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Coking Reaction by Anthracene on Acidic Aluminas and Silica–Aluminas

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Coking by anthracene was studied on aluminas and silica–aluminas of varying acidities. An increase of the alumina acidity by chloride addition leads to an increase of coke deposits at low temperatures (673–773 K), whereas the opposite effect occurs at high temperatures. Under the same conditions, the amounts of coke are greater on silica–alumina than on alumina, but the higher the coking temperature, the lower the amount of coke. Hence the coking reaction appears to be the result of a competition between polymerization of coke precursors and their destruction, which is more activated at higher temperature. The different behaviour between alumina and silica–alumina is explained by the presence of Brønsted acidic sites on silica–alumina, whereas alumina retains only Lewis acidic sites. The determination of the acidity after the coking reaction and tests carried out on catalysts where acidic sites were neutralized by ammonia adsorption bear out such a hypothesis.

INTRODUCTION

Coke deposition is a complex reaction resulting from both production and destruction of coke precursors. On supported metallic catalysts, the metal produces dehydrogenated species which can polymerize on the metallic function or on the support. On the other hand, coke precursors can be destroyed by hydrogenolysis on the metal or by cracking on the acidic sites of the support (*1–7*).

In previous work on bifunctional Pt/Al_2O_3 catalysts, Barbier *et al.* (*8*) proved that acidic sites of the support are mainly responsible for coke deposition by polymerization of olefinic compounds. Analysis by TPO (temperature-programmed oxidation) of coke deposits indicates that inhibition of the basic sites of the alumina by boric acid does not change significantly the amount and the location of coke deposits, whereas neutralization of the acidic sites by potassium hydroxide induces a drastic drop in the amount of coke deposited on the support.

Furthermore, during isomerization of methyl-1-naphthalene on HY zeolites exchanged with Na (*9*), the rate of coke formation decreases as the exchange ratio increases and therefore as the zeolite acidity decreases. In the same way, Tejada (*10*) showed that exchange of an HY zeolite by Na, Cs, Ba, or La improves strongly its stability during the transformation of *m*-xylene or 1,2,4-trimethylbenzene. Finally, during the cracking of anthracene on a nonacidic silica showing the same BET area as a silica–alumina, the amount of carbon deposited on silica–alumina was 23 times higher than that accumulated on the nonacidic support (*11*).

It therefore appears that polymerizaton of dehydrogenated species mainly occurs on acidic catalysts. The aim of this paper is to define the role of the acidic sites during the coking reaction with anthracene, which appears as a coke intermediate whatever the nature of the original coking agent (*12*). In order to define the effects of the number, the strength, and the nature of the active sites, the coking reaction was carried out on alumina catalysts modified by addition of

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chloride, potassium, or silica. In such silica–alumina catalysts, Lewis acidic sites prevail with high alumina contents, while for high silica contents the acidic sites are mainly of Brønsted type (*13*).

To define the nature and the strength of the acidic sites involved, the coking reaction by anthracene was also carried out on catalysts the acidic sites of which were partly inhibited by ammonia adsorbed at 323 K and desorbed at different temperatures. Moreover, assuming that coke deposits remain on the acidic sites responsible for their formation, we measured the acidity of the catalysts after coke deposition.

EXPERIMENTAL

Materials

The materials were γ-alumina (GFS C, Rhône-Poulenc, 210 m^2/g), three silica–aluminas (silica–aluminas 24–76 (24 wt% SiO_2; 76 wt% Al_2O_3) and 50–50 (50 wt% SiO_2; 50 wt% Al_2O_3), Rhône-Poulenc, 340 m^2/g and 380 m^2/g, respectively, and a silica–alumina 75–25 (75 wt% SiO_2; 25 wt% Al_2O_3), Ketjen, 650 m^2/g) and a silica (Aerosil 200 Degussa, 130 m^2/g). The alumina was modified by addition of chloride (HCl) or potassium (KOH) following the procedure of pore volume saturation. All the catalysts were pretreated at 773 K under flowing dry air for 4 h and at 823 K under flowing hydrogen for 8 h. The Cl and K concentrations on the modified samples were determined after the same thermal treatments.

Surface Acidity Measurements

Alumina and silica–alumina samples were subjected to a pretreatment under a helium flow at 793 K for 10 h. After cooling to 323 K, ammonia was made to pass for 0.25 h, then the samples were purged with a helium stream.

Ammonia desorption by stages at different temperatures within the range from 323 to 773 K was carried out with flowing helium and was followed by gas chromatographic analysis. The whole amount of ammonia which desorbs between 373 and 773 K was trapped at the exit of the chromatograph in a 0.01 *M* HCl solution and was determined by titration with NaOH.

