Korean J. of Chem. Eng., **5**(1) (1988) *14-18*

DEACTIVATION PHENOMENA OF SUPPORTED PLATINUM CATALYSTS DURING THE HYDROGENATION OF CYCLOPROPANE

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(Received 25 February 1987 • accepted 29 May 1987)

Abstract—Cyclopropane hydrogenation reaction was performed in a differential reactor operating at atmospheric pressure, 50°C and H_2/C_3H_6 ratio of 9, and the deactivation of the catalysts during the reaction was investigated by observing the effects of the supports and the size of platinum crystallites. Owing to the accumulation of the carbonaceous materials the platinum catalysts dispersed on the acidic supports such as γ-Al_2O_3, SiO_2-Al_2O_3 and Y-zeolite deactivated significantly, while no detectable deactivation was observed for the catalysts on the non-acidic supports of SiO_2 and active carbon. In addition smaller platinum particles on acidic supports were more vulnerable to the catalyst deactivation.

INTRODUCTION

Reactions of hydrocarbons over group VIII metal catalysts are always accompanied by the formation of carbonaceous deposits on the active surface, and the amounts of deposits depend on the operating conditions of temperature, pressure and feed composition.

Platinum catalysts are known to be active for many hydrogenation reactions, and their deactivations have received considerable attention[1,2]. Although cyclopropane hydrogenation reaction over supported platinum catalysts was studied in several papers[3-6], little works have been done on the deactivation of the platinum catalysts during cyclopropane hydrogenation.

The aim of the present study was to investigate the influence of both the support and the size of the platinum metal particles on the deactivation of the supported platinum catalysts during cyclopropane hydrogenation.

EXPERIMENTAL

Materials and Catalysts

Hydrogen(Matheson, 99.999%) and helium (Matheson, 99.999%) were further purified by passing them through an Oxytrap(Alltech) followed by a molecular sieve trap. A cupper-amine trap was used to remove the impurity of propylene present in cyclopropane (Matheson, 99.5%). Oxygen (Matheson 99.95%) was used without further purification.

The supports used in the present study were γ-Al_2O_3 and NaY zeolite from Strem Chemicals, and SiO_2 and SiO_2-Al_2O_3 from Ventron Corp.. Active carbon-supported platinum catalyst of 1wt% loading was provided from Engelhard.

All the catalysts except for zeolite-supported one were prepared by an aqueous impregnation method. Filling the pores of the supports with an aqueous solution of $H_2PtCl_6 \cdot 6H_2O$ (Strem Chemicals), the catalysts were dried in air at 85°C for 24 h. Zeolite-supported platinum catalyst was prepared through a conventional ion exchange method. An aqueous 0.04 N Pt(II) $(NH_3)_4Cl_2$ (Strem Chemicals) solution was mixed with 5 g sample of NaY zeolite, and the mixtures were stirred continuously at 50°C for 12 h. After being ion exchanged, the catalyst was filtered and washed sufficiently with deionized water to remove remaining metal salt solution which was not yet ion exchanged, and was dried in air at 85°C for 24h.

After preparation all the catalysts were precalcined with air at 400°C for 3 h and were reduced with hydrogen at 480°C for 2 h.

Thermogravimetric Analysis

To obtain a better understanding of the carbonaceous deposits, temperature programmed oxidation of the deposits was performed in a thermogravimetric flow system (Dupont Instruments 951). About ten milligram samples were placed in a platinum container and were reduced with hydrogen at 480°C for 2 h. The

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stream of hydrogen was then switched to that of helium and the sample was remained at the temperature another 30 min followed by cooling to the reaction temperature. After the hydrogenation of cyclopropane being performed for 2 h, temperature programmed oxidation of the deposits was carried out with flowing air at 20 cc/min by heating the sample linearly at 20°C/min.

Chemisorption

The adsorption isotherms of hydrogen were measured at room temperature in a conventional Pyrex glass volumetric adsorption apparatus.

