One-step facile method to prepare Ni/MgO-Al₂O₃ catalysts via high frequency cold plasma in N₂, H₂ or N₂/H₂ atmosphere for CO₂ reforming with CH₄

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Abstract: With the increasingly serious situation of air pollution, catalytic conversion has become a hot research direction, and the efforts were focused on the preparation of catalysts greenly and effectively. The catalysts were prepared by plasma-assisted method in our work. Different gases were introduced to the plasma system. The catalyst treated by a mixture of nitrogen and hydrogen plasma (PNH) catalyst behaved badly in activity and coke resistance, but the hydrogen plasma (PH) and nitrogen plasma (PN) samples displayed fine activity. The catalyst treated by nitrogen plasma (PN) exhibited high activity compared to the C sample. The amount of coke over PN sample was less than that of the NMA-PH catalyst. Whereas, the PN catalyst presented as good activity and coke resistance in carbon dioxide reforming with methane as the conventional calcined catalyst.

1. Introduction
In order to mitigate the greenhouse effect with reducing carbon dioxide and methane, catalytic reforming with these two gases into the valuable syngas is of great strategic significance. For the reason that the reaction is strongly endothermic, high efficient catalyst is aimed to develop with better low-temperature activity and longer lifetime with less coke, which plays a decisive role in the industrialization of CH₄/CO₂ reforming. Bunches of studies have proved that the nickel catalyst would be the substation of noble metal catalyst for this reaction. However, the regular preparation method is tedious and the high calcination temperature would lead to the aggregation of active species. We could turn to a facile and tender way to produce the catalyst.

The low temperature arc plasma was an effective technique for the catalyst modification [1], by which the physicochemical properties of heterogeneous catalysts have been greatly changed[2-8]. Whilst, the catalyst could be directly decomposed and reduced in plasma, which is not only shorter in time costing than conventional calcination-reduction method, but also with the advantage of preventing the metal cluster from sintering. At the same time, catalytic activity is improved by the increase of active sites [9-13].

Different plasma working gases have great difference in material handling. The nitrogen arc plasma was applied to decompose the nickel nitrate in glow discharge plasma by Zhang et al [14]. In this process, the color of the catalyst changed obviously from green to gray white. The conversion rate of natural gas was 98.2%, and the selectivity of H₂ and CO was 97.3% and 96.5%, respectively, under the temperature of at 850 °C, when the catalyst was used in the partial oxidation of methane to syngas. Whereas, the catalyst was reduced to black in the process of hydrogen plasma. The catalyst exhibited high catalytic
activity and good stability.

The hydrogen, nitrogen and hydrogen/nitrogen mixture were introduced into the plasma treatment with Cu/Co catalysts for the synthesis of low carbon alcohols in the previous work[15, 16]. It was believed that the nitrogen was bombarded by high-energy electrons and ions in the plasma, which mainly made the nitrate precursor decompose into metal or metal oxide. Compared with the nitrogen plasma, the energy and temperature of hydrogen plasma system is lower. Therefore, The hydrogen treatment need longer time with the nitrate decomposition and the oxide reduced to a certain extent. Liu [17] et al proposed that the Ar or O2 plasma can be used to directly decompose the supported metal (Pt, Pd, Ag, Au) catalysts with the reduction of ionic-state noble metal precursor to zero-valence metal catalyst without the reductive substance. They believed that the free electrons in the plasma working atmosphere (Ar and O2) lead to the reduction of catalysts, with no relation to the existence of reducing substances. The size of the active component on the catalyst obtained by plasma decomposition and reduction is smaller than that in the conventional calcination in H2 atmosphere. At the same time, the catalyst can be completely reduced after 60-min treatment. The Ar plasma also used to prepare the reduced Ir/Al2O3 catalyst by [18]. It was confirmed that the metal existed with the zero valence state by XRD and XPS characterization. The catalyst produced by one step reduction of plasma showed high activity in the methane carbon dioxide reforming reaction.

In the previous work [19-22], the Ni/Al2O3 catalyst was treated by plasma technology in 3 different ways, and 3 kinds of catalysts were obtained respectively: (1) first roasted and then reduced NA-CPR catalyst for plasma treatment; (2) the plasma technology replaced the calcined process, that is, the direct plasma treatment and reduction NA-PR Catalyst; (3) NA-P catalyst prepared by plasma treatment instead of roasting and reduction process. NA-PR showed superior catalyst activity, but it is also noted that the NA-P catalyst, which was not in-situ reduction, was also active in the CH4/CO2 reforming reaction, though the activity was not high. The previous research work compared the catalyst prepared by one step reduction treatment of high frequency hydrogen plasma and the conventional calcination reduction. The grain size of the catalyst obtained by the plasma treatment is small, the dispersion of the active component is high, and the low temperature activity of the ammonia catalytic decomposition reaction is obviously improved. When the treatment time is only 10 min, the reduced catalyst [21] can be obtained. Based on the absence of reductive gas in the literature, plasma treatment can reduce the catalyst of precious metals (Pt, Pd, Ir, etc.). The previous study shows that MgO modification can reduce the reduction activation energy of Ni species in the Ni/Al2O3 catalyst and reduce the activation energy of the catalyst in the reaction. The Ni/MgO-Al2O3 catalyst was prepared from the plasma without the traditional calcination and reduction step, and the activity of different catalysts in the CH4/CO2 reforming reaction was investigated in this study.

