperatures[9]. In this communication, H-BEA type zeolite with a microporous structure was used as the support and the activation of methane and carbon dioxide over Rh/H-BEA at low temperatures (⩽573 K) was investigated by *in situ* ^{13}C MAS NMR and *in situ* FT-IR. This provides useful information for developing novel reforming catalysts for operation under mild conditions.

Rh/H-BEA containing 2%Rh was prepared by the incipient wetness impregnation method. H-BEA (5 g, $n(Si)/n(Al)=12.5$, Nankai University) was impregnated with 10 ml of $RhCl_3 \cdot 3H_2O$ (98%, Aldrich) solution (0.1 mol/L). After drying under an infrared lamp, the catalyst was calcined at 573 K in air with a flow rate of 100 cm^3/min for 30 min and then reduced at 773 K in H_2 with a flow rate of 20 cm^3/min for 60 min. The XRD patterns of Rh/H-BEA show good crystallinity and featured peaks of the BEA type zeolite.

In a typical *in situ* ^{1}H-decoupling ^{13}C MAS NMR experiment, a sealed NMR cell containing catalyst and 1～3 molecules of ^{13}C-labelled reactant (99% $^{13}CH_4$ or 99% $^{13}CO_2$, Icon) with an equal amount of unlabelled reactant (CO_2 or CH_4) was heated at the desired temperature for a certain time. After rapid cooling of the cell in liquid nitrogen, the NMR spectra were recorded on a Bruker Avance DSX-300 spectrometer using a probe head with 7 mm zirconia rotors, operating at 75.45 MHz with 90° pulses and recycling delays of 10 s.

For the cell with Rh/H-BEA that only contained $^{13}CH_4$ or $^{13}CO_2$ and treated at 473 and 573 K, the *in situ* ^{13}C MAS NMR spectra showed the $^{13}CH_4$ or $^{13}CO_2$ peak itself. No other species was detected. In the reaction system containing $^{13}CH_4$ and $^{12}CO_2$ in a

---

Received date: 2005-03-18. **First author:** QIAN Linping, male, born in 1977, MS student.
Corresponding author: HE Heyong, YUE Bin. Tel: (021)65643916; E-mail: heyonghe@fudan.edu.cn, yuebin@fudan.edu.cn.
Foundation item: Supported by the National Natural Science Foundation of China (20025310, 20371013, 20273017, 20421303), the National Basic Research Program of China (2003CB615807), and the Shanghai Science and Technology Committee (03DJ14004).

molar ratio of 1∶1, the spectra showed the $^{13}CH_4$ peak at around $\delta=-9$ at ambient temperature and when treated at 473 K (Fig 1). However, the carbon atom exchange reaction between $^{13}CH_4$ and $^{12}CO_2$ occurred when the catalyst was treated at 573 K for 20 min. A peak of $^{13}CO_2$ appeared around $\delta=125$ and its intensity increased significantly when the reaction time was increased to 240 min. The intensity ratio of the $^{13}CH_4$ to $^{13}CO_2$ finally reached a value of 1, which is consistent with that the equilibrium constant of this carbon exchange reaction is equal to 1.

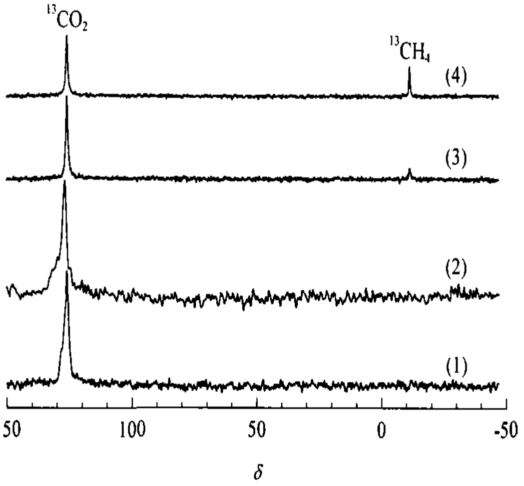


Fig 1 *In situ* ^{13}C MAS NMR spectra for the reaction of $^{13}CH_4$ and $^{12}CO_2$ ($^{13}CH_4$/$^{12}CO_2$ molar ratio = 1) over 2%Rh/H-BEA under different reaction conditions

(1) RT; (2) 473 K, 20 min; (3) 573 K, 20 min; (4) 573 K, 240 min; (5) 573 K, 400 min; (6) 573 K, 800 min

