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RESEARCH PAPER

Effect of support on the performance of Ni-based catalyst in methane dry reforming

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Abstract: Ni-based catalysts with different supports were prepared and characterized by N_2 physisorption, XRD, H_2-TPR, H_2 chemisorption, and so on; the effect of support on the performance of Ni-based catalyst in methane dry reforming was then investigated. The results indicated that the support has a significant influence on the state of NiO species. SiO_2, TiO_2 and ZrO_2 as a support have a weak interaction with NiO, which facilitates the reduction of the corresponding catalysts; however, the weak interaction may also lead to quick deactivation due to the agglomeration of active metal species. Al_2O_3 and MgO have a strong interaction with NiO, which may promote the formation of $NiAl_2O_4$ spinel and NiO-MgO solid solution, respectively, and make the reduction of corresponding catalysts very difficult. Al_2O_3 modified by MgO is provided with both proper textural properties and interaction strength between metal and support, which are in favor of the dispersion and stabilization of NiO species. As a result, NiO supported on MgO-modified Al_2O_3 exhibits superior catalytic performance in methane dry reforming even under very high gas hourly space velocity; it is quite stable during a long term test of more than 100 h.

Key words: methane; carbon dioxide; dry reforming; syngas; support effect

Methane dry reforming is able to convert two inexpensive carbon-containing compounds, viz., CH_4 and CO_2, into syngas, which is a valuable raw material for the synthesis of various fuel and chemicals. In comparison with the steam reforming of methane, dry reforming gives a relatively low H_2/CO ratio in the syngas product, which is more suitable for certain synthesis processes[1–3]. In addition, methane dry reforming, as an effective way to utilize of both CH_4 and CO_2, may have great economical, social and environmental benefits when putting into industrial application[4].

Early in 1928, Fischer and Tropsch[5] had proposed the reforming of methane with CO_2 to produce syngas; however it did not get enough attention until 1991, when Aschroft et al published a paper in *Nature*[6]. Since then, the methane dry reforming has attracted extensive attention from worldwide researchers.

Noble metal catalysts, such as Pt, Ru, Rh, etc., exhibited high activity and good resistance to carbon deposition in the methane dry reforming, but cannot be applied industrially in large scale because of their high price and limited resources[7,8]. Ni-based catalyst had comparable activity with the noble metal one; however, it deactivated rapidly due to the metal sintering and carbon deposition, which hindered the pace to its commercial utilization. Therefore, the development of a good catalyst with high activity and anti-coking capability is essential for methane dry reforming and the selection of a suitable support may be a pivotal step to prepare the catalyst with high performance.

In the present work, Ni-based catalysts with different supports were prepared for methane dry reforming with CO_2. To investigate the influence of support on the performance of Ni-based catalyst, the state of NiO species on various supports and the interaction between metal and support were characterized. This work is then conducive to the selection of suitable supports to prepare practical Ni-based catalysts for methane dry reforming.

1 Experimental

1.1 Catalyst preparation

SiO_2, MgO, TiO_2 and ZrO_2 were supplied by Beijing Chemical Co. Ltd; Al_2O_3 and its derivative, viz., MgO-modified Al_2O_3 (denoted as MA) were developed by the Research Institute of Petroleum Processing (RIPP). They were calcined at 750°C for 3 h prior to being used as the support for

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Ni-based catalysts. The supported Ni catalysts were prepared by wet impregnation method. Typically, a required amount of support was immersed in an aqueous solution of nickel nitrate and then aged for a certain time. After that, the catalyst sample was then dried and calcined at 600°C. The loading of nickel element is 8% for all Ni-based catalysts.

1.2 Characterization

The textural properties of catalyst samples such as BET surface area, pore volume and average pore diameter were measured by N_2 physisorption at 77 K on a Micromeritics ASAP-2010C adsorption apparatus. The crystalline structures present in the calcined catalysts were analyzed by X-ray diffraction (XRD) on a Bruker D8 Advance X-Ray Diffractometer. Temperature-programmed reduction (H_2-TPR) was performed on a Micromeritics 2950 chemisorption analyzer.

