Remarkable Enhancement in the Low-temperature Activity of Catalysts Prepared via Novel Plasma Reduction-Calcination Method for Methane Conversion

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Introduction

Methane valorization is very important to the present world. Due to the stability of methane molecule, methane conversion normally requires a high temperature operation, which induces an intense energy input and poor selectivity. We previously reported a novel plasma catalyst preparation, with which the catalyst is first treated by a glow discharge and then the plasma treated catalyst is calcined thermally [1-8]. During the plasma treatment, the metal ions loaded will be normally reduced. A plasma reduction is thereby occurred. And, during calcination thermally after plasma treatment (no plasma employed in this step), the metal particles will be oxidized again. We nominated this preparation as Plasma Reduction and Calcination method (PR&C). This PR&C preparation can lead to a better catalyst preparation with a high dispersion of metal active species, a significantly enhanced acidity, an improved low-temperature activity and a remarkable promotion of catalyst stability.

The Plasma Reduction and Calcination Method

The catalyst preparation using PR&C method has been reported elsewhere [1-8]. The procedure for this method includes: the conventional incipient wetness impregnation, drying (sometimes no drying needed), plasma treatment and calcination thermally. For the plasma treatment, several plasma phenomena, e.g., glow discharge, dielectric-barrier discharge and microwave discharge, can be employed. The different discharge plasma treatment would induce a very different catalytic performance. In this work, we focus on the discussion of PR&C method with glow discharge plasma treatment. Glow discharge is a kind of plasma that is created by inserting two electrodes in a cell filled with gas at low pressure (e.g.,1 Torr). During the glow discharge plasma treatment, the catalyst was hold in a quartz container and placed in a glow discharge tube. A high-voltage (DC or AC) generator is used to generate the glow discharge plasma. The catalyst powder or particles are usually placed in the "positive column" of glow discharge where it was characterized with highly energetic electrons at low gas temperature [2]. Argon, helium, nitrogen, hydrogen, carbon dioxide and others can be applied as the plasma-forming gas for PR&C preparation. In the following discussions, we focus the use of argon as the plasma-forming gas. After the plasma treatment, the catalyst is then calcined thermally. The calcination temperature exhibits a significant effect on the dispersion and other catalytic performances that will be discussed in the future.

As mentioned above, during plasma treatment, the catalyst is normally reduced. Figure 1 exhibits XRD patterns of plasma treated catalyst samples. Evidently, some metal species present after the plasma treatment. A plasma reduction is thereby addressed. XPS analysis of the plasma treated catalysts gives us further evidences of the plasma reduction [2,8]. The reduced metal species would play an important role in the plasma-enhanced dispersion. During the oxidation of the reduced metal species in calcinations thermally, the new-formed metal oxide will induce an intense electric field. The metal species with the same electric properties will therefore exclude each other, which induces a highly dispersion [8].

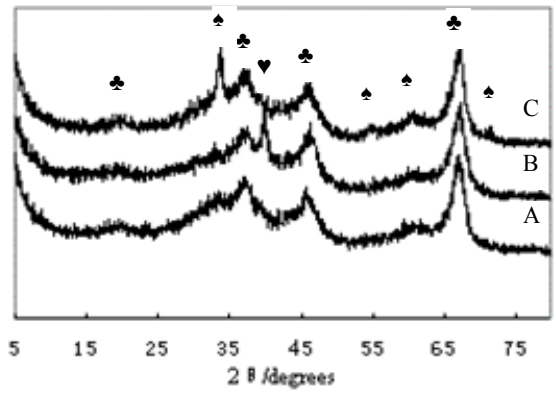

Figure 1. The XRD patterns of Pd/Al_2O_3 catalysts by different preparations
A: Pd/Al_2O_3 (conventional catalyst); B: Pd/Al_2O_3 (catalyst after plasma treatment); C: Pd/Al_2O_3 (PR&C prepared) [8]

Plasma Enhanced Acidity

The catalysts prepared with PR&C method normally show a plasma-enhanced acidity [2-4]. We used IR–pyridine adsorption to analyze the effect of plasma treatment on the Brönsted and Lewis acidities for further understanding the plasma enhanced catalytic performance. The PR&C preparation normally leads to enhanced Brönsted and Lewis acidities of the supported catalyst. For example, the amount of Brönsted acid sites of the plasma prepared Pd/HZSM-5 catalyst is 1.13 times larger than that of the catalyst prepared thermally, while the amount of Lewis acid sites is 1.21 times higher. Table 1 presents the results obtained over Pt/NaZSM-5 catalyst [4].

Table 1. Acid site amount of Pt/NaZSM-5 catalysts based on the IR-pyridine adsorption [4]

	0.1wt%Pt/Na ZSM-5 (conventinal)	0.1wt%Pt/Na ZSM-5 (PR&C prepared)	The increased amount of acidic sites
Lewis acid (mmol/g)	1.944	2.147	10%
Brönsted acid (mmol/g)	0.0332	0.0369	11%

Plasma Enhanced Dispersion

Remarkable plasma enhanced dispersion has been achieved from the PR&C preparation. Tables 2 and 3 present some comparisons of the dispersion between Pd/HZSM-5 and Pt/NaZSM-5 catalysts prepared by PR&C and by the conventional way [3,4]. The results were obtained from hydrogen chemisorption. The calculations from XRD give us further supporting evidence, as shown inTable 4 [2].

