RF Plasma Modification of Supported Pt Catalysts for CO_2-CH_4 Reforming

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Introduction

Numerous studies dealing with CO_2/CH_4 reforming have been recently published. Edwards and Maitra (1), in a detailed review, have suggested that further catalyst development is the major hurdle before this reforming can be widely commercialized. Literature shows that the supported Group VIII elements in their reduced forms, especially Ni, Co, Ru, Rh, Pd, Ir and Pt, are active for CO_2/CH_4 reforming. Among these metals, Ni, Pt, Ru and Rh are the most studied elements.

Many different support materials, such as SiO_2, Al_2O_3, ZrO_2, TiO_2 and mixed oxides, have been studied for CO_2/CH_4 reforming. Results suggest that supports have a strong effect on the activity and the stability of CO_2 reforming catalysts. For example, replacing γ-Al_2O_3 by single crystal MgO as support material for Ni results in low coking and high catalytic activity (2). The support materials apparently influence the growth of carbon by controlling the type of metallic clusters that are sites for carbon formation (1). The acid/base properties of the support material are also important to the activity and stability of the catalysts. Tang et al. report that the increase in base strength of catalysts decreased the coke deposition rate on both SiO_2 and Al_2O_3 supported Ni catalysts (3). Ferreira-Aparicio et al have suggested that surface hydroxyl groups are involved with the reaction mechanism (4).

Strong support-metal interactions can result in changes in catalytic activity, selectivity, and stability. For example, Ni/Al_2O_3 forms $NiAl_2O_4$ (which is inactive for CO_2 reforming with CH_4) at high temperatures. Modifiers such as La_2O_3 and CeO_2 promote the activity of alumina supported Ni catalysts for CO_2 reforming. It is reported, by Bitter et al., that the available perimeter around Pt-ZrO_2 interfaces is critical for the reforming activity in that CO_2 reduction occurs close to the metal-support boundary (5). Verykios also proposed that active carbon containing species on Rh/Al_2O_3 are in the reaction pathway of CO formation during CO_2/CH_4 reforming (6). These results confirm the importance of metal-support interactions.

Recently, non-thermal plasma based techniques for catalyst preparation have attracted significant attention (7,8). Materials with unusual and highly advantageous catalytic properties, including high metal dispersion and enhanced metal-support interaction resulting in better catalyst stability, have been achieved via the plasma route. These advances have been documented in symposia and detailed in recent reviews (9-11). For example, Zhang et al. reported plasma activation of a Ni/α-Al_2O_3 catalyst for methane conversion to synthesis gas using a radio-frequency (RF) argon plasma for the decomposition of $Ni(NO_3)_2$. The resulting catalyst exhibited improved activity and catalytic lifetime compared to material obtained using conventional high temperature methods (12). More recently, a Ni-Fe/Al_2O_3 catalyst, prepared first by glow discharge plasma treatment followed by calcination, was studied for partial oxidation of methane by Wang et al. (13). The resultant catalyst exhibited overall improved performance compared to a catalyst of identical composition prepared via calcination. In addition, the plasma treated Ni-Fe/Al_2O_3 catalyst also exhibited better resistance to carbon deposition (13).

The present study examines further the utility of plasma processing in developing improved catalysts for eventual use in CO_2/CH_4 reforming operations. Specifically, we report plasma modification effects on metal-support interactions of 1%Pt/Al_2O_3 catalysts. By substituting plasma treatment for the conventional high temperature calcination step, both higher metal dispersions and improved sintering resistance are observed with the resultant catalysts. Additionally, the distribution of CO_2 adsorption sites on the catalyst is observed to be strongly regulated by various plasma treatments.

Experimental

Catalyst Synthesis. Alumina pellets, 1/8 in., (from Alfa Aesar) with 1.14 ml/g pore volume and a 255 m^2/g surface area were crushed and screened to 20-40 mesh. The 20-40 mesh alumina particles were dried at 200°C for one hour then cooled in a dissicator to room temperature. The resultant alumina particles were then impregnated with H_2PtCl_6 solution based on the incipient wetness technique to provide 1% Pt loading. The materials were dried at 120°C for 2 hours and are designated as 1%Pt/Al_2O_3(A).
Powder aluminum hydroxide (from Aldrich) was used as the alumina precursor to prepare impregnated Pt catalysts for acid/base studies. Aluminum hydroxide and the Pt precursor were mixed in water and heated until dry. The dried sample was then calcined at 500°C in air for 3 hours and it is designated as 1%Pt/Al_2O_3(H).

Plasma Treatment. Plasma treatments were carried out in a custom-designed 360° rotating RF plasma system. The system consists of three major components: power supply, reaction chamber, and a gas delivery and pumping system. The power supply includes an ENI A-300 amplifier, Tetronix pulse generation (Model 2101), and a Wavetech function generation (Model 166). A custom designed matching network was employed to minimize the reflected power. Power wattage is measured by the combination of a Bird watt meter (Model 4412), and a Leader oscilloscope (Model LS1020). This system is operable from milli-torr to a few torrs, with a base pressure of 10 mtorr. For O_2 plasma, 150W peak power and a 10ms/10ms plasma on/off cycle was used. For H_2 plasma, 200W and 10ms/10ms on/off cycle was employed. Typically, one gram of catalyst was loaded into the plasma chamber for treatment. The times for plasma treatment ranged from 1 to 3 hours. Both O_2 and H_2 gases were UHP grade.

