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Analysis of Gd Level and Pt Dispersion on Ceria Support for Isobutane Steam Reforming

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Abstract Ceria-supported platinum catalysts were used to produce hydrogen by isobutane steam reforming. The influence of gadolinia, as a trivalent cationic oxide (M_2O_3) dopant at 0–20%, is investigated here. The gadolinia content in the catalysts did not correlate well with reforming activity. The platinum dispersion ranged from 29 to 38% as measured by the propylene hydrogenation method and it did correlate well with reforming activity.

Keywords Steam reforming · Isobutane · Ceria-gadolinia · Platinum dispersion · Propylene hydrogenation · Chemisorption

1 Introduction

Autothermal and steam reforming of higher hydrocarbons can be catalyzed by noble metals supported by reducible oxides (redox supports). These catalysts gained importance as three-way catalysts because of their wide usage in vehicle exhaust treatment to achieve simultaneous control of CO, hydrocarbons, and NO_x emissions [1]. Redox supports like ceria undergo oxidation/reduction, acting as an oxygen buffer, releasing oxygen in times of oxygen deficiency and storing oxygen in times of oxygen surplus [2, 3].

Gorte et al. [4, 5] carried out steam reforming of various hydrocarbons like *n*-butane, *n*-hexane, *n*-octane, benzene, and toluene on Pd/ceria and Pd/alumina catalysts between 620 and 700 K. The Pd/ceria catalysts exhibited a higher rate and selectivity compared to the Pd/alumina catalysts. They proposed a dual-function mechanism to explain steam reforming on noble metal/ceria catalysts. According to the mechanism, CeO_2 transfers oxygen to the supported metal and is reduced to Ce_2O_3. The reduced ceria is in turn re-oxidized by water to CeO_2. This way ceria supplies oxygen to the hydrocarbons adsorbed on the supported metal for oxidation.

Another key property that enhances the steam reforming activity of noble metal/ceria catalysts compared to the noble metal/alumina catalysts is the oxygen mobility from the support to the active metal. One method of increasing the oxygen mobility is by doping ceria with a trivalent cationic oxide (M_2O_3) like gadolinia. Addition of gadolina creates extrinsic vacancies based on the principle of charge compensation. This increases the oxygen conduction in the ceria support, as observed by Cho et al. [6] Wiemhofer et al. [7] estimated the oxygen ion conductivity of $Ce_{0.8}Gd_{0.2-x}Pr_xO_{1.9}$ by impedance measurements. They observed an improvement in the overall ionic conductivity after doping ceria with the rare earth metals.

Argonne National Laboratory (ANL) investigated autothermal reforming of higher hydrocarbon fuels like isooctane, toluene, 2-pentene, gasoline, diesel, etc. using a flexible fuel processor [8, 9]. They used group VIII metals on redox supports doped with rare earth metals, like Pt/ceria doped with gadolinia [10, 11]. The doped-ceria supported catalysts have a higher activity for many reactions compared to the alumina supported catalysts [12, 13].

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But Gorte et al. [14, 15] have noted that, depending on the reaction considered, the dopants in ceria have a wide range of influence on the rate of the reaction (higher, lower, and similar to an undoped ceria). The influence of the gadolinia doping in ceria for isobutane steam reforming is addressed here.

Another factor that can influence the reforming activity of a catalyst is the metal dispersion on a support. For example, Kikuchi et al. [16] carried out steam reforming on *n*-heptane using an Rh/Al_2O_3 (noble metal/non reducible support) catalyst. They found that the activity of the catalyst for the reaction decreased as the degree of rhodium dispersion increased. The activity depended on the proportion of face atoms, which decreased with an increase in the degree of dispersion. But, the activity for the aromatization reaction of *n*-heptane increased with the dispersion of rhodium. It becomes important to find a correlation between the metal dispersion and the reforming activity of the catalysts. So, a suitable method has to be found to estimate the metal dispersion on a support.

The most common method adopted to estimate the metal dispersion on supports like alumina, silica, and magnesia is by chemisorption of gas probes like CO or H_2 at room temperature [17, 18]. The dispersion can be calculated by measuring the amount of CO or H_2 chemisorbed, assuming a specific stoichiometry of adsorption.