Coking reaction. The coking reaction was carried out at atmospheric pressure in a classical glass flow reactor for 1 h; 1 g of catalyst was treated again under hydrogen at 793 K for 2 h and then brought to the coking temperature. After the coking reaction, the different samples were treated under pure hydrogen at the coking temperature for 1 h.

Anthracene (Fluka, purum) was employed as a coking agent with a hydrogen: hydrocarbon ratio of 19.

Analysis of coke. Coke deposits were analyzed by temperature-programmed oxidation, the temperature being increased from room temperature to 973 K at 7 K min^{-1}. Oxygen, diluted 1/100 in helium, was used. The combustion gas was led through a Pt/Al_2O_3 catalyst heated at 573 K in order to oxidize into CO_2 any CO which formed. The determination of the oxygen consumed and the carbon dioxide produced was carried out at intervals of 1 min by gas chromatography. The integration of these two amounts allowed the hydrogen content (H/C) of coke to be defined (*14*).

The extraction of coked catalysts was carried out with benzene for 48 h in a Soxhlet apparatus.

RESULTS

Acidity of Fresh Catalysts

The determination of the acidity of the different catalysts by ammonia thermodesorption shows that addition of chloride increases the acidity of alumina while potassium causes an opposite effect (Table 1).

The examination of the shapes of the curves relating the amount of desorbed base versus the desorption temperature indicates that chloride increases mainly the weak sites and to a minor degree the strong sites, while potassium inhibits chiefly the medium and strong sites (Fig. 1).

With regard to the SiO_2–Al_2O_3, the overall acidities and the shapes of the desorption

TABLE 1

Determination of the Acidity of Different Al_2O_3 and SiO_2–Al_2O_3 Catalysts by NH_3 Thermodesorption (NH_3 Desorbed by Stages between 373 and 773 K)

Catalyst	Acidity (meq H^+/g × 10^2)
Al_2O_3	44.1
Al_2O_3 0.5% Cl	51.2
Al_2O_3 1.0% Cl	57.8
Al_2O_3 0.2% K	37.1
Al_2O_3 0.6% K	33.2
SiO_2–Al_2O_3 (24 wt% SiO_2; 76 wt% Al_2O_3)	68.7
SiO_2–Al_2O_3 (50 wt % SiO_2; 50 wt% Al_2O_3)	60.2
SiO_2–Al_2O_3 (75 wt% SiO_2; 25 wt% Al_2O_3)	82.7

FIG. 2. Acidity distribution determined by NH_3 thermodesorption on: (○) SiO_2–Al_2O_3 24–76; (□) SiO_2–Al_2O_3 50–50; (●) SiO_2–Al_2O_3 75–25.

curves of NH_3 versus temperature are recorded in Table 1 and Fig. 2, respectively.

Coking Reaction on Al_2O_3 and Al_2O_3–Cl

The coking reaction with anthracene on GFS alumina modified by addition of chloride leads to the results recorded in Fig. 3. Note that the amount of coke increases with temperature; however, the apparent activation energy of the reaction decreases when the amount of chloride on alumina increases. An isokinetic temperature appears at about 840 K. At lower temperatures, the addition of chloride promotes the polymerization of anthracene, whereas at higher temperatures, the higher the chloride content the lower the amount of deposited coke.

The gas chromatographic analysis of light products formed during the coking reaction shows traces of methane and ethane when the reaction is carried out at 793 K, whereas no product appears at 673 K.

The effect of the coking temperature on

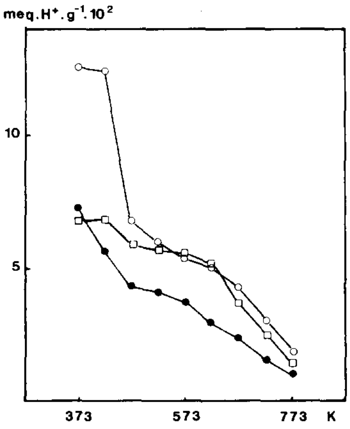

FIG. 1. Acidity distribution determined by NH_3 thermodesorption on: (□) Al_2O_3; (○) Al_2O_3 1% Cl; (●) Al_2O_3 0.6% K.

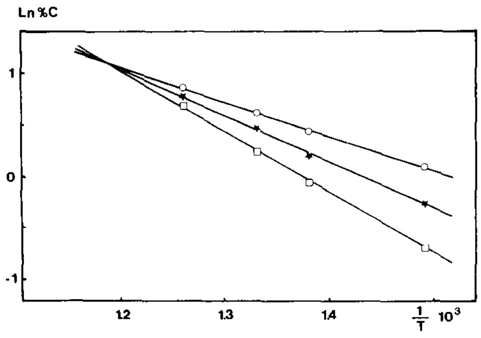

FIG. 3. Arrhenius plots of the coking reaction by anthracene on: (□) Al_2O_3; (★) Al_2O_3 0.5% Cl; (○) Al_2O_3 1.0% Cl.