The adsorption uptakes were obtained by extrapolating the straight portion of the isotherms to zero pressure, and the dispersions of platinum metal were calculated from the uptakes at zero pressure by assuming the adsorption stoichiometry of H/Pt to be one. The dispersions of the catalysts used in the present study are listed in Table 1.

Hydrogenation of Cyclopropane

Hydrogenation of cyclopropane was performed in a quartz tubular microreactor operating at atmospheric pressure, temperature of 50°C and H_2/C_3H_6 ratio of 9. To obtain a reactant of homogeneous composition, a premixer was employed. Conversions were always kept below 5 % to minimize the heat and concentration gradients across the catalyst bed. The activity was expressed in terms of turnover number for cyclopropane conversion, i.e., the number of cyclopropane molecules converted per catalytic site per second. The product gases were separated in a 1/8 in. × 15 ft. column packed with Porapak Q at the temperature of 80°C and were analyzed by using a gas chromatograph (Gowmac 750, FID) with a digital integrator (Hewlett Packard 3388A).

Table 1. Dispersions of the supported platinum catalysts used in the present study.

catalyst	Pt loading (wt %)	dispersion* D(%)
Pt/γ-Al_2O_3	2	97
	5	63
	10	50
Pt/SiO_2	0.5	93
	1	84
	2	33
Pt/SiO_2-Al_2O_3	2	54
Pt/Y-zeolite	2	55
Pt/Active carbon	1	69

* Dispersions were calculated from the hydrogen chemisorption.

RESULTS AND DISCUSSION

Support Effects

The changes in the activity with reaction time are shown in Figure 1 and 2. The activities of the alumina-,silica-alumina- and zeolite-supported platinum catalysts continue to decrease with reaction time, while the activities of the silica- and active carbon-supported platinum catalysts remains almost constant.

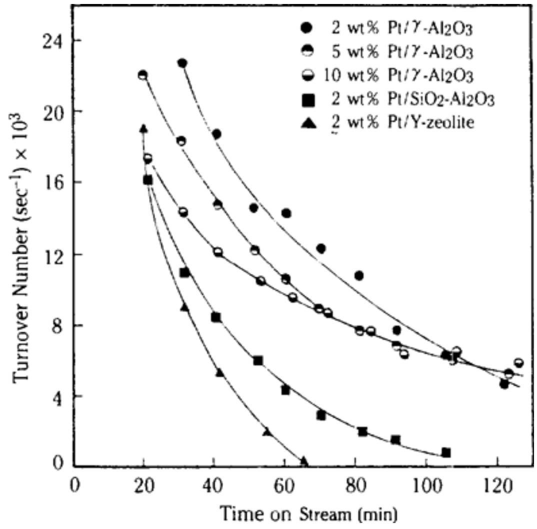

Fig. 1. The changes in activity with reaction time on the γ-Al_2O_3, SiO_2-Al_2O_3 and Y-zeolite supported platinum catalyst.

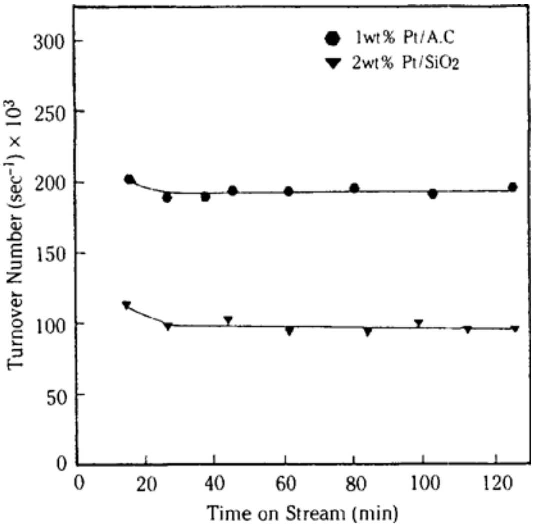

Fig. 2. The changes in activity with reaction time on the silica and active carbon-supported platinum catalysts.