H_2-Chemisorption. H_2-Chemisorption tests were performed with the automatic catalyst characterization system, AMI-200 (Altamira Instruments). Approximately 70mg samples were heated in H_2, with a 5°/min ramping rate, to 450°C or 600°C before cool down in argon to 35°C. Hydrogen-chemisorption was carried out by pulsing H_2 over clean metal surfaces until saturation. The consumption of H_2 due to chemisorption is measured by TCD for metal dispersion determination.

CO_2/NH_3-TPD. Catalyst samples (~70 mg) were heated in UHP helium at 20°C/min to 500°C before cooling down to 50°C for adsorption with 10% CO_2/NH_3 in helium for an hour. CO_2/NH_3-TPD is recorded with TCD using a ramp rate of 10°C/min from 50°C to 500°C in helium.

Results and Discussion

Pt Dispersion. Pt metal dispersions of 1%Pt/Al_2O_3(A), determined by H_2-chemisorption after reduction at different temperatures, are summarized in Table 1. After hydrogen reduction at 450°C, both O_2 and H_2 plasma treated samples show higher dispersions than the plasma untreated control sample. The O_2 plasma is more effective than the H_2 plasma in promoting the dispersion with 39.5% (O_2) vs 34.1% (H_2) compared to 31.1% for the untreated sample. After 600°C reduction for 5 hours, both O_2 and H_2 plasma treated samples show much higher dispersions than the untreated sample. The Pt dispersions are 34.1%, 34.7% and 24.4% for O_2 plasma, H_2 plasma and untreated samples, respectively. These results suggest that the sintering resistance of these catalysts is improved by the plasma treatments. The relative improved resistance is even more prominent after extended reductions at 600°C. After reduction at 600°C for 12 hours, H_2 plasma treated sample shows superior sintering resistance over O_2 plasma treated and untreated samples. As shown in Table 1, no apparent decrease in Pt dispersion is detected for the H_2 plasma treated sample while metal dispersion on the O_2 plasma treated sample decreased by 22% while the untreated one decreased by 34.7%. These results demonstrate that both O_2 and H_2 plasmas are effective in promoting increased metal dispersion, with the H_2 treated materials also exhibiting improved sintering resistance.

NH_3-TPD. The NH_3-TPD results of calcined, H_2 plasma treated and O_2 plasma treated 1%Pt/Al_2O_3(H) are shown in Figure 1. Both H_2 and O_2 plasmas modify the acidic sites for NH_3 adsorption. The O_2 plasma shows a stronger effect on 1%Pt/ Al_2O_3(H) increasing strongly the surface density of weak, medium and strong sites for NH_3 adsorption. In contrast, the H_2 plasma treatment apparently results in a more selective increase in the concentration of the weakly acidic sites, relative to smaller increases in the medium and strong NH_3 adsorption sites.

CO_2-TPD. CO_2-TPD results of calcined, H_2 plasma treated and O_2 plasma treated 1%Pt/Al_2O_3(H) are listed in Figure 2. As shown in Figure 2, H_2 plasma has little effect on the population and the distribution of CO_2 adsorption sites. O_2 plasma, on the other hand, is highly effective in the generation of strong and medium CO_2 adsorption sites on 1%Pt/Al_2O_3(H). Oxygen plasmas are well known for etching ability and are used extensively for that purpose. It is likely that O_2 plasma creates vacancies which serve as new sites for CO_2 adsorption. H_2 plasma, on the other hand, is known for passivation effects (14) and is less efficient for site generation. However, after site generation by O_2 plasma, a subsequent H_2 plasma treatment alters the properties of generated sites, as shown in Figure 3. Figure 3 lists the CO_2-TPD results of samples with the 3-h O_2 plasma treatment followed by H_2 plasma treatments of 1 to 6 hours. As shown in Figure 3, one hour of H_2 plasma treatment largely reduces the strong sites generated by the 3-h O_2 plasma treatment and simultaneously increases the sites with less strength (mainly weak sites) for CO_2 adsorption. As the H_2 plasma time increases from 1 hour to 3 hours, the strong site population further decreases and, simultaneously, both weak and medium sites decrease. Further increase of the H_2 plasma treatment time to 6 hours results in further decease of the weak sites, with relatively no changes of medium sites. These results indicate that H_2 plasma is effective in reducing the strength of CO_2 adsorption sites while O_2 plasma generates CO_2 adsorption sites with medium to high strengths. Thus, it appears the combination of O_2 and H_2 plasma treatments, especially an initial O_2 plasma followed a subsequent H_2 plasma, can manipulate the population and distribution of CO_2 adsorption sites. It is anticipated that regulation of the nature and surface density of active sites should affect the activity and stability of catalysts employed in CO_2/CH_4 reforming. Present studies involve a continuation of this work and they include examination of the effect of similar plasma treatments on CH_4 adsorption site densities. The RF plasma treatment approach described offers a viable route to evaluation of the role of active surface site densities on the CO_2/CH_4 reforming process, and thus a potentially important route to synthesis of improved catalysts for this purpose.