2. Experimental

The γ-Al2O3 (40-60 mesh) support was calcined at 550 °C for 3 h before use. The improved support was obtained by impregnation method with Mg(NO3)2 solution and γ-Al2O3. The Ni/MgO-γ-Al2O3 catalyst in this work was also prepared by wetness impregnation method. Impregnation process: the γ-Al2O3 was impregnated with an aqueous solution of Mg(NO3)2 or Ni(NO3)2 for 1 h, evaporated at 80 °C water bath and then dried in oven at 110 °C for 12 h. The obtained sample was separated into four parts. One was calcined at 550 °C for 3 h first and then reduced in pure hydrogen for 2 h in situ (denoted as C). The second part was directly reduced using the atmosphere high frequency plasma jet in a mixture of nitrogen and hydrogen for only 10 min (labeled as PNH). The third part was directly reduced using the atmosphere high frequency plasma jet in nitrogen for only 10 min (labeled as PN). And the last part was directly reduced using the atmosphere high frequency plasma jet in hydrogen for only 10 min (labeled as PH). The process of plasma treatment and the apparatus have been illustrated in detail during the previous work as Ref. [22].
3. Results and Discussions

3.1 The performance of catalysts in CH₄/CO₂ reforming reaction

The CH₄/CO₂ reforming reaction was performed at 700 ℃ with the gas velocity of 36,000 mL·g⁻¹·h⁻¹. And the function of time and conversion of CH₄ and CO₂ was drawn in Fig. 1. It was observed that the plasma atmosphere has great influence on the activity of the catalyst. In terms of methane conversion, the activity and stability of pH catalyst and PN catalyst are similar, higher than C sample, while PNH catalyst has the worst activity and poor stability.

In this study, the plasma treated samples were directly used in the reforming reaction. After being treated by plasma, the catalysts decomposed from nitrate to oxidized Ni species and were partially reduced Ni species.

Due to the absence of high-temperature calcination, the correlation between Ni component and the support is weak, which makes the Ni species easy to be reduced. The modification of MgO reduces the activation energy of the catalyst, which makes it easier to activate the catalyst for methane. Methane cracking produces hydrogen, which can easily reduce the Ni species. The freshly reduced Ni becomes the active center of CH₄/CO₂ reforming. Therefore, it is speculated that the reforming of methane and carbon dioxide over the plasma treated catalyst is a process of reduction and reaction.

3.2 The results and analysis of the coke resistance over the catalysts

The temperature programmed surface reaction with CO₂ (CO₂-TPSR) was adopted to study the coke over the catalysts. There would be reaction between the coke and CO₂: C + CO₂ → 2CO. The detective CO amount would refer to the coke deposition.
The results of temperature programmed carbon dioxide decarbonization over different catalysts are shown in Figure 2. It can be seen from the figure that the initial formation temperature of CO is different, which indicates that different surface carbon species with different activity are formed on different catalysts. The higher the activity of carbon species is, the easier it is to react with activated CO$_2$. Therefore, a carbon removal reaction will occur at a lower temperature, so that the carbon deposition on the catalyst surface can be eliminated in time, which will extend the service life of catalysts. At the same time, the area of the peak can indicate the amount of carbon deposition. It can be seen that the carbon deposition over the PH sample is the most which is much more than that of conventional calcined catalyst. At the same time the carbon deposition ranged mainly at higher temperature which is not easy to be eliminated. The carbon deposition amount over the PNH is also in a second large scale. For the PN and C sample, the coke amount is less.

4. Conclusions
The catalysts were prepared by plasma-assisted method. Different gases were introduced to the plasma system. The catalyst with hydrogen plasma (PH) treatment could obtain a good performance equaled to the conventional catalyst (C) in the reforming reaction. However, the coke deposition was excessive over the PH sample. The catalyst treated by nitrogen plasma (PN) also exhibited high activity compared to the C sample. The amount of coke over PN sample was less than that of the NMA-PH catalyst. It could be elucidated that the plasma method would make the catalysts be decomposed and reduced to some extent which is a very facile and effective way to prepare catalysts.

