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Coking Characteristics of Reforming Catalysts

Coking rates were measured for two different γ-aluminas, each with and without platinum, under near commercial conditions using a gravimetric reactor. Coke on catalyst was characterized by a Temperature-Programmed Oxidation (TPO) technique. With a naphtha feed, coke formed on both aluminas at rates related to the respective population of α-sites as measured by IR. For the corresponding Pt on alumina catalysts, coke, as measured by TPO, predominantly formed on sites associated with alumina ("alumina coke"), while coke associated with Pt ("Pt coke"), was relatively minor. With a *n*-heptane feed, under the same conditions, coke formation on both aluminas was much less than with the naphtha feed. However, the corresponding Pt on alumina catalysts generated comparatively more coke with a higher proportion associated with Pt. A correspondence between this proportion of "Pt coke" and the decline in reforming activity was observed. It is postulated that most of the coke produced during naphtha reforming with an active catalyst is formed by a reaction between α-sites on alumina and certain components in the feed via a polymerization mechanism. This type of coke has minimal effect on the reforming reactivity of the catalyst. However, in *n*-heptane reforming, about 50% of the coke also results from precursors formed from reactions with Pt. In either case, coke associated with Pt appears to be the probable cause of deactivation. © 1986 Academic Press, Inc.

INTRODUCTION

Modeling catalytic industrial processes requires a knowledge of both the kinetics of coking and catalyst deactivation (*1–3*). This is particularly important in cases of rapid deactivation and high coke deposition, such as Pt cyclic reforming of naphtha feedstocks under high severity conditions (*4*). Relating coking to deactivation could simplify the deactivation kinetics but this assumes all decline in activity is caused by coke and this may not always be true. However, if such a relationship exists, it is better derived from a fundamental understanding of the deactivation process rather than from empirical data obtained from a small window of process conditions.

Attempts have been made to model the coking process of catalysts (*5, 6*) and some insight into the kinetics has been gained, however these studies have not provided an understanding of the origin, the nature, or the location of the coke deposited. The nature of reforming coke is complex and is very much dependent on reaction conditions and the nature of the catalyst and feed (*7, 8*). Coke location on a bifunctional reforming catalyst where several possibilities for deposition exist, appears equally complex (*9, 10*). In addition Pt sites are not all equivalent as shown by the large distribution of CO binding states in TPD studies (*11, 12*), and alumina is equally multisited as observed by Infrared (*13*).

Recently a Temperature-Programmed Oxidation (TPO) method has been reported which claims to differentiate coke formed on Pt from that formed on alumina (*14, 15*). This study uses this technique in conjunction with a microgravimetric reactor to investigate the coking characteristics of Pt catalysts and alumina supports with two different feeds and under different conditions.

METHODS

Gravimetric reactor. The gravimetric reactor system consisted of a Cahn 2000 Microbalance housed in a stainless-steel pres-

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sure casing, similar in design to the glass housing normally supplied with Cahn balances. The actual reactor was a 45-cm-long, 2.5-cm-o.d. stainless-steel tube hanging from the balance chamber. A stainless-steel wire mesh basket centrally positioned down the reactor was suspended from the weighing arm of the balance via a quartz fiber.

Reactant gases were fed in below the basket and exited through a sidearm about 5 cm above the catalyst. A separate flow of He passed continuously through the balance chamber and down to the same upper sidearm outlet where the reacted gases exited, thus allowing the balance to be isolated from the products of reaction. Flow rates and pressures were maintained by mass and pressure control valves. The reactor effluent was depressurized through a heated valve and into an in-line gas chromatograph for analysis. Reforming activities are reported in terms of the weight percentage of aromatics produced.

Briefly the procedure consisted of weighing out 1 g of catalyst (14–20 mesh) into the wire mesh basket. The catalyst was then pretreated within the reactor by heating to 504°C in hydrogen for 3 h. Heat was supplied by a split-tube furnace surrounding the reactor with temperature controlled by a thermocouple placed directly beneath the basket. On introducing the feed, via a Ruska pump, a sharp increase in weight of the catalyst was observed (~2 mg) due to hydrocarbon adsorption. After this initial increase all weight gains were assumed to be caused by coke lay-down.