This confirms that the deactivation is favored for the catalysts dispersed on the acidic supports. Although NaY zeolite alone is almost neutral by the compensation of the negative charges of the aluminosilicate framework with Na cations, the reduction of platinum ion in zeolite-supported catalyst with hydrogen accompanies the production of Brønsted acids sites ($Pt^{2+} + H_2 \rightarrow Pt^0 + 2H^+$), thereby making the reduced zeolite-supported catalyst acidic[7,8].

In Figure 1 it is also noted that the decreasing rate of the activity for alumina-supported catalysts becomes less severe with increasing platinum loading. Since the increase in platinum loading resulted in the increase in the size of platinum crystallites (Table 1), the size of platinum crystallites is also believed to affect the deactivation of the catalysts.

Effect of Crystallite Size

To observe the effect of platinum crystallite size on the catalyst deactivation, catalysts having various sizes of platinum crystallites were obtained by sintering the 2wt% Pt/γ-Al_2O_3 catalysts at different temperatures under oxygen stream.

With increasing sintering temperature the platinum particle size increased and the catalyst deactivation became slower (Figure 3). But since the treatment of γ-Al_2O_3 at high temperature may accompany the phase transformation, the effect of the morphological changes should be considered. When γ-Al_2O_3 is transformed to the α-state, surface area and pore volume of the support decrease[9-10]. Such morphological changes in a catalytic support accompanied a loss of catalytic activity by encapsulation of the metal[9]. Kozlov et al.[10] have shown that γ-Al_2O_3 with dispersed platinum metal did not change morphologically up to the temperature of 800°C. To verify this the surface areas and pore volumes were measured and the results are shown in Table 2. As expected, little changes are observed. Therefore the possible effect of morphological changes in γ-Al_2O_3 must be negligible.

Table 2. Surface areas and pore volumes of the 2 wt% Pt/γ-Al_2O_3 catalysts treated with oxygen at various temperatures.

temperature* (°C)	surface area (m^2/g)	pore volume (cc/g)
**	205	0.21
600	201	0.21
700	194	0.19

* Temperatures at which the catalysts were treated with oxygen.

** The catalyst which was not further treated with oxygen.

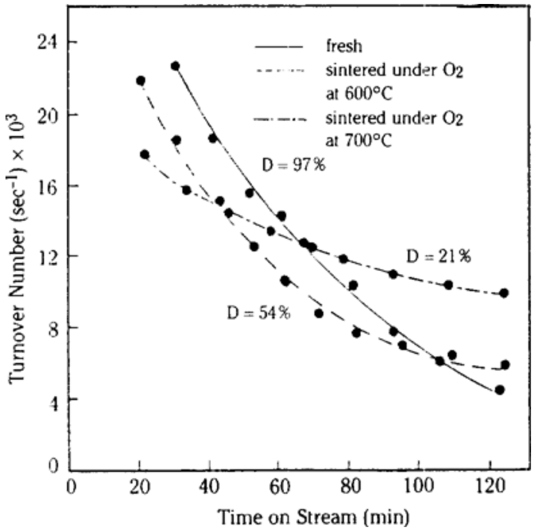

Fig. 3. Effect of the size of platinum crystallites on the catalyst deactivation over 2 wt% Pt/γ-Al_2O_3.

Thermogravimetric Analysis

Figure 4 shows the accumulation of carbonaceous materials on the supported platinum catalysts. The amounts of cyclopropane and hydrogen adsorbed on the supports and platinum container, which were measured from the independent experiments on the supports and platinum container alone, were subtracted from the total amounts of carbonaceous materials accumulated on the supported platinum catalysts. Their contributions, however, were always small (less than 5%) irrespective of the species of the support.

