DRY REFORMING OF METHANE ON NANO-ZIRCONIA SUPPORTED NICKEL CATALYST

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Introduction

Catalytic reforming of carbon dioxide with methane to synthesis gas has been proposed as one of the most promising technologies for the utilization of these two greenhouse gases. Moreover, this route produces synthesis gas with a suitable CO/H_2 ratio for the production of hydrocarbons and oxygenated derivatives. Supported noble metals catalysts have characteristic of high activity, selectivity and resistance to coke formation. Nevertheless, consideration of high cost and limited availability of noble metals makes the development of a nickel-based catalyst more feasible for industrial practice, but it is rapidly deactivated by carbon deposition.

Nanosized catalysts possess more edges, corners, defects, small-sized particles, large surface area and high metal dispersion, as a result exhibit the good catalytic performance. In this work, we synthesized nano-zirconia and used it as the support of Ni-based catalyst for dry reforming of methane.

Experimental

Preparation of Nano-zirconia Support and Catalysts. The nano-zirconia was synthesized by solid state reaction method. Zirconyl chloride, sodium hydroxide, CTMABr were milled respectively and mixed together. The reaction product was then transferred to the autoclave to age. Finally, the sample was washed and dried.

The nano-zirconia supported nickel catalyst, denoted as NZ, was prepared by incipient wet impregnation method using nickel nitrate as the precursor. For comparison, the catalyst of the same component was prepared by conventional co-precipitation method, denoted as CZ.

Catalytic evaluation. The catalysts behavior was carried out in the continuous flow quartz-fixed-bed reactor under atmospheric pressure. The catalyst was reduced in situ at 673K during 5h with H_2, then the reaction was preformed at 973K with CH_4:CO_2 ratio (mol) of 1:1 and space velocity of 5000cm^3/g·h.

Results and Discussion

Characterization of the Support. Figure 1 exhibits the XRD pattern of nano-zirconia. Evidently, the four peaks appearing at high degrees show that the synthesized zirconia is of tetragonal structure, and the particle size calculated by Sherrer equation is about 3.5 nm.

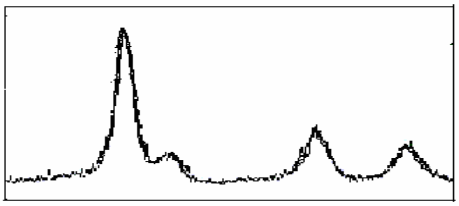

Figure 1. The XRD pattern of nano-zirconia

Figure 2 shows that nano-zirconia possesses mesopore of about 3.6 nm and large specific surface area of about 381.8 m^2/g. Moreover, it is seen that the isotherm exhibits a shape of type Ⅳ with a hysteresis of type H3. It is thought that the mesopore formed by aggregates of plate-like nanasized particles is slit-like.

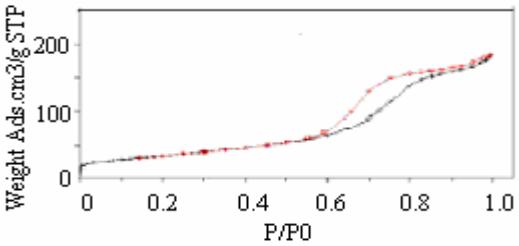

Figure 2. N_2 adsorption / desorption isotherm of nano-zirconia

Two weight loss stages are observed in the TG profile of nano-zirconia as shown in Figure 3. The first one, before 373K, corresponds to desorption of water physically adsorbed in the sample. The second one, after 473K, corresponds to loss of hydroxyl groups bonded on the surface of zirconia. No further weight loss is observed after 773K.

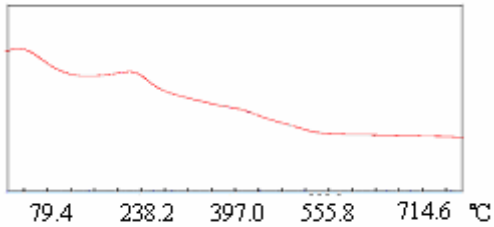

Figure 3. TG profile of nana-zirconia

Characterization of the Catalysts

Figure 4 shows that the pattern of NZ catalyst is the characteristic peaks of nano-zirconia and has no that of NiO, which indicates the dispersion of NiO on the support of nano-zirconia is uniform. However, NZ catalyst is amorphous. At the same time, the surface area, above 125.4 m^2/g, of NZ catalyst is about 2 times higher than that of CZ catalyst.