Table. 2. Results of H_2-chemisorption measurement of

catalysts	Metal dispersion/%	Active particle diameter/nm
Pd/HZSM-5 (conventional)	4.57	24.5
Pd/HZSM-5 (PR&C prepared)	5.92	18.9

2wt%Pd/HZSM-5 [12]

Table 3. The results of H_2-chemisorption for dispersion of 0.1wt%Pt/NaZSM-5 [4]

	0.1wt%Pt/NaZSM-5 (conventional)	0.1wt%Pt/NaZSM-5 (PR&C prepared)
Pt dispersion	4.2	63.3
Surface area of Pt (m^2/g sample)	0.02	0.28
Surface area of Pt (m^2/g metal)	18.5	281.8
Diameter of Pt particle (nm)	27.0	1.8

Table 4. Particle size of PdO obtained by Scherrer formula for 2wt%Pd/HZSM-5 [2]

	Full width at half maximum / rad	Particle size / nm
Pd/HZSM-5 (conventional)	0.00691	21.0
Pd/HZSM-5 (PR&C prepared)	0.00904	16.0

The Ni-supported catalysts prepared via PR&C method exhibit an unusual dispersion characteristic. From hydrogen chemisorption, XRD characterization and TEM analysis, no metal particles can be identified [5,6]. One possibility is that the metal species is ultra-highly dispersed over the support. Another possibility is that the Ni species changes to amorphous species after the plasma treatment. Further investigation is being conducted to study this unusual dispersion performance.

Plasma Enhanced Low-temperature Activity

All the catalysts prepared by PR&C method and tested by far show a better low-temperature activity, esp., those for methane conversion. We reported a comparison between methane combustion over Pd/HZSM-5 catalysts prepared via PR&C and the conventional catalyst [2,3]. Obviously, the plasma prepared catalyst presents a better low-temperature activity and an enhanced stability over the catalyst prepared conventionally. The methane conversion over the plasma treated catalyst is close to 100% at 450 °C, but it is only 50% at the same temperature over the conventional catalyst. The alumina supported Pd catalysts exhibit a similar plasma-enhanced low-temperature activity. The light-off temperature of the plasma prepared catalyst is 370 °C, 50 °C lower than that obtained from the conventional catalyst [7,8].

Ni-Fe/Al_2O_3 catalyst for partial oxidation of methane prepared via PR&C exhibits a better low-temperature activity too over the catalyst prepared thermally [5]. The conversion of methane and the selectivity of CO and H_2 over the plasma prepared catalyst are 97.44%, 100% and 100% at 875 °C, while, at the same temperature, they are 90.09%, 97.28% and 97.09%, respectively, over the catalyst prepared without plasma treatment. At the same methane conversion, the reaction temperature with the plasma prepared Ni-Fe/Al_2O_3 is at least 80 °C lower.

The PR&C prepared Pt/NaZSM-5 catalyst for NO reduction by CH_4 exhibits a highly dispersion of metal active species and a remarkable improvement in the low-temperature activity, compared to the catalyst prepared conventionally [4]. The conventional 0.1wt%Pt /NaZSM-5 catalyst shows no activity at temperatures below 673 K, while at 673 K, the NO conversion to nitrogen reaches 61.3% over the plasma prepared 0.1wt%Pt /NaZSM-5 catalyst. The initiated temperature for the plasma prepared 0.1wt%Pt/NaZSM-5 catalyst can be as low as 548 K.

Plasma Enhanced Stability

During our investigation on methane combustion, we have confirmed a remarkable enhanced stability of catalysts from the PR&C preparation. The investigations for partial oxidation of methane to syngas [5] and carbon dioxide reforming of methane [6] over Ni supported catalysts give us further evidences for the plasma-enhanced stability. The Ni supported catalyst is active for both reactions but this catalyst suffers from a deactivation, principally due to the carbon deposit. The catalysts prepared via PR&C presents a very different carbon species, compared to the conventional catalyst. A plasma-enhanced stability has also been observed over the Pt/NaZSM-5 catalyst for NO reduction by methane [4]. It is well known that the catalyst for NO reduction is structure-sensitive. The PR&C preparation would make an improvement too with the structure-sensitive catalyst.

From the present understanding, the plasma-enhanced acidity plays a very important role in the plasma-enhanced dispersion and stability, which makes the catalyst prepared via PR&C method exhibit better low-temperature activity and better thermal stability.

Conclusions

The principal procedure of the catalyst preparation using PR&C method can be summarized: 1) impregnation conventionally; 2) drying or no drying; 3) plasma treatment; and 4) calcination thermally. The PR&C preparation will normally induce a significantly plasma-enhanced acidity and dispersion, which further leads to a low-temperature catalytic activity. A remarkable improved in the stability of catalysts has also obtained with the PR&C catalyst preparation. This improved stability is achieved principally thanks to the plasma-enhanced acidity and the improvement in the interaction between metal species and the support. Further improvement in the PR&C preparation is leading to a development of a novel and practical catalyst preparation technology.

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