Study on methane conversion to synthesis gas over nano Pt/MgO catalysts III. Influence of the precursors on the physico-chemical properties of the catalysts

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Abstract. Using different precursors, two series of nano Pt/MgO catalysts (Pt-II and Pt-IV, respectively) loaded with Pt in a wide range from 0.1 wt% to 2.2 wt% were prepared by using wet impregnation methods. The physico-chemical properties of catalysts were characterized by using BET, XRD, TPD-CO₂, and other techniques. The results revealed that the precursor and content of Pt, especially the acid/base properties of the precursor solution, had a big influence on the structure, and surface properties of the catalysts. The loaded Pt is in metallic state in all the catalysts calcined at 1073 K. The Pt-II catalysts had larger surface areas and relatively narrow pore size distribution range. The MgO crystals in the calcined Pt-II-3 catalyst had more regular structure than that in the calcined Pt-IV-3 catalyst.

1. Introduction
Methane is the principal constituent of natural gas. Conversion of methane to more useful and easily transportable chemicals (liquids) has therefore been given high priority by chemical scientists. Since Sabatier and Senderens [1] discovered the formation of synthesis gas from methane by steam reforming, different routes have been developed to convert methane to synthesis gas [2].

The conversion of methane into value-added products is a challenging task and the main reason is the high CH₃–H(g) bond dissociation energy (439.3 kJ/mol). Nickel and other transition metals are active for methane conversion but quickly deactivate due to deposits of carbon limits their utilization [3–5]. Certain noble metals (Rh, Ru, Pt, Pd) exhibit much higher intrinsic activities for dry reforming than Ni and are much less susceptible to carbon formation, and become more attractive [6-8]. Our earlier work showed that Pt supported on MgO has highly catalytic activity and stability for methane conversion to syngas due to the high stability of dispersed Pt and the low carbon deposition [9-11]. In this paper, we report about the comparison of the characterization results of two series of catalysts with different Pt content.

2. Experimental

2.1 Catalysts Preparation
Two series of nano Pt/MgO catalysts were prepared by the wet impregnation method using different precursors of Pt, i.e. Pt(NH₃)₄(NO₃)₂ and H₂PtCl₆, for Pt-II and Pt-IV, respectively. The catalyst was dried at 393 K for 24 h, then, calcined in air at the desired temperature (473 – 1073 K) for 6 h. The Pt content of the catalysts calcined at 1073 K were detected by ICP-AES and showed in Table 1.
Table 1. Pt content of the catalysts calcined at 1073 k detected by ICP-AES.

| Catalyst  | Pt-II-1 | Pt-II-2 | Pt-II-3 | Pt-II-4 | Pt-IV-1 | Pt-IV-2 | Pt-IV-3 | Pt-IV-4 |
|-----------|---------|---------|---------|---------|---------|---------|---------|---------|
| Pt content, wt% | 0.11    | 0.56    | 1.05    | 2.19    | 0.09    | 0.47    | 0.84    | 1.51    |

2.2 Characterization techniques

The textural analysis of catalysts was tested by N₂ adsorption at 77 K on the automatic adsorption analyzer ASAP 2000 (Micrometric, USA). The specific surface area, and the pore size distribution were calculated from the adsorption isotherm according to the BET model.

X-ray powder diffraction (XRD) was carried out as described in earlier paper [11].

The AMI 100 system (Zeton Altamira, USA) equipped with a TCD detector was used to carry out the temperature programmed desorption of CO₂ (TPD-CO₂). For each experiment, the first step was the activation of the catalyst in a flow of He (25 ml/min) from room temperature to the desired temperature at a rate of 10 K/min, and kept for 60 min. After activation, the temperature was cooled down to 308 K, and then, a test of TPD-CO₂ was performed, the TCD signal was recorded and saved by the computer.