But, when a noble metal such as platinum is dispersed on a reducible support such as niobia or ceria, chemisorption of gas probes such as CO or H_2 at room temperature is complicated due to the spillover of the gas probes to the support or the metal-support interface from the metal sites [19–21]. As a result the amount of CO or H_2 chemisorbed can be greater than the number of metal atoms dispersed on the surface of the support leading to an overestimation of the metal dispersion [17, 22].

To overcome the spillover problem, Andersson et al. [17] carried out the CO chemisorption on a Pt/ceria catalyst at –78.5 °C (dry ice), a temperature expected to hinder the spillover process. They observed a remarkable decrease in the CO chemisorption at that temperature compared to the CO chemisorption at room temperature (25 °C), but they were not sure of the complete hindrance of the spillover process at that temperature and also the CO uptake by ceria. So, an alternative method for estimating the metal dispersion on a reducible support was considered.

Gavalas et al. [23] suggested an indirect method for the estimation of metal dispersion on a ceria support. They estimated the metal dispersion on an alumina support by chemisorption at room temperature (25 °C) and carried out propylene hydrogenation, a structurally insensitive reaction, on both the alumina and the ceria supported noble metal catalysts at 0 °C under differential conditions. A relationship was established between the dispersion and the rate of propylene hydrogenation on the alumina supported catalyst, which was used to estimate the metal dispersion on the ceria supported catalyst.

In a previous paper [23], we investigated the kinetics of isobutane steam reforming on 0.5 wt% platinum on gadolina-doped ceria catalysts (hereafter designated Pt/CGO). Our objective here is to analyze the influence of the gadolinia content and platinum dispersion on the activity and activation energy of isobutane steam reforming. The reason for carrying out isobutane steam reforming is that, when hydrocarbons like gasoline are reformed autothermally, they quickly break down to lower hydrocarbons like C_4 during the partial oxidation stage and subsequently undergo steam reforming as the rate limiting step [24]. Isobutane was hence used as a model fuel for carrying out steam reforming.

2 Experimental

The isobutane steam reforming reactor was a 0.35 inch quartz tube containing a quartz wool bed that supported the catalyst. A furnace encompassing the quartz tube supplied the heat for the reaction. The furnace was controlled using the temperature from a thermocouple at the top of the catalyst bed. There was also a thermocouple at the bottom of the catalyst bed, which was connected to a temperature recorder. The flow rate of isobutane (99.9%) and nitrogen (99.99%), which was used as an internal standard gas and a diluent, was controlled by mass flow controllers (UNIT, 8100 series). The deionized water was supplied by a syringe pump (KD Scientific, model 100). The reactants were mixed and vaporized by a heating tape before flowing into the reactor. The products went to a condenser maintained at room temperature and a drierite bed (anhydrous calcium sulfate), where the water was removed. After removing most of the condensable water, a sample was taken in a six-way valve and injected into an HP 5890 Gas Chromatograph (GC), which had a Haysep DB packed column and a TCD detector. The GC was connected to an SRI Peak-Simple data acquisition system.

The catalyst formulations were developed at ANL [11]. The catalysts considered in this study were 0.5% Pt-CeO_2 (Pt-CGO-0), 0.5% Pt-$Ce_{0.95}Gd_{0.05}O_{1.975}$ (Pt-CGO-5), 0.5% Pt-$Ce_{0.9}Gd_{0.1}O_{1.95}$ (Pt-CGO-10), 0.5% Pt-$Ce_{0.85}Gd_{0.15}O_{1.925}$ (Pt-CGO-15), 0.5% Pt-$Ce_{0.8}Gd_{0.2}O_{1.9}$ (Pt-CGO-20), and a larger amount of 0.5% Pt-$Ce_{0.8}Gd_{0.2}O_{1.9}$ (Pt-CGO-20 (B)) catalyst for screening experiments.

For use in the propylene hydrogenation method, a 0.5% Pt–Al_2O_3 catalyst was prepared by impregnating a platinum precursor, dihydrogen hexachloroplatinate ($H_2PtCl_6 \cdot 6H_2O$, 99.99% metal basis) on an Al_2O_3 support (basic, gamma, 99.99% metal basis). The precursor and the support were obtained from Alfa AESAR. Deionized water was used as the solvent for the precursor material for impregnation by incipient wetness method. The catalyst was dried in air at 120 °C for 5 h and then calcined for 3 h at 500 °C. The platinum dispersion was measured to be 41 ± 2%.