Accelerated coking conditions were used for most of the reforming runs so that a measurable amount of coke could be obtained within a 20-h period. These conditions were a pressure of 786 kPa, a temperature of 504°C, a weight hourly space velocity (WHSV) of 6, and a hydrogen-to-hydrocarbon mole ratio of 3. The hanging basket reactor configuration allowed a certain amount of bypassing, hence the reported space velocity was only approximate. Duplicate runs with a catalyst of different particle sizes confirmed that the system was not limited by diffusion.

Temperature-programmed oxidation (TPO). The method used was essentially that of Parera *et al.* (*15*). The apparatus consisted of a DTA instrument (a DuPont 1090 Thermal Analyzer with a 1600°C cell). Each coked catalyst was finely ground and approximately 25 mg was packed into a Pt sample cup. With a constant flow of dry air at 50 cm^3/min, the sample was heated rapidly to 200°C and held at this temperature until a stable baseline was obtained, and then heated at 20°C/min to 900°C or until the coke had been completely oxidized.

Materials. Two different commercial γ-aluminas were used, Cyanamid's Aero 1000 and Kaiser's SAS. Pt catalysts were prepared by the incipient wetness technique of impregnating each alumina with chloroplatinic acid to a level of 0.5 wt% of equivalent Pt. Each catalyst was dried and then calcined at 500°C for 2 h in air. In addition, two commercial Pt/Al_2O_3 catalysts, Cyanamid's PHF5 and PHF5A were used in two sets of runs. Designations and properties of each catalyst and alumina are given in Table 1 along with acidity measurements determined by TPD of the second or β peak of *t*-butylamine (*16*). Exposed Al ions or α-sites were measured by strongly held CO_2 adsorption bands at 2360 cm^{-1} in the infrared (*17*). Spectra are shown in Fig. 1. The hydrocarbon feeds were *n*-heptane (Aldrich Chemical, 99%) and a Mid-Continent heavy virgin naphtha of API gravity 54.9 and boiling range of 204 to 386°F. Prior to use both feeds were dried over 4A molecular sieve.

RESULTS

Differences in coking rates with the naphtha feed are shown in Fig. 2a for the two γ-alumina supports, A and B and the corresponding Pt catalysts C and D. The presence of Pt significantly increases the coking rate of alumina B but only slightly affects the rate of coking of alumina A. The related coke profiles shown in Fig. 2b re-

TABLE 1

Catalyst Properties

Catalyst	Source	SA ($M^2\ g^{-1}$)	PV ($cm^3\ g^{-1}$)	wt% Pt	Relative acidity (β peak) equivalent amine moles × 10^5 (*16*)
A Alumina	Cyanamid-Aero 1000	240	0.54	0	6.1
B Alumina	Kaiser-SAS	272	0.94	0	6.9
C Pt/Alumina	Impregnated A	—	—	0.50	—
D Pt/Alumina	Impregnated B	—	—	0.50	—
E Pt/Alumina	Cyanamid PHF5A	210	0.56	0.74	—
F Pt/Alumina	Cyanamid PHF5	252	0.56	0.40	—

flect the difference in the coking rates. Only one peak with a maximum at near 520°C is observed in the TPO for the alumina samples but an additional small peak at about 420°C occurs with the Pt catalysts.

The coking rates and the resulting TPO profiles obtained on aluminas, A and B, and the corresponding Pt catalysts C and D, with a *n*-heptane feed are shown, respectively, in Figs. 3a and b.

The amount of coke produced with the aluminas during these runs is considerably less than with the naphtha feed and again only one peak at 520°C is observed in the TPO spectra. The corresponding Pt catalysts, C and D, on the other hand show a large increase in coke formation compared to that produced by the aluminas, while the resulting TPO profiles show a significant difference in character. A higher proportion of the 420°C peak is shown in both cases compared to the equivalent naphtha runs.