3. Results and Discussion

3.1. Textural analysis of the catalysts

The BET surface areas for all Pt-II and Pt-IV catalysts calcined at 1073 K and the pore size distributions of the Pt-II-3 and Pt-IV-3 catalysts are presented in figure 1. It is shown that the two series of catalysts have different surface behavior compared to the support MgO. There was a big difference between the Pt-II samples and the support MgO. After loading Pt, the surface area showed large increases, between about two to four times. The surface area decreased with an increase of the Pt content. For the Pt-IV samples, the amount of Pt content had little influence on the surface area.

For the Pt-II-3 catalyst, most of the pores had diameters of 10 ~ 100 nm, different from the support MgO. But Pt-IV-3 catalyst had similar pore size distribution to the support MgO. The pore size distributions of other catalysts give the similar results. This is the first difference in pore size distributions between the two catalyst series. Another difference lies in the influence of Pt content. For Pt-II catalysts, the amount of Pt content did not influence the pore size distribution. For Pt-IV catalysts, the amount of Pt content had no influence on the pore size distribution (not showed here) when it was below 1.0 wt%. When the Pt content reached 1.5 wt%, the pore size distribution showed a relatively narrow range (10 ~ 100 nm).

The above results indicate that the two precursors of Pt had different influence on the texture of the support MgO. Pt(NH₃)₄(NO₃)₂ had a big influence, whereas H₂PtCl₆ had only a small influence. The reason for this may be the acid-base properties of the impregnation solutions. The impregnation solution of H₂PtCl₆ is acidic (pH = 6~7), whereas the impregnation solution of Pt(NH₃)₄(NO₃)₂ is basic (pH = 7~8).
In order to verify the above idea, the support MgO was treated with acidic and basic water solutions at the equivalent pH values as the impregnation solutions and under similar condition as impregnation, which were named MgO$^a$ and MgO$^b$, respectively, and their pore size distributions and surface areas are showed in figure 1 also. The BET results of MgO$^a$ and MgO$^b$ show that the pH value of the impregnation solution influenced the texture of MgO. After treating with basic solution, MgO had similar BET surface and pore size distribution as the Pt-II-3 catalyst. MgO$^b$ showed similar BET surface and pore size distribution as the Pt-IV-3 catalyst. This supports above idea that the textural differences between the Pt-II and Pt-IV catalysts mainly result from the acid-base properties of the impregnation solution.

3.2. Phase composition of the catalysts

As showed in figure 2, all the patterns have similar XRD patterns as the support MgO, but, new peaks appear in the patterns of catalysts having high Pt content. These new peaks at $2\theta=40, 46, 67, 81$ and $86$ belong to Pt crystallites. For the Pt-II series, these peaks appeared when the Pt content is more than 0.5 wt%, and their intensities increased with an increasing Pt content. For the Pt-IV catalysts, only Pt-IV-4 (1.5 wt% Pt) showed Pt diffraction peaks. This means that the dispersed Pt on the surface of the support MgO existed in the metallic state after calcination at 1073 K in both catalyst series.

The phase composition of the dried catalysts was complicated. The XRD patterns (not showed here) of the dried Pt-II-3, Pt-IV-3, and, Pt-IV-4 catalysts show that the supports consisted of Mg(OH)$_2$ and MgO. The relative amount of the two phases depended on the acid/base properties of the impregnation solution, as supposed. The impregnation solution for Pt-II-3 was basic, and was weakly acidic for Pt-IV-3. The XRD patterns of both catalysts show that a large amount of Mg(OH)$_2$ existed in these catalysts. Whereas, the impregnation solution for the Pt-IV-4 catalyst was relatively strong acidic, about two times as that of the Pt-IV-3 catalyst. The XRD pattern of Pt-IV-4 catalyst shows that there was only a small amount of Mg(OH)$_2$ in it. In these dried catalysts, there was no indication of a phase of Pt. XPS results show that Pt existed in the Pt$^{2+}$ state in the dried Pt-II-3 catalyst, and, in the dried Pt-IV-3 catalyst, Pt may exist in the halide state.

