

## Catalytic Action of Platinum on Coke Burning

Bifunctional catalysts are used for different hydrocarbon processes, like naphtha reforming. Among these catalysts Pt/Al<sub>2</sub>O<sub>3</sub> is a very important one. The metallic function, Pt, is supported on the acid function, Al<sub>2</sub>O<sub>3</sub>, whose acidity is promoted by chlorine addition. During reforming many reactions take place (cracking, isomerization, dehydrocyclization) and coke is simultaneously deposited on the catalyst decreasing its activity. This coke is burnt out with diluted air.

The objective of this note is to study the influence of Pt on the burning temperature of the coke produced during pure hydrocarbon reforming.

### EXPERIMENTAL

**Catalysts.** Several catalysts, whose properties are shown in Table 1, were used. Some of them have both metallic and acidic functions, and others have only one function. Catalyst A, Al<sub>2</sub>O<sub>3</sub> CK 300 provided by Cyanamid Ketjen from Amsterdam, was chlorinated following the method of Castro *et al.* (1). Catalysts B and C were prepared following (2) with Al<sub>2</sub>O<sub>3</sub> CK 300 as support. Catalyst D was also prepared following (2) but using as support a previously sinterized Al<sub>2</sub>O<sub>3</sub> obtained heating CK 300 in air during 48 h at 900°C. Catalyst E is a commercial dehydrogenating catalyst whose acidity was destroyed by adding Li. Catalyst F is Pt/SiO<sub>2</sub> and is free of chlorine; it is the catalyst identified as 63.5-SiO<sub>2</sub>-Ion X-L in (3) and was provided by Professor J. Butt from Northwestern University.

**Reactants.** Analytical-reagent-grade *n*-hexane and methylcyclopentane were used,

and pure AGA hydrogen dehydrated previously was the reactants' carrier.

**Catalytic activity.** Activity was measured at 500°C and atmospheric pressure in a flow equipment using 1 g of 30- to 60-mesh catalyst. The feed was hydrogen saturated with the hydrocarbon at a proper temperature to obtain a H<sub>2</sub>-to-hydrocarbon molar ratio of 2. The length of the run was 2 h.

**Temperature-programmed oxidation (TPO).** The coke burning was studied by TPO in catalysts used in runs where *n*-hexane or methylcyclopentane were fed. The TPO was done with an Aminco Thermoanalyzer with oxygen as dynamic gas, and fresh catalysts as references. In this way the signal of the differential thermal analysis was due to the oxidation of the carbonaceous material at programmed temperature. The heating rate was 24°C/min and the oxygen flow rate 60 cm<sup>3</sup>/min. To see if the internal diffusion process controls the rate of combustion, a problem studied by Weisz and Goodwin (4), the catalyst sample containing more coke was ground and sieved and the TPO of the samples thus obtained were performed. All the TPO have the same shape, ruling out the possibility of diffusion control.

### RESULTS AND DISCUSSION

Figure 1 shows the TPO obtained when *n*-hexane was fed. Catalyst A, with only the acid function present, produced a very small coke deposition (so that the signal was very small) with a peak at around 490°C. Catalyst B, with both functions present, showed peaks at 280 and 490°C. From that difference it can be assumed that the burning at 280°C corresponds to coke on the metallic function and that the burn-

TABLE I  
Catalyst Properties

Catalyst:	A	B	C	D	E	F
Pt (%)	0	0.37	1.6	0.37	0.75	0.49
Support	Al <sub>2</sub> O <sub>3</sub> 0.9% Cl	Al <sub>2</sub> O <sub>3</sub> 0.9% Cl	Al <sub>2</sub> O <sub>3</sub> 0.9% Cl	Al <sub>2</sub> O <sub>3</sub> 0.3% Cl	Al <sub>2</sub> O <sub>3</sub> 0.5% Li	SiO <sub>2</sub>
Surface area (m <sup>2</sup> /g)	180	165	165	56	140	285
Porosity (cm <sup>3</sup> /g)	0.50	0.48	0.46	0.80	1.4	1.2

ing at 490°C corresponds to coke on the acidic function (5). This result is similar to that of Barbier *et al.* (6), who found two peaks in the TPO of the coke obtained from cyclohexane on Pt/Al<sub>2</sub>O<sub>3</sub>. Catalyst C presented the peak at a lower temperature than that found in B. Catalyst D had a metal-to-acid ratio similar to that in catalyst C and its coke burnt at a similar temperature. When catalyst E was used, the coke burnt at a lower temperature. In all cases, when the metal-to-acid ratio increased the temperature of coke burning decreased. When only Pt was present, as was the case of catalyst F, the coke burnt at the lowest temperature.