Similarly, the *in situ* ^{13}C MAS NMR spectra only show the $^{13}CO_2$ peak around $\delta=125$ for the Rh/H-BEA containing $^{12}CH_4$ and $^{13}CO_2$ in a molar ratio of 1∶1 at ambient temperature and treated at 473 K (Fig 2). Carbon exchange between $^{12}CH_4$ and $^{13}CO_2$ was also observed after the system was treated at 573 K for 20 min. The peak intensity of $^{13}CH_4$ appeared at around $\delta=-9$, and increased with increased reaction time. During the whole heating treatment, no significant decrease in the total absolute intensity of the ^{13}C labels was observed. The NMR results, therefore, show a reversible carbon exchange between CH_4 and CO_2 over Rh/H-BEA. However, the spectra did not give any peaks of any intermediates due to the low time resolution of the NMR technique.

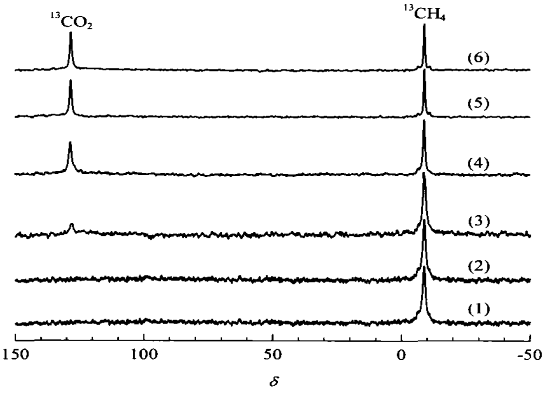


Fig 2 *In situ* ^{13}C MAS NMR spectra for the reaction of $^{12}CH_4$ and $^{13}CO_2$ ($^{12}CH_4$/$^{13}CO_2$ molar ratio = 1) over 2%Rh/H-BEA under different reaction conditions

(1) RT; (2) 473 K, 20 min; (3) 573 K, 20 min; (4) 573 K, 240 min

In situ FT-IR was used to study the formation of intermediates. The experiments were performed on a Bruker Vector 22 IR spectrometer equipped with a DTGS detector and a homemade high temperature *in situ* IR cell with quartz lining and CaF_2 windows. Self-supporting discs containing 10 ~ 20 mg catalyst were used. The catalyst was reduced *in situ* in the IR cell with H_2(99.99%) at 723 K, cooled down to room temperature in the H_2 atmosphere, then kept in He for 1 h for the removal of the physically adsorbed H_2. After that, the gas was switched to a flow of CH_4 and CO_2 with a molar ratio of 1∶1 and at a total flow rate of 35 cm³/min. Under this atmosphere, the system was heated to the desired temperature at a rate of 5 K/min, and maintained at this temperature for 1 h prior to recording the IR spectra.

As shown in Fig 3, the FT-IR spectra exhibited two bands at 2 111 and 2 047 cm^{-1}, which are as-

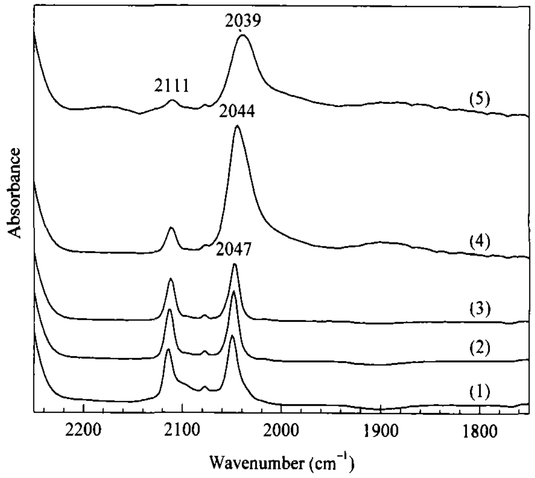
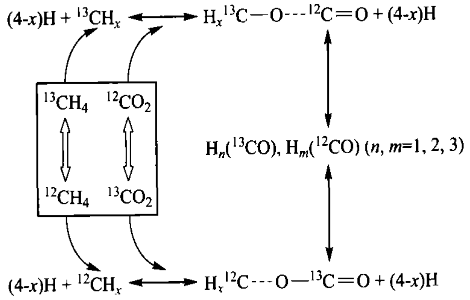


Fig 3 *In situ* FT-IR spectra for the reaction of CH_4 and CO_2 over 2%Rh/H-BEA at different reaction temperatures

(1) 343 K, (2) 433 K, (3) 523 K, (4) 573 K, (5) 623 K

signed to carbonyls formed on isolated Rh^{+} and Rh^{0}[10~13]. Their intensity decreased with increasing temperature. A new band at 2 044 cm^{-1} appeared above 573 K, which may be due to the formation of hydrocarbonyl RhH$_n$(CO) (n=1, 2, 3)[11, 13] in the carbon atom exchange between CH_4 and CO_2. This suggests that the intermediates formed on the catalyst possibly are analogues of formaldehyde.