The reactions were carried out under differential and integral conditions. Under differential conditions, 0.1 g of a catalyst mixed with 0.1 g of SiC (diluent) was subjected to steam reforming at five temperatures 450, 480, 500, 530 and 550 °C, 1.09 atm total pressure, 55,400 h^{-1} GHSV and 146 mL/min (STP) total flow rate. The H_2O to C molar ratio was 2 (stoichiometric ratio). The conversion was always less than 10%. The measurements were taken after 1 h of reaction at a particular temperature until reproducible results were obtained. The integral conditions were 550 °C, 1.09 atm total pressure, 12,000 h^{-1} GHSV and 107 mL/min (STP) total flow rate. The catalyst weight used was 0.5 g.

The chemisorption studies were carried out in a Quantachrome CHEMBET-3000. A total of 2 g catalyst was placed in the sample holder. The catalyst was cooled down to room temperature after heating it in H_2 at 500 °C to remove the physisorbed water and to reduce the platinum to its metallic state. A total of 2 mL CO was injected into the He stream at the injection port for the chemisorption. A TCD measured the CO gas that was not chemisorbed on the catalyst. The CO injection was continued until saturation, which was indicated by a constant CO peak in the SRI PeakSimple data acquisition system. The CO chemisorption at –78.5 °C was carried out by immersing the sample holder in a dry ice bath.

The propylene hydrogenation reactor consisted of a 0.25-inch quartz U tube containing a quartz wool bed that supported the catalyst. The flow rate of propylene, hydrogen and nitrogen were controlled by the UNIT mass flow controllers. The gases were mixed before entering the reactor. The heat required for pretreatment was supplied by a furnace encompassing the reactor. The furnace was controlled using the temperature from a thermocouple at the top of the catalyst bed. The temperature required to carry out the propylene hydrogenation reaction (0 °C) was achieved by immersing the reactor in an ethylene glycol cooling bath. A sample of the product gases was taken in the six-way valve and injected into the GC which was used to analyze the product gases of the steam reforming reactions.

The propylene hydrogenation was conducted under differential conditions. A total of 20 mg 0.5% Pt–Al_2O_3 catalyst was mixed with 200 mg of SiC and used as a catalyst for the reaction. The catalyst was pretreated by reducing it in H_2 at 500 °C for 1 h. It was then cooled down to room temperature. The reactor was then immersed in an ethylene glycol cooling bath to maintain the reaction temperature at 0 °C. The total flow rate and the space velocity were 128 mL/min and 48,700 h^{-1}, respectively. The reaction product was sampled after 1 h of reaction until reproducible results were obtained. The same procedure was adopted for the ceria supported catalysts.

3 Results and Discussion

The purpose of doping gadolinia in the ceria support was to increase the oxygen mobility by creating vacancies, which leads to an increase in the catalytic activity. This hypothesis was tested here. To test the effect of gadolinia doping on the activity of the catalysts, the activation energy was calculated from the Arrhenius plot which is shown in Fig. 1. The slope of the straight lines was used to calculate the activation energy of the catalysts. It was then compared to the corresponding steam reforming activity (hydrogen yield) at 550 °C, as shown in Fig. 2. The hydrogen yield was measured as soon as the integral steam reforming reactions were stabilized. The error bars in the figure represent the standard deviation of the data, obtained by multiple experiments. Figure 3 shows the correlation of hydrogen yield to Pt dispersion.

The correlation tests between the various parameters such as gadolinia composition, activation energy, H_2 yield, isobutane conversion (at 550 °C), and platinum dispersion (discussed later) are shown in Fig. 4. Even though, the H_2 yield and the isobutane conversion are not necessarily coupled to each other, Fig. 4(a) shows that there was a very good correlation between them (R^2 = 0.99). Therefore, H_2 yields were chosen to analyze the activation energies of the catalysts in Fig. 2.