![Figure 2. XRD patterns of MgO and Pt/MgO catalysts](image1)

![Figure 3. CO$_2$-TPD profiles of MgO (a), Pt-IV-3 (b) and Pt-II-3 (c) catalysts](image2)

When the dried catalysts were calcined at high temperatures (>393 K), the phase transformation from Mg(OH)$_2$ to MgO took place. After calcination at 573 K, there was no Mg(OH)$_2$ detected. Although the phase transformation from Mg(OH)$_2$ to MgO was completed after calcination at 573 K, higher calcination temperatures (> 573 K) still had influence on the MgO phase, i.e. the MgO diffraction intensities increased with the temperature increase in the XRD patterns.

Pt appeared as phase at different temperatures for the Pt-II-3 and Pt-IV-4 catalysts. The Pt phase appeared when the Pt-II-3 catalyst was calcined at 473 K, and higher calcination temperatures (>473 K) had only a small influence on it. For the Pt-IV-4 catalyst, the Pt phase began to appear after calcination at 573 K, and the XRD peak intensities of the Pt phase increased with an increase in the calcination.
temperature. The above results indicate that there was difference in the formation of the Pt phase between the two catalysts. In the Pt-II-3 catalyst, the Pt phase was formed completely after calcination at 473 K, whereas in the Pt-IV-4 catalyst, the Pt phase was formed step by step above a calcination temperature of 573 K.

3.3. Basicity of the catalysts

The basicity of the calcined catalysts was investigated by TPD-CO$_2$. Figure 3 shows that there were two CO$_2$ desorption peaks in the TPD-CO$_2$ profile of support MgO. One was at 413 K, and the other at 540 K. This indicates that there were two kinds of basic sites on the surface of the support MgO, but they were only weak basic sites as judged from the low desorption temperatures. For the Pt-II-3 catalyst, the TPD-CO$_2$ profile had also two CO$_2$ desorption peaks, and the desorption temperatures were almost identical to that in the TPD-CO$_2$ profile of the support MgO, but the amount of desorbed CO$_2$ at both temperatures increased greatly after loading of Pt. This means that the loading of Pt did not change the basicity of the support MgO, but increased the amount of the basic sites, resulting in the increase of the amount of desorbed CO$_2$.

Different to the TPD-CO$_2$ profile of Pt-II-3, Pt-IV-3 catalyst had similar TPD-CO$_2$ profile as that of the support MgO, with respect to both the basicity and the amount of the desorbed CO$_2$. Therefore, for Pt-IV catalyst, the loading of Pt did not change the basic property of the support MgO.

The TPD-CO$_2$ results show that both series of catalysts had only two kinds of weak basic sites. But the two series of catalysts exhibit a big difference in the number of the basic sites. The number of the basic sites in all the Pt-II catalysts were about 2 ~ 3 times higher than in the support MgO, whereas all Pt-IV catalysts had a similar amount of basic sites as the support MgO.

As shown in figure 1, the surface area of the Pt-II catalysts were two times of that of the support MgO, but there was only small difference in these parameters between the Pt-IV catalysts and the support MgO. These results are in accordance with the difference in the TPD-CO$_2$ results. So, the big difference in the number of the basic sites may be caused by the difference in the textural properties of the two series of catalysts.

4. Conclusion

All catalysts calcined at 1073 K showed the typical XRD pattern of the support MgO. The precursor, especially the acid/base properties of the precursor solution, had a big influence on the structure of the catalysts. The Pt-II catalysts had larger surface areas than the Pt-IV catalysts. The MgO crystals in the calcined Pt-II-3 catalyst had more regular structure than that in Pt-IV-3 catalyst. Both series of catalysts had a similar basicity as the support MgO, but the Pt-II catalysts had more weak basic centers than the Pt-IV catalysts.

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