Conclusions

Both O_2 and H_2 plasmas are effective in promoting increased metal dispersion. Additionally, H_2 plasma treatments results in catalysts having improved resistance to sintering. The CO_2-TPD study indicates that the combination of O_2 and H_2 plasma treatments, especially the O_2 plasma first followed by H_2 plasma, can manipulate the population and distribution of CO_2 adsorption sites. Further studies of these effects are currently in progress in our labs.

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Table 1. Metal dispersion results of 1%Pt/Al_2O_3(A).

Catalyst	Reduction at 450°C for 2 hr	Reduction at 600°C for 5 hr	Reduction at 600°C for 12 hr
Uncalcined	31.1	24.5	20.3(-34.7%)
H_2 plasma, 1 hr	34.1	34.7	35.1(~0)
O_2 plasma, 1hr	39.5	34.1	30.8 (-22.0%)

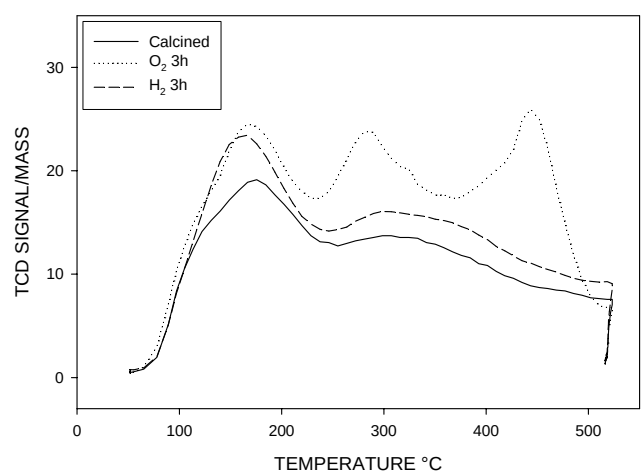

Figure 1. NH_3-TPD of calcined, O_2 treated and H_2 plasma treated 1%Pt/Al_2O_3(H).

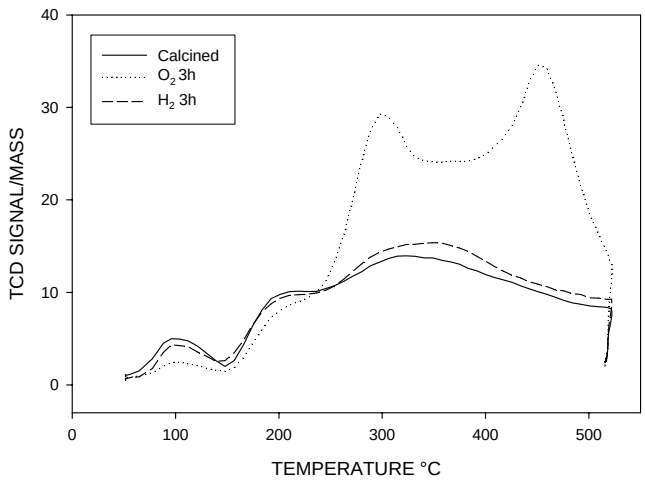

Figure 2. CO_2-TPD of calcined, O_2 treated and H_2 plasma treated 1%Pt/Al_2O_3(H).

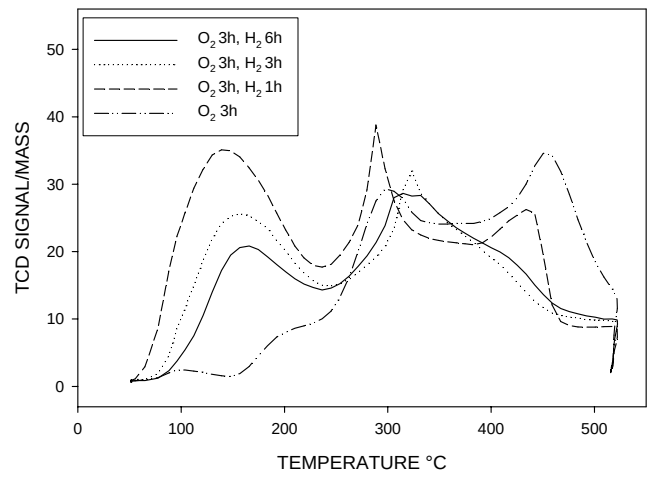

Figure 3. CO_2-TPD of calcined 1%Pt/Al_2O_3(H) with combinations of O_2 plasma and H_2 plasma treatments.

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