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Reference
[1] Yu K L, Liu C J, Xia Q, Zou J J. Applications of Low Temperature Plasma in Catalysis [J]. Progress in Chemistry, 2002, 14(6): 456-461
[2] Pan Y X, Liu C J, Shi P. Preparation and characterization of coke resistant Ni/SiO$_2$ catalyst for carbon dioxide reforming of methane [J]. Journal of Power Sources, 2008, 176: 46-53
[3] Dadashova E A, Yagodovskaya T V, Shpiro E S, Belin L A, Lunin V V, Kiselev V V. The synthesis of Fe$_2$O$_3$/ZSM-5 catalyst for carbon monoxide hydrogenation in glow discharge of oxygen and argon [J]. Kinetics and Catalysis, 1993, 34(4): 670-673
[4] Gheorghii P Vissokov, Petar S Pirgov. Experimental studies on the plasma-chemical synthesis of a catalyst for natural gas reforming [J]. Applied Catalysis A: General, 1998, 168(2): 229-233
[5] Liu C J, Vissokov G P, Jang B W L. Catalyst preparation using plasma technologies [J]. Catalysis Today, 2002, 72(3-4): 173-184
[6] Pietruszka B, Heintze M. Methane conversion at low temperature: the combined application of catalysis and non-equilibrium plasma [J]. Catalysis Today, 2004, 90(1-2): 151-158
[7] Kobayashi M, Konno K, Nagazoe H. Decomposition of biomass by microwave plasma process [J]. Studies in Surface Science and Catalysis, 2006, 159(1): 821-824
[8] Dadashova E A, Yagodovskaya T V, Shpiro E S, Belin L A, Lunin V V, Kiselev V V. The regeneration of the Fe$_2$O$_3$/ZSM-5 catalyst for Fischer-Tropsch synthesis in oxygen glow discharge [J]. Kinetics and Catalysis, 1993, 34(4): 670-673
[9] Chen M H, Chu W, Zhang X W. Catalytic Performance of Pd/Al$_2$O$_3$ Catalyst Prepared by Glow Discharge Plasma Method for Selective Hydrogenation of Acetylene [J]. Chinese Journal of Catalysis, 2003, 24(10): 775-778
[10] Cheng D G, Zhu X L, Ben Y H. Carbon dioxide reforming of methane over Ni/Al$_2$O$_3$ treated with glow discharge plasma [J]. Catalysis Today, 2006, 115(1-4): 205-210.
[11] Chen M H, Chu W, Dai X Y, Zhang X W. New palladium catalysts prepared by glow discharge plasma for the selective hydrogenation of acetylene [J]. Catalysis Today, 2004, 89(1-2): 201-204.
[12] Khodakov A Y, Chu W, Fongarland P. Advances in the development of novel cobalt Fischer-Tropsch catalysts for synthesis of long-chain hydrocarbons and clean fuels. Chemical Reviews, 2007, 107(5): 1692-1744.
[13] Chu W, Wang L N, Chernavskii P A, Khodakov A Y. Glow-discharge plasma-assisted design of cobalt catalysts for Fischer-Tropsch synthesis [J]. Angewandte Chemie International Edition, 2008, 47(27): 5052-5055.
[14] Zhang Y, Chu W, Cao W M, Luo C R, Wen X G, Zhou K L. A plasma-activated Ni/α-Al2O3 catalyst for the conversion of CH4 to syngas [J]. Plasma Chemistry and Plasma Process, 2000, 20 (1): 137-144.
[15] Xu H Y, Chu W, Ci Z M. Effect of Glow Discharge Plasma on Copper-based Catalysts for Methanol Synthesis[J]. Acta Physico-Chimica Sinica, 2007, 23(7): 1042-1046.
[16] Xu H Y, Chu W, Shi L M, Zhang H, Zhou J. Preparation of Copper-Cobalt Catalyst by Glow Discharge Plasma for Lower Alcohols Synthesis[J]. Acta Physico-Chimica Sinica, 2008, 24(6): 1085-1089.
[17] Zou J J, Zhang Y P, Liu C J. Reduction of supported noble-metal ions using glow discharge plasma [J]. Langmuir, 2006, 22: 11388-11394.
[18] Zhao Y, Pan Y X, Xie Y B, Liu C J. Carbon dioxide reforming of methane over glow discharge plasma-reduced Ir/Al2O3 catalyst [J]. Catalysis Communications, 2008, 9: 1558-1562.
[19] Guo F, Chu W, Xu H Y. Glow Discharge Plasma-Enhanced Preparation of Nickel-Based Catalyst for CO2 Methanation [J]. Chinese Journal of Catalysis, 2007, 28(5): 429-434.
[20] Guo F, Chu W, Xu J Q, Zhong L. Glow discharge plasma-assisted preparation of nickel-based catalyst for carbon dioxide reforming of methane [J]. Chinese Journal of Chemical Physics, 2008, 21, 5: 481-486.
[21] Huang L Q, Chu W, Zhang T, Yin Y X, Tao X M. Preparation of novel Ni-Ir/γ-Al2O3 catalyst via high-frequency cold plasma direct reduction process [J]. Journal of Natural Gas Chemistry, 2009, 18 (1): 35-38.
[22] Liu G H, Li Y L, Chu W, Shi X Y, Dai X Y, Yin Y Y. Plasma-assisted preparation of Ni/SiO2 catalyst using atmospheric high frequency cold plasma jet [J]. Catalysis Communications, 2008, 9(6): 1087-1091.