It is well known that supported rhodium catalysts are active for the decomposition of CH_4 to give CH_x species at low temperatures[9, 14]. Based on the results above, we proposed a possible pathway for the reversible carbon atom exchange between methane and carbon dioxide shown in Scheme 1.



Scheme 1　Carbon atom exchange between CH_4 and CO_2 through a possible intermediate of H_n(CO) (n=1, 2, 3)

The decomposition of $^{13}CH_4$ on the Rh surface is considered as the initial step involving the formation of the intermediates of $^{13}CH_x$ and H. Next, the adsorbed species of $^{13}CH_x$ that have high activity reacted with $^{12}CO_2$ and H to form $H_n(^{13}CO)$ and $H_m(^{12}CO)$ (n, m=1, 2, 3) on Rh observed in the IR study. The reversible steps occurred by the decomposition of $H_n(^{13}CO)$ and $H_m(^{12}CO)$ on Rh into ^{13}C-labelled and non-labelled intermediates that further convert to $^{12}CH_4$ and $^{13}CO_2$.

The carbon atom exchange between $^{12}CH_4$ and $^{13}CO_2$ can occur in the same way to form $^{13}CH_4$ and $^{12}CO_2$. The carbon atom exchange between methane and carbon dioxide molecules over Rh/H-BEA found by the ^{13}C MAS NMR technique in this work provides useful information for the development of reforming catalysts operated under mild conditions.

References

1　Iyer M V, Norcio L P, Punnoose A, Kugler E L, Seehra M S, Dadyburjor D B. *Top Catal*, 2004, **29**(3-4): 197
2　Richardson J T, Garrait M, Hung J-K. *Appl Catal A*, 2003, **255**(1): 69
3　Bhat R N, Sachtler W M H. *Appl Catal A*, 1997, **150**(2): 279
4　Hickman D A, Schmidt L D. *Science*, 1993, **259**(5093): 343
5　Huang W, Wang X H, Wang J P, Yin L H, Xie K Ch. *Cuihua Xuebao* (*Chin J Catal*), 2001, **22**(4): 321
6　Huang W, Xie K-C, Wang J-P, Gao Z-H, Yin L-H, Zhu Q-M. *J Catal*, 2001, **201**(1): 100
7　Raskó J, Solymosi F. *Catal Lett*, 1997, **46**(3-4): 153
8　Raskó J, Solymosi F. *Catal Lett*, 1998, **54**(1-2): 49
9　Erdohelyi A, Cserényi J, Solymosi F. *J Catal*, 1993, **141**(1): 287
10　Sachtler W M H, Ichikawa M. *J Phys Chem*, 1986, **90**(20): 4752
11　Fisher I A, Bell A T. *J Catal*, 1996, **162**(1): 54
12　Kusama H, Okabe K, Arakawa H. *Appl Catal A*, 2001, **207**(1-2): 85
13　Sciè S, Crisafulli C, Maggiore R, Minicò S, Galvagno S. *Catal Lett*, 1998, **51**(1-2): 41
14　Sakagami H, Ogata S, Takahashi N, Matsuda T. *Phys Chem Chem Phys*, 2001, **3**(10): 1930

Rh/H-BEA 催化剂上甲烷和二氧化碳的碳交换反应

钱林平,　曹　勇,　岳　斌*,　任　瑜,　陈柏龄,　贺鹤勇*
(复旦大学化学系上海市分子催化和功能材料重点实验室, 上海 200433)

摘要: ^{13}C 原位魔角旋转固体核磁共振光谱研究发现, 573 K 时甲烷和二氧化碳在 Rh/H-BEA 催化剂上发生碳交换反应. 原位红外光谱检测到 H_nCO(n=1, 2, 3)中间体, 说明甲烷与二氧化碳在 Rh/H-BEA 上可以发生低温活化. 提出了发生碳交换反应的可能途径.

关键词: 铑, H-BEA 沸石, 负载型催化剂, 甲烷, 二氧化碳, 碳交换, ^{13}C 魔角旋转核磁共振

(Ed LYX)