TABLE 2

Effect of the Coking Temperature on the Characteristics of Coke Deposited on Different Catalysts

Catalyst	793 K			753 K			723 K			673 K		
	% C	H/C	Ext.[a] coke (%)	% C	H/C	Ext.[a] coke (%)	% C	H/C	Ext.[a] coke (%)	% C	H/C	Ext.[a] coke (%)
Al_2O_3 1% Cl	2.32	0.39	3	1.85	0.43	—	1.56	0.47	—	1.08	0.51	44
Al_2O_3 0.5% Cl	2.15	0.42	6	1.57	0.47	—	1.23	0.48	—	0.76	0.51	35
Al_2O_3	1.95	0.44	12	1.30	0.48	—	0.95	0.51	—	0.50	0.57	34
Al_2O_3 0.2% K	0.85	—	—	0.54	—	—	0.39	—	—	0.28	—	—
Al_2O_3 0.6% K	0.16	—	—	0.15	—	—	0.12	—	—	0.10	—	—
SiO_2–Al_2O_3 24–76	3.74	0.36	6	4.26	0.40	—	4.51	0.40	—	5.32	0.44	20
SiO_2–Al_2O_3 50–50	6.57	0.33	4	7.12	0.40	—	7.24	0.46	—	8.01	0.50	15
SiO_2–Al_2O_3 75–25	7.16	0.30	3	7.44	0.30	—	7.62	0.44	—	8.41	0.45	10

[a] Extractable coke.

the chemical nature of the deposits was also investigated. The characteristics of coke deposited on alumina with different amounts of chloride are summarized in Table 2. The H/C ratio and the amount of extractable coke decrease when the temperature of the reaction increases, showing a higher level of graphitization at 793 K.

Coking Reaction on Al_2O_3–K

The addition of a low amount of potassium leads to a large decrease in the amount of coke (Table 2). Figure 4, giving the amounts of coke deposits at different temperatures versus the acidity of the various modified alumina catalysts, shows that that break in the curves is all the more obvious when the reaction temperature is high. This trend can be explained by assuming the acidic sites promoted by chloride are different from sites inhibited by potassium. This explanation agrees with the shapes of the acidity curves (Fig. 1) which show an inhibition of the medium and strong acidic sites by potassium, whereas chloride increases mainly the weak sites and to a minor degree the strong sites.

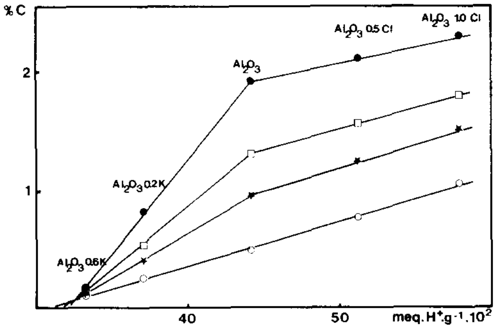

FIG. 4. Amount of deposited coke at different temperatures versus total acidity (acidity modified by potassium or chloride): (○) 673 K; (★) 723 K; (□) 753 K; (●) 793 K.

Coking Reaction on SiO_2–Al_2O_3

In opposition to results obtained on aluminas, the coking reaction with anthracene on silica–aluminas leads to a decreasing coke deposit with an increasing working temperature (Fig. 5). Figure 6, giving the change of the amount of deposits coke per unit surface area versus the SiO_2 content of SiO_2–Al_2O_3 catalysts at different temperatures shows that a maximum is reached for materials with almost 50 wt% Al_2O_3–50 wt% SiO_2 and that coke deposits are higher on silica–alumina than on alumina. However, at higher temperature (793 K) the amounts of

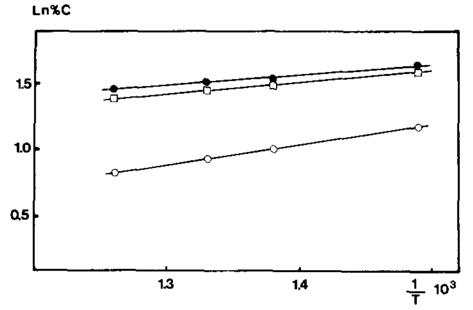

FIG. 5. Arrhenius plots of the coking reaction by anthracene on: (○) SiO_2–Al_2O_3 24–76; (□) SiO_2–Al_2O_3 50–50; (●) SiO_2–Al_2O_3 75–25.