The Pt-CGO-5 catalyst had the smallest activation energy and it increased with the gadolinia content. The

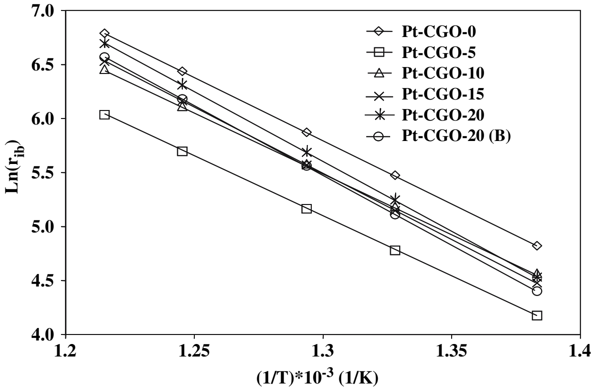


Fig. 1 Arrhenius plot to calculate the activation energy of 0.5% Pt-CGO-0 to 20 catalysts. The unit of the rate of isobutane consumption (r_{ib}) is millimol/s g

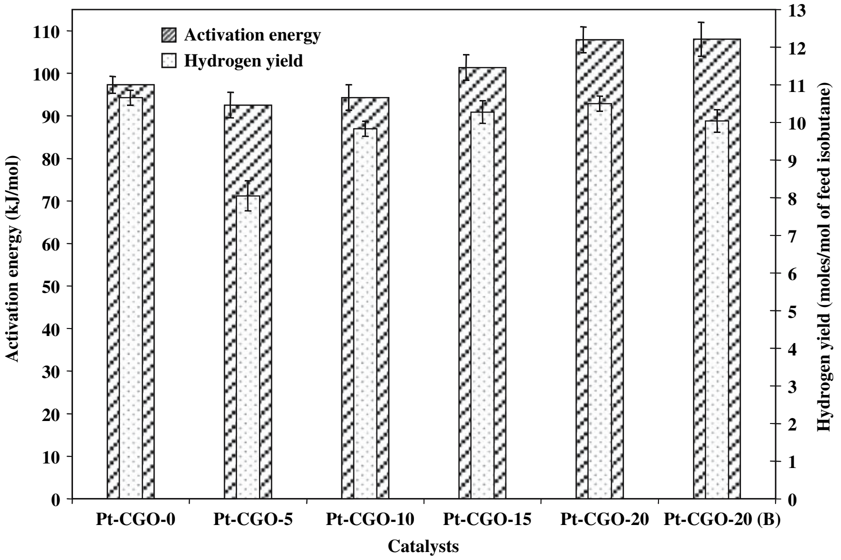


Fig. 2 Comparison of activation energy and hydrogen yield of 0.5% Pt-CGO-0 to 20 catalysts. The error bars represent the standard deviation of the data, obtained by multiple experiments