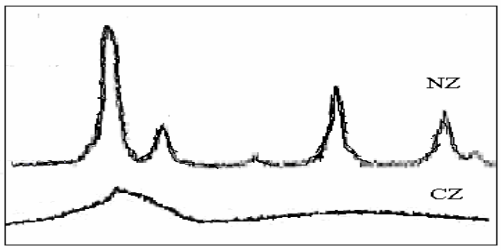

Figure 4. XRD patterns of the catalysts prepared with different method

Figure 5 shows that the weigh loss of NP is slow, has no obvious exothermic spectra, and the reduction temperature is relatively low, which indicate that NiO dispersion is uniform and the interaction of NiO and support is relatively weak. However, the weigh loss of CP is fast, has no obvious exothermic spectra, and the reduction temperature is relatively high, which indicate that the interaction between NiO and ZrO2 is strong and NiO is not easily reduced, this is in accordance with the amorphous phase shown in XRD pattern.

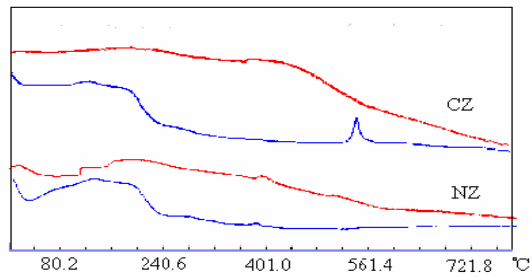

Figure 5. TG profiles of the catalysts prepared with different method in the atmosphere of H_2

Figure 6 shows that the particles of NZ catalyst are small and uniform, have no conglomeration, so the catalyst is considered as the compound of nanosized nickel oxide and zirconia. However, CN catalyst has obvious aggregates.

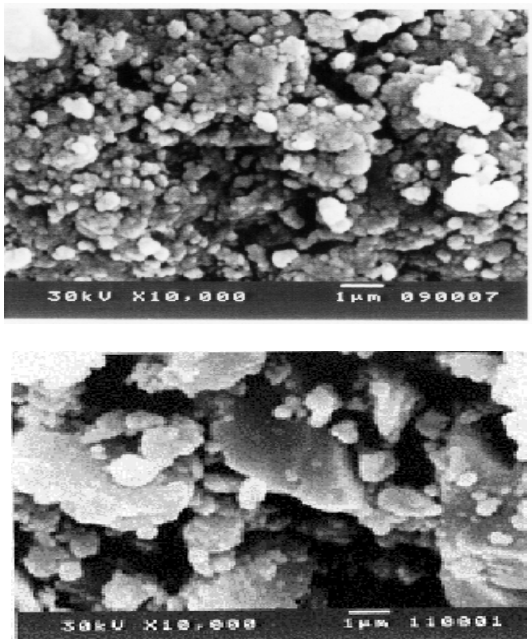

Figure 6. SEM images of the catalysts prepared with different method

Catalytic activity and stability

Figure 7 shows that the conversion of CH_4 on NZ catalyst is much high than that of CZ catalyst. NZ catalyst exhibits high stability, the conversion of CH_4 is 77.8% at the beginning and decreases by about 8% after reacting 170h., however, the conversion of CH4 is 59.22 on average over CZ catalyst. This indicates that the nano-sized catalyst with small-sized particles, large specific surface area and high metal dispersion possesses good catalytic property.

Conclusion

The results of catalytic activity and stability on dry reforming of methane reveals the important role of nano-zirconia to the catalyst. It makes the catalyst possess the characteristic of nana-particles such as more edges, corners, defects and abundant exposed atoms and so on. So nano-zirconia is the proming support of reforming catalysts.

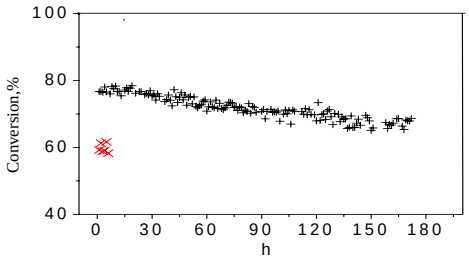

Figure 7. The variation of CH4 conversion on the catalysts prepared with different method as a function of time

References

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