The activity, extent of deactivation, and levels of coke after 18 h of the Pt catalysts C and D, with both the naphtha and the *n*-heptane feeds are given in Table 2. While

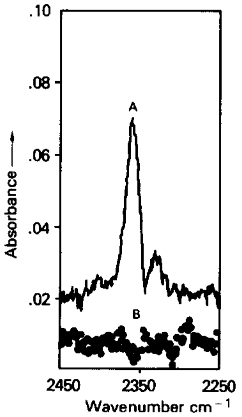

FIG. 1. Spectra of CO_2 on alumina A and B (precalcined and evacuated at 500°C). CO_2 adsorbed and then evacuated at room temperature. Background subtracted by computer.

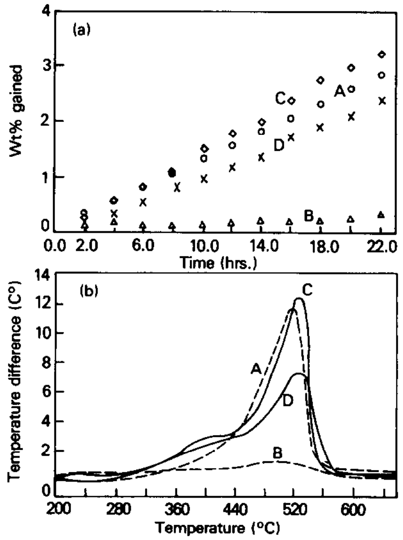

FIG. 2. (a) Coking rates on alumina A and B and Pt/alumina C and D with naphtha. Conditions: 504°C, 786 kPa, 6 WHSV, and 3/1 = H_2/hydrocarbon. (b) TPO's of coked A, B, C, and D.

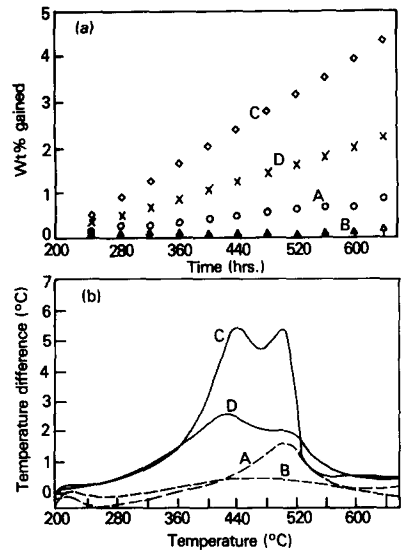

FIG. 3. (a) Coking rates on alumina A and B and Pt/alumina C and D with *n*-heptane. Conditions: 504°C, 786 kPa, 6 WHSV, and 3/1 = H_2/hydrocarbon. (b) TPO's of coked A, B, C, and D.

the activity and decline of catalyst C is similar for both feeds, there is a marked increase in the deactivation rate for catalyst D during heptane reforming.

Some further runs were also made to observe the effects of run length and chloride level with the naphtha feed and Pt catalysts, E and F.

TABLE 2

Catalyst Deactivation

Catalyst	Aromatics produced (wt%)		% Deactivation over 18 h	wt% Coke after 18 h
	1 h	18 h		
During naphtha reforming				
C (Pt/Al_2O_3A)	41	29	30	2.8
Al_2O_3A				2.3
D (Pt/Al_2O_3B)	29	18	38	1.9
Al_2O_3B				0.2
During heptane reforming				
C (Pt/Al_2O_3A)	47	31	35	3.7
Al_2O_3A				0.6
D (Pt/Al_2O_3B)	37	7	81	2.0
Al_2O_3B				0.1

The extended run was made over a period of 2 days with catalyst E, at more accelerated coking conditions than those used previously. Figures 4a and b show the coking rate and subsequent TPO profile for this run. The TPO spectrum shows broader peaks with maxima occurring at higher temperatures than the others made at lower coke levels.

The effect of chloride level on the coking rate and activity of Pt catalyst F is shown in Figs. 5a and b. The activity plotted as a function of coke level shows an increase for the higher chlorided catalyst of about 20% throughout the duration of the runs, however there is only a small increase in coking rate. Duplicate runs were made on the catalyst with the lower chloride level.