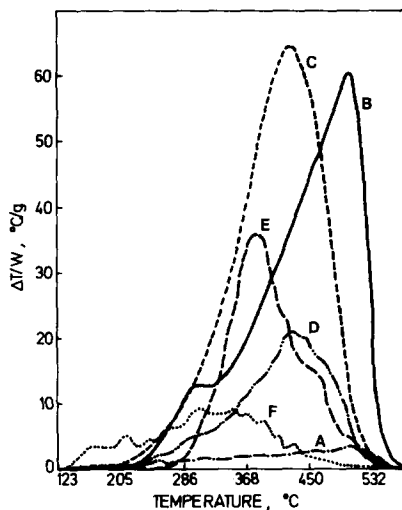


FIG. 1. TPO of the coke on catalysts used in *n*-hexane reforming.

Figure 2 shows the TPO of the coke on the catalysts when the feed was methylcyclopentane. Al<sub>2</sub>O<sub>3</sub> showed a peak at high temperature. In that case, in order to obtain a greater amount of coke, the run lasted 10 h. For the other catalysts the length was 2 h. Similar to the results found when *n*-hexane was fed, the catalysts with higher metal-to-acid ratio have lower burning temperatures.

The curves of Figs. 1 and 2 show different peak heights. This is because of the dif-

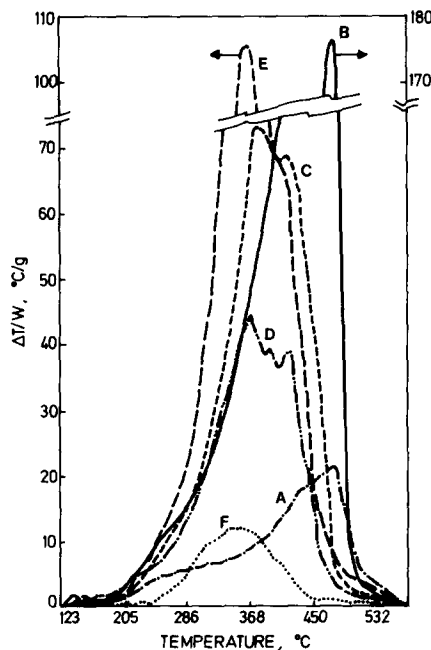


FIG. 2. TPO of the coke on catalysts used in methylcyclopentane reforming.

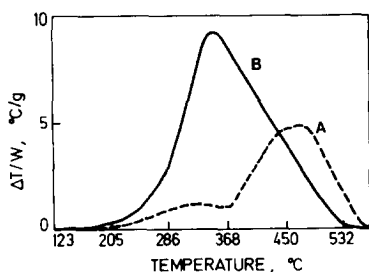


FIG. 3. TPO of the benzene-methanol-soluble fraction of coke produced on Pt/Al<sub>2</sub>O<sub>3</sub> during naphtha reforming when it was impregnated on Al<sub>2</sub>O<sub>3</sub> (curve A) and Pt/Al<sub>2</sub>O<sub>3</sub> (curve B).

ferences on the reactant conversion levels, on the kind of products obtained with each of the catalysts, and on their different tendencies to produce coke deposition. Pt/Al<sub>2</sub>O<sub>3</sub> is catalytically more active than Al<sub>2</sub>O<sub>3</sub> and a greater amount of coke is produced on it.

The differences in the coke oxidation temperatures could be due to the fact that the nature of the coke formed when using different catalysts was not the same. In order to see whether these differences in temperature exist even when the carbonaceous deposit is the same, other experiments were carried out. Catalysts A and B were impregnated with a soluble part of the coke produced when reforming a 60–160°C range naphtha (5) on catalyst B. The soluble part was obtained by extraction with a benzene-methanol solution (7) during 24 h in a Soxhlet. After the impregnation on A and B and evaporation of the solvent, the TPO of both samples were performed. The results are shown in Fig. 3, where it can be seen that on Pt/Al<sub>2</sub>O<sub>3</sub> the same coke fraction is oxidized at lower temperatures than on Al<sub>2</sub>O<sub>3</sub>. The presence of Pt decreased the burning temperature of the carbonaceous material. The same results were found impregnating catalysts A and B with solutions of pure compounds, like naphthalene.

Comparing the TPO of catalysts with different metal-to-acid ratios and the oxidation of the same product on different catalysts, it can be accepted that Pt catalyzes

the oxidation of the coke. The higher the metal-to-acid ratio, the lower the oxidation temperature. Similar results for Pt/Al<sub>2</sub>O<sub>3</sub> were reported by Bacaud *et al.* (8), who found that Pt decreases the oxidation temperature of graphite. For silica-alumina used in hydrocarbon cracking Weisz and Goodwin (9) showed that the presence of oxides of transition metals decreases the coke burning temperature and Chester *et al.* (10) stated that the platinum-group metals added to promote CO oxidation might also promote coke oxidation.

There is an additional factor that can reduce the coke burning temperature: when higher amounts of Pt are present, the coke can be less polymerized because of the hydrogenation of coke precursors produced during the reaction and catalyzed by Pt. The less polymerized deposit would oxidize at a lower temperature. But the catalytic action of Pt exists because even for the same carbonaceous material there is a decrease in the oxidation temperature when Pt is present.

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