No apparent accumulation is observed during the first 5 minutes after which a rapid increase in the accumulation occurs. The elapsed time from beginn-

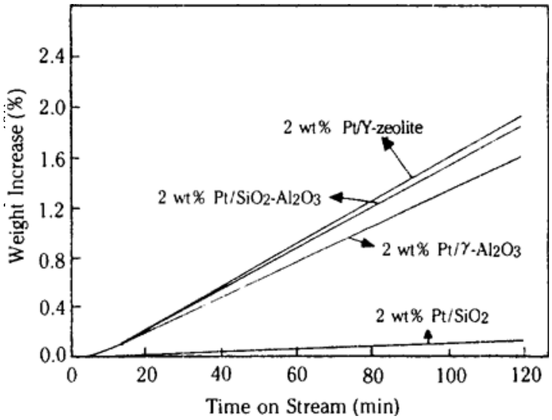

Fig. 4. The accumulation of the carbonaceous materials on the supported platinum catalysts.

ing to when the carbonaceous materials begin to accumulate seems to be required in order for enough nucleates to be formed and to accelerate the accumulation of carbonaceous materials. It is noted from Figure 4 that the accumulation of carbonaceous materials is significant for the platinum catalysts dispersed on the acidic supports. On the silica- and active carbon-supported platinum catalysts, however, no detectable amounts of carbon deposits were observed. The deactivation of the platinum catalysts on the acidic supports is then undoubtedly believed to be due to the accumulation of the carbonaceous deposits on the active surfaces.

The results of the temperature programmed oxidation of the accumulated carbonaceous materials are shown in Figure 5. The oxidation rate was defined by the amount of carbonaceous materials which disappeared through the reaction with air per weight of the aged catalyst and time. Most of the carbonaceous materials are shown to be oxidized at around 120°C.

Regeneration

The aged catalysts were regenerated with oxygen at 300°C for 30 minutes and their activities were measured again (Figure 6 and 7). The dispersion of the 2 wt% Pt/γ-Al_2O_3 catalyst decreased with regeneration, which is believed to result from the sintering of platinum under oxygen atmosphere. The activity of the regenerated catalysts was not restored to the value of the fresh catalyst. In the 5 wt% Pt/γ-Al_2O_3 catalyst which contains larger platinum particles than 2 wt% Pt/γ-Al_2O_3, both the dispersion and activity were influenced by regeneration only slightly. This implies that the activity may probably depend on the size of platinum particles. In Figure 8 are shown the changes in activity with dispersion of the silica-supported platinum catalysts on which no detectable catalyst deactivation occurred. The dispersions of the silica-supported catalyst were controlled by changing the platinum loading and by sintering the 0.5 wt% Pt/SiO_2 catalyst with oxygen at different temperatures. The activity does not change at low dispersion level, while at high dispersion level about two-fold increase in activity is shown with increasing dispersion.

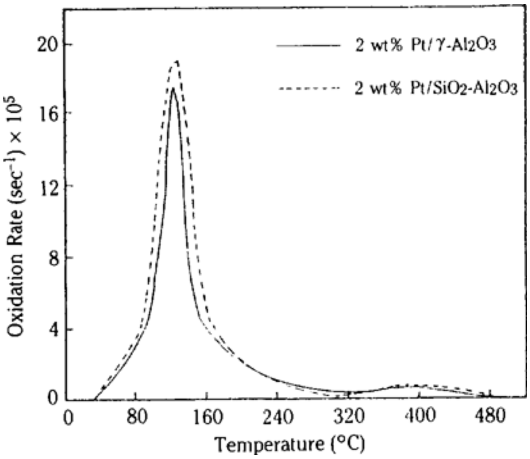

Fig. 5. The curves of temperature programmed oxidation of the carbonaceous materials.

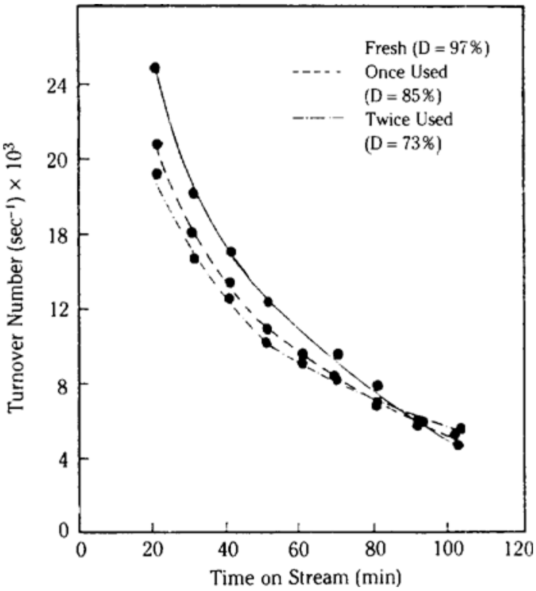

Fig. 6. Effect of regeneration on the activity of 2 wt% Pt/γ-Al_2O_3 catalyst.