DISCUSSION

The extent of coking obtained on γ-alumina during runs with the naphtha feed as shown in Fig. 2a was unexpected, for apart from some trace amounts of gas formation, no reforming activity was observed. Furthermore a previous run with an α-alumina

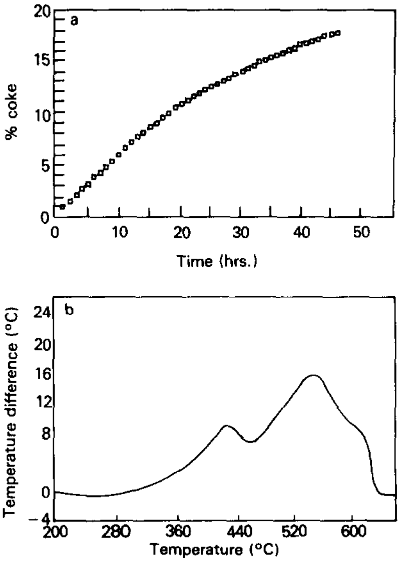

FIG. 4. (a) Coking rate on Pt/alumina E over extended period. Conditions: 516°C, 786 kPa, 6 WHSV, and 3/1 = H_2/hydrocarbon (naphtha). (b) TPO of coked E.

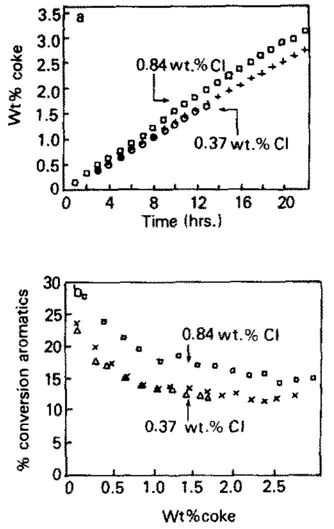

FIG. 5. (a) Coking rates on Pt/alumina F at two levels of chloride. (additional chloride was provided by HCl impregnation). Condition: 504°C, 786 kPa, 6 WHSV, and 3/1 = H_2/hydrocarbon (naphtha). (b) Deactivation as a function of coke level.

sample under the same conditions had produced no coke. The results strongly suggest the existence of sites, probably acidic, on the alumina surface which will react directly with constituents in the naphtha feed to form coke. The absence of chloride on both aluminas shows that the sites responsible for coking must be generated from the alumina itself. In addition results in Table 1 shows that the general acid character of the aluminas, as represented by the extent of interaction with an amine does not correlate with the rate of coking. However measurements of α-sites obtained by the infrared spectrum of strongly held CO_2 at 2360 cm^{-1} (i.e., CO_2 held after a 5-min evacuation and after a 500°C pretreatment) as shown in Fig. 1 clearly illustrates the proportionality between these sites and the coking occurring on the respective aluminas. α-Sites are exposed aluminum ions of the Lewis acid–base type produced by the dehydration of two adjacent hydroxyl groups and contain reactive oxide ions closely adjoining an exposed aluminum ion as discussed by Peri (*13*). They can readily polymerize olefins and as such are potential sites for coke formation. These results also indicate that all aluminas are not the same in either coking potential or acid site population.

The corresponding coking rates for the catalysts with Pt, (Fig. 2a) shows an increase of an order of magnitude over the less active alumina B, but with only a small increase (20%) over the more active alumina A. This result shows that for a catalyst made from a support containing more α-sites, more of the coke is generated independent of the Pt.

With the *n*-heptane feeds, there is however a significant increase in the rate of coking when Pt is present for both aluminas as shown in Fig. 3a. There is also an increase (35%) for the more active catalyst C than during the naphtha run. This finding is consistent with the more demanding reaction of dehydrocyclization compared to dehydrogenation, the latter process predominating during naphtha reforming (*18*).

