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)

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The conversion of methane and carbon dioxide into useful products is a challenging subject in the field of C1 chemistry. The catalytic dry reforming of CH₄ with CO₂ at high temperatures (generally $>1073$ K) yields syngas with a low H₂/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. [5-8] 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 CH₄ and CO₂ 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 ($\leq 573$ 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 RhCl₃·3H₂O (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 cm³/min for 30 min and then reduced at 773 K in H₂ with a flow rate of 20 cm³/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% $^{13}$CH₄ or 99% $^{13}$CO₂, Icon) with an equal amount of unlabelled reactant (CO₂ or CH₄) 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 $^{13}$CH₄ or $^{13}$CO₂ and treated at 473 and 573 K, the in situ $^{13}$C MAS NMR spectra showed the $^{13}$CH₄ or $^{13}$CO₂ peak itself. No other species was detected. In the reaction system containing $^{13}$CH₄ and $^{12}$CO₂ in a
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.

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.

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 cm$^3$/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 2111 and 2047 cm$^{-1}$, which are as...
signs to carboxyls formed on isolated Rh⁺ and Rh⁰ [10-13]. Their intensity decreased with increasing temperature. A new band at 2044 cm⁻¹ appeared above 573 K, which may be due to the formation of hydroxocarbonyl RH₃(CO) (n = 1, 2, 3) in the carbon atom exchange between CH₄ and CO₂. 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 CH₄ to give CH₃ species at low temperatures [8, 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.

The decomposition of ¹³CH₄ on the Rh surface is considered as the initial step involving the formation of the intermediates of ¹³CH₃ and H. Next, the adsorbed species of ¹³CH₃ that have high activity reacted with ¹²CO₂ and H to form Hₙ(¹³CO) and Hₘ(¹²CO) (n, m = 1, 2, 3) on Rh observed in the IR study. The reversible steps occurred by the decomposition of Hₙ(¹³CO) and Hₘ(¹²CO) on Rh into ¹³C-labelled and non-labelled intermediates that further convert to ¹²CH₄ and ¹³CO₂.

The carbon atom exchange between ¹²CH₄ and ¹³CO₂ can occur in the same way to form ¹³CH₄ and ¹²CO₂. The carbon atom exchange between methane and carbon dioxide molecules over Rh/H-BEA found by the ¹³C MAS NMR technique in this work provides useful information for the development of reforming catalysts operated under mild conditions.

References

4. Hickman D A, Schmidt L D. Science. 1993, 259(5093), 343

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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)