The activity pattern at high dispersion level can be

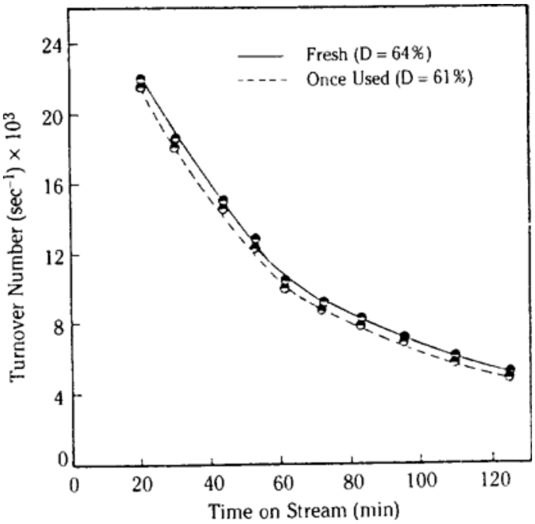

Fig. 7. Effect of regeneration on the activity of 5 wt% Pt/γ-Al_2O_3 catalyst.

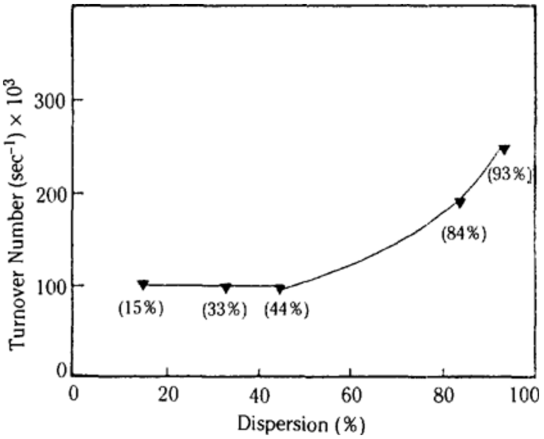

Fig. 8. The changes in activity with the dispersion of platinum metals of silica-supported catalysts.

interpreted in terms of structure-sensitive nature of the reaction, i.e., higher activity on lower coordination sites. Boudart et al.[11], however, showed that the hydrogenation of cyclopropane on platinum metal is a structure-insensitive reaction. The changes in activity by two-fold is so small that it can not be ascribed to the structure-sensitive nature of the reaction. About two-fold changes in activity with dispersion can result from the morphological changes in platinum which may occur during catalyst treatments or an interaction between small platinum particles and support.

The incomplete restoration of the activity by regeneration in the 2 wt% Pt/γ-Al_2O_3 catalyst seems then to be due to the changes in platinum morphology, interaction between platinum and support, or some other phenomena which can result from the sintering under oxygen atmosphere.

CONCLUSIONS

The deactivation of the supported platinum catalysts was significantly influenced by the nature of the supports and the size of the platinum crystallites.

During cyclopropane hydrogenation the catalyst deactivation by the accumulation of the carbonaceous materials was observed for the platinum catalysts dispersed on the acidic supports such as γ-Al_2O_3, SiO_2-Al_2O_3 and Y-zeolite, while for the platinum metal dispersed on the non-acidic supports such as silica and active carbon no detectable amounts of carbonaceous materials were accumulated and the activity remained almost constant.

Catalyst deactivation was also affected by the size of platinum crystallites. Smaller platinum particles on acidic supports were more vulnerable to the catalyst deactivation by the accumulation of carbonaceous materials.

By regeneration the activity of the smaller platinum particles was not restored to that of the fresh catalysts, while in the larger platinum particles the activity was recovered almost completely.

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