In general, the coke rates observed in the gravimetric reactor are characterized by an apparent linearity up to about 4 wt% coke. Above this value obtained over an extended period at higher temperatures (Fig. 4), a decrease in the coke rates is observed. A recent TEM study of a Pt/alumina catalyst coked to a level of 6.8 wt% indicates that coke forms a mixture of porous carbon particles with localized stacks of aromatic rings 10 atoms arranged high around the alumina crystallites (*10*). This agrees well with the observed linearity of the coke accumulation with time up to relatively high levels which suggests that coke formation occurs by a polymerization chain mechanism on special sites of the support as has been proposed previously (*19*).

Results in Figs. 5a and b show that increasing the chloride content of a Pt catalyst only slightly affects the coking rate but that at each level of coke the reforming activity is substantially increased over the low chloride case. Since it is generally accepted that chloride addition increases the

Brønsted acidity (*20*) then Brønsted acid sites do not appear to be involved in the coking of the catalyst. A study by Parera *et al.* (*21*) however showed that coking was not entirely independent of the chloride level, but that there was a minimum at a level of 0.6% chloride which is midway between the two levels seen in Fig. 5.

TPO data. The size of each TPO profile reflects the amount of coke produced, while the character of the spectra should provide information about the location and type of coke formed. TPO profiles of coked aluminas (Fig. 2b) exhibit only one peak at the maximum of 520°C. The equivalent spectra for the Pt-containing catalysts show some increase of coke over the corresponding aluminas, but it is the appearance of a second peak at around 420°C which is more significant. This new peak is almost certainly associated with the Pt, while the higher temperature peak is related to alumina. A similar argument for these assignments has been given by others (*13, 14*).

The coke represented by this 420°C peak is most probably not coke entirely adsorbed on Pt but a combination of this with coke on alumina sites adjacent to Pt; but whatever the nature of the 420°C peak, it represents the most likely source for deactivation. Some confirmation of this is seen in the results of Table 2 with a naphtha feed, which show equivalent deactivation rates for catalysts C and D, in agreement with the similar sized 420°C peaks (Fig. 2b).

Further evidence for the existence of at least two forms of coke is seen in the quite different results obtained with the *n*-heptane feed. The higher ratio of "Pt to alumina coke" observed with catalysts C and D (Fig. 3b) compared to the equivalent naphtha runs (Fig. 2b) is again reflected in the higher deactivation rates reported in Table 2 with the same catalysts. Similarly, differences between Pt and alumina coke ratio for catalysts C and D, show the same trend. However, the absolute amount of Pt coke as observed in the TPO profiles does not correlate directly with the deactivation. This could be due to the two possible forms of "Pt coke," i.e., coke on Pt and coke adjacent to Pt. Coke precursors generated from reactions around Pt centers are more likely to be at higher concentrations in normal paraffin than in naphtha reforming since in the process of dehydrocyclization, olefinic intermediates are produced (*18*) which is consistent with the findings of other workers which shows that *n*-heptane deactivates Pt at a faster rate than methyl cyclohexane (*19*) and toluene (*22*). The coke in the vicinity of the Pt probably represent coke of a less deactivating form similar to the "alumina coke" and therefore a direct relation between deactivation and "Pt coke" does not exist, especially when coke bordering on Pt sites is present to any great extent.

In conclusion, it has been shown that:

(1) In naphtha reforming with an active Pt catalyst the rate of coking is only slightly more than with the alumina support inferring that coke is deposited predominantly on alumina. This is confirmed by TPO analysis of the subsequent coke which appears to be largely associated with alumina only. Moreover there exists a correspondence between the coking rates and the α-site or exposed aluminum ion population on different aluminas. Coke is probably formed on these sites by a polymerization mechanism as indicated by the almost constant coke rates obtained. In addition, the TPO results also show that catalysts producing similar amounts of coke associated with Pt have similar deactivation rates.

(2) In *n*-heptane reforming the difference between the amount of coke formed on a Pt catalyst and the corresponding alumina support is larger than in naphtha reforming. The subsequent TPO analysis of the coke formed on the Pt catalysts shows a higher proportion of coke associated with Pt than with the naphtha runs reflecting the localized production of more coke precursors in the vicinity of the Pt.

While a higher ratio of Pt coke to alumina coke is observed for the catalyst exhibiting

a higher activity decline, no precise relationship between the coke associated with Pt and the reforming deactivation exists.

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