Metal dispersion was determined on another Micromeritics 2950 chemisorption analyzer. The catalyst sample was first reduced in a H_2/N_2 mixture at 700°C for 2 h, and then cooled down to 40°C for H_2 chemisorption. The amount of chemisorbed H_2 was then obtained and the metal dispersion was calculated according to following formula:

$$D(\%)=\frac{V_{ad}}{W_s}\times\frac{FW_{Ni}\times 2}{F_{Ni}\times V_m}\times 100 \qquad (1)$$

where V_{ad} refers to the monolayer adsorption capacity of H_2 under the standard state; FW_{Ni} is the molar mass of metal Ni, i.e. 58.7 g/mol; W_s is the mass of catalyst sample in g; F_{Ni} is the metal percentage loading; V_m is the molar gas volume under the standard state, i.e. 22.4 L/mol.

The amount of coke deposited on the catalyst after reaction was determined by using a Sulfur-Carbon analyzer (HORIBA, EMIA-320V). The carbon deposition rate was calculated according to the reaction time.

1.3 Catalytic tests

The catalytic activity measurement was carried out in a tubular fixed-bed continuous-flow reactor made of quartz with an inner diameter of 8 mm under atmospheric pressure. 0.1 g of the catalyst sample (40–60 mesh) was packed in the middle of the reactor. Prior to the reaction, the catalyst was reduced in a H_2/N_2 mixture at 700°C for 1 h. After reduction, the temperature was raised to 750°C and a reactant gas consisted of equal molar ratio of CH_4 and CO_2 was introduced into the reactor. The gas composition of reactants and products were analyzed by using a gas chromatograph (Agilent GC-140) equipped with a TCD detector. In all tests, the catalyst performances were evaluated by the conversion of CH_4 and CO_2 and selectivity to H_2 and CO, which are calculated as:

CH_4 and CO_2 conversion:

$$x(\%)=\left(\frac{M_{in}-M_{out}}{M_{in}}\right)\times 100\% \qquad (2)$$

Selectivity to H_2 and CO:

$$s_{CO}=\frac{M_{CO,out}}{M_{product}-M_{CH_4,out}-M_{CO_2,out}}\times 100\% \qquad (3)$$

$$s_{H_2}=\frac{M_{H_2,out}}{2\times(M_{product}-M_{CH_4,out})}\times 100\% \qquad (4)$$

where M_{in} is the amount of CH_4 or CO_2 introduced into the reactor, M_{out} is the amount of CH_4 or CO_2 outflow from the reactor, while $M_{product}$ is the total amount of the product, s_{H2} and s_{CO} are the product selectivity.

2 Results and discussion

2.1 Textural properties

The textural properties of various supports measured by N_2 physisorption are listed in Table 1. The surface area of SiO_2 is 239 m^2/g, the highest one among all the supports used in this work. The surface areas of Al_2O_3 as well as MA (obtained by modifying Al_2O_3 with MgO) are slightly lower than that of SiO_2. Comparatively, ZrO_2, MgO and TiO_2 have much lower surface areas, in accordance with the results reported in the literatures[9–11]. After loading with NiO, the supported Ni-based catalysts only exhibit a minor change in the textural properties, in comparison with the corresponding supports.

Table 1 Textural properties of supports

Support	BET surface area $A/(m^2\cdot g^{-1})$	Pore volume $v/(cm^3\cdot g^{-1})$	Average pore size d/nm
SiO_2	239(235*)	0.76	12.8
TiO_2	9(7*)	0.030	13.8
Al_2O_3	167(161*)	0.60	14.3
MA	145(142*)	0.58	15.9
ZrO_2	25(21*)	0.10	15.2
MgO	29(23*)	0.093	12.6

*: the specific surface areas of catalysts after loading NiO