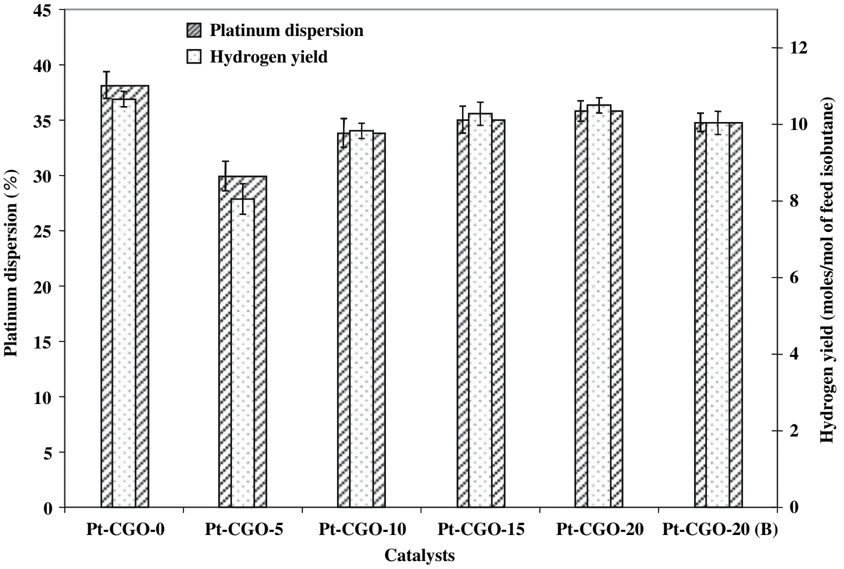


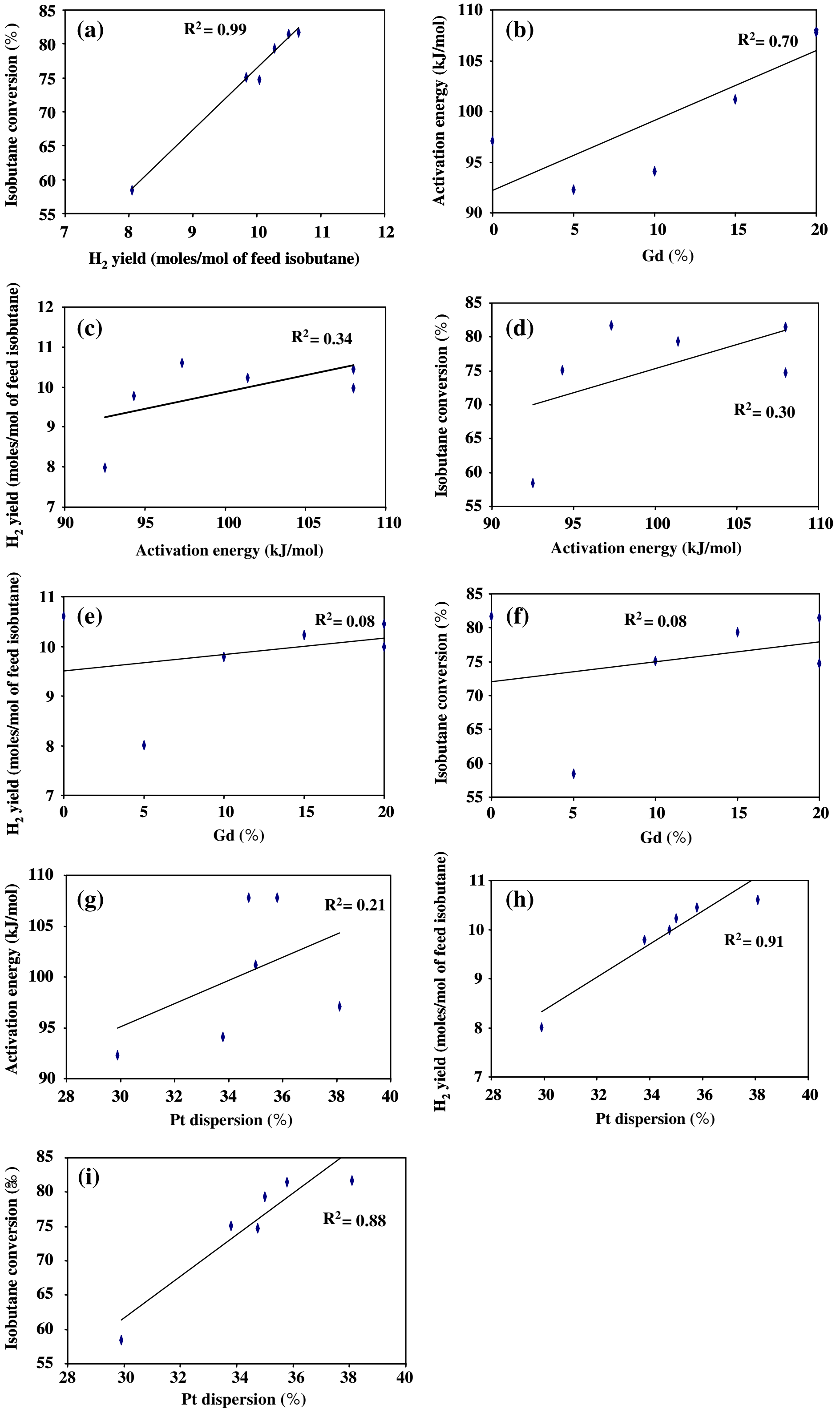
Fig. 3 Comparison of platinum dispersion and hydrogen yield of 0.5% Pt-CGO-0 to 20 catalysts. The error bars represent the standard deviation of the data, obtained by multiple experiments

activation energies of the catalysts with gadolinia content more than 10% were greater than the catalyst without any gadolinia doping. The activation energies of the Pt-CGO-20 and the Pt-CGO-20 (B) catalysts were the same, which could be because of the same gadolinia composition in the catalysts. The activation energy of the Pt-CGO-5 catalyst was the lowest among the catalysts considered, which could be due to the presence of gadolinia. However, this difference was very small and was within the margin of experimental error. The correlation between the gadolinia doping and activation energies of the catalysts as shown in Fig. 4b was not very good ($R^2 = 0.70$). Consequently, the influence of gadolinia composition on the activation energy of the catalysts was minimal.

The hydrogen yields and the isobutane conversion of the catalysts did not correlate well with the activation energies and gadolinia composition of the catalysts as shown in Fig. 4c–f. The catalysts with lower activation energies had lower activity for the hydrogen production compared to the catalysts with higher activation energies as shown in Fig. 2. Even though the Pt-CGO-20 and the Pt-CGO-20 (B) catalysts had the same activation energies, they had different activity. The catalysts with lower activation energy should have higher catalytic activity according to our previous work [24]. This suggests another parameter influenced the activity of the catalysts in addition to the activation energies. The platinum dispersion on the supports was considered as a possible factor, and it was not incorporated in our previous work [24]. The correlation between platinum dispersion and activation energies will also be analyzed.

The platinum dispersion on the fresh catalysts shown in Fig. 3 was estimated by the propylene hydrogenation

Fig. 4 Correlation tests between isobutane conversion (at 550 °C), H_2 yield (550 °C), activation energy, gadolinia composition, and platinum dispersion



method. The catalyst without the gadolinia doping had the highest platinum dispersion and the catalyst with the 5% gadolinia doping had the least platinum dispersion. The platinum dispersion on the Pt-CGO-20 catalyst was slightly higher than the Pt-CGO-20 (B) catalyst. The platinum dispersion in all the catalysts ranged between 29 and 38%. The correlation between platinum dispersion and activation energy was not good ($R^2 = 0.21$), which is shown in Fig. 4g. This suggests that the influence of the platinum dispersion on the activation energy was not significant.

There was a good correlation between the platinum dispersion and the activity of the catalysts, as shown in Fig. 4h and i. The hydrogen yield of the catalysts increased with an increase in the platinum dispersion as shown in Fig. 3. Even though the Pt-CGO-20 and the Pt-CGO-20 (B) catalysts had the same gadolinia doping they had different reforming activity because of the different platinum dispersions. So, the platinum dispersion on the CGO supports appears to influence the activity of the catalysts for the steam reforming reaction, and its influence overwhelmed any influence from the gadolinia composition. The correlation tests show that the hydrogen yield and the isobutane conversion follow the platinum dispersion much better than the gadolinia content.

The platinum dispersion on the CGO-20 (B) support was also estimated by CO chemisorption at room and dry ice temperature assuming a 1:1 stoichiometry of the CO chemisorbed and the platinum dispersed on the surface of the support. Primet et al. [25] also used the same assumption to calculate the platinum dispersion on ceria and niobia supports by O_2 or H_2 chemisorption. The platinum dispersion was 65± 3% and 59 ± 2% at room and dry ice temperature, respectively. The platinum dispersion estimated at dry ice temperature was lower than the room temperature chemisorption, suggesting a hindrance of CO spillover from the metal to the support. Further studies must be done to corroborate the complete hindrance of the spillover phenomena at –78.5 °C. However, the platinum dispersion of the catalyst estimated by the propylene hydrogenation method was much lower than the numbers obtained by the chemisorption methods. This indicated a significant amount of spillover of the CO from the metal to the support at room and even dry ice temperature.

To estimate the amount of CO chemisorbed on the CGO support in the absence of the platinum, the CO chemisorption on the CGO support was carried out at room and dry ice temperature. There was negligible chemisorption at both the temperatures.

4 Conclusion

The gadolinia content in Pt/CGO catalysts on steam reforming activity was compared to the activation energy. In the right proportion (5%), the gadolinia doping marginally lowered the activation energy of the catalyst compared to that without any gadolinia doping. The activation energy of the catalysts slightly increased with the gadolinia composition, and the catalysts with the same gadolinia composition had the same activation energy. However, the influence of gadolinia composition on the activation energy of the catalysts was minimal. The activation energies of the catalysts did not correlate well with the reforming activity of the catalysts.

The platinum dispersion on all the catalysts estimated by the propylene hydrogenation method and the reforming activity of the catalysts showed a good correlation. The activity of the catalysts increased with the platinum dispersion. The influence of platinum dispersion on the activity of the catalysts overwhelmed the influence of gadolinia doping on the catalysts.

The platinum dispersions on the CGO-20 (B) support estimated by CO chemisorption at room and dry ice temperature were higher than the value estimated by the propylene hydrogenation method because of the spillover of the CO from the metal to the support. This confirms that CO chemisorption is not a good method to estimate the platinum dispersion on CGO supports.

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