TABLE 3

Chromatographic Analysis of Light Cracking Products during Coking Reaction with Anthracene on Silica–Aluminas

Catalyst	Molecule h^{-1} at 793 K × 10^{-19}			Molecule h^{-1} at 673 K × 10^{-19}		
	Me	Et	Bu	Me	Et	Bu
SiO_2–Al_2O_3 24–76	2.25	0.80	0.15	0.29	0.54	0.07
SiO_2–Al_2O_3 50–50	4.97	1.54	0.39	0.67	0.58	0.23
SiO_2–Al_2O_3 75–25	4.55	1.44	0.43	0.52	0.46	0.23

Note. Me, methane, Et, ethane; Bu, butane.

carbon (%C/m^2) are comparable on alumina and silica–aluminas 24–76 and 75–25 because of the opposite activation energies of the coking reaction on alumina and silica–alumina.

On the other hand, whatever the reaction temperature, the amount of deposited coke would be the same for catalysts loaded with about 87.5 wt% Al_2O_3–12.5 wt% SiO_2. For lower silica contents the activation energy of the coking reaction would be positive, while for higher silica contents it would be negative (Fig. 6).

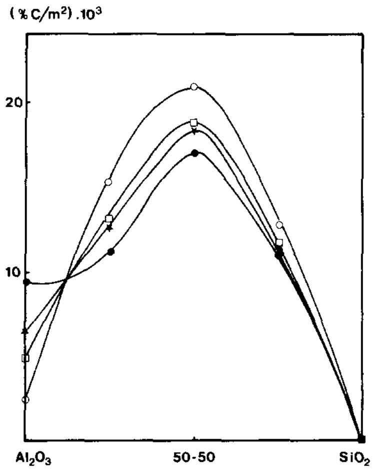

FIG. 6. Amount of deposited coke per square meter versus the silica content of the SiO_2–Al_2O_3 at different temperatures: (○) 673 K; (□) 723 K; (★) 753 K; (●) 793 K.

The determination of the H/C ratio shows that coke deposited on silica–alumina is more dehydrogenated at 793 K, although the amount of deposits at 793 K is lower than that at 673 K (Table 2). Extractions of coked catalysts with benzene bear out that the chemical nature of deposits varies with temperature. Thus the extractable coke increases as the temperature of the coking reaction decreases, proving a greater graphitization of carbonaceous deposits at high temperature (Table 2). Furthermore, during the coking reaction with anthracene on silica–alumina, light gaseous products such as methane, ethane, or butane appear, what ever the working temperature (Table 3).

Coking Reaction on Catalysts Treated by NH_3

Alumina catalysts. The amounts of coke deposited on alumina saturated by NH_3 at 323 K and then treated under pure hydrogen at different temperatures are recorded in Table 4. From these results it can be deduced that the strong acidic sites of alumina are the most active for the coking reaction with anthracene, since 75% of coke grows on acidic sites which desorb NH_3 at temperatures higher than 673 K. The same conclusion can be deduced from Table 5 on chlorinated alumina catalysts. Finally, for

TABLE 4

Effect of the Temperature of NH_3 Desorption on Coke Deposits at 673 K on Alumina and Silica–Alumina 75–25

Desorption temperature of NH_3 (K)	% C deposited at 673 K	
	Alumina	Silica–alumina 75–25
Without NH_3 treatment	0.50	8.41
773	0.25	8.25
723	0.17	8.03
673	0.13	6.10

alumina modified by potassium, the treatment by ammonia has a very low effect on coke deposits, showing that the strong acidic sites are neutralized by potassium itself (Table 5).

Silica–alumina catalysts. Different samples of silica–alumina 75–25 catalyst saturated by ammonia at 323 K and then treated under pure hydrogen at various temperatures between 673 and 773 K were submitted to the coking reaction with anthracene at 673 K. The results recorded in Table 4 show that the amounts of coke are slightly decreased for a desorption temperature of ammonia higher than or equal to 723 K. Hence, contrary to the results previously shown for alumina catalysts, the acidic sites which desorb ammonia at a temperature lower than 723 K would be responsible for the coking reaction on silica–alumina.

TABLE 5

Effect of the Treatment by Ammonia on the Amounts of Coke Deposited on Al_2O_3–Cl and Al_2O_3–K Catalysts

Catalyst	% C deposited at 753 K	% C deposited at 753 K after NH_3 desorption at 773 K
Al_2O_3	1.30	0.60
Al_2O_3 0.5% Cl	1.57	0.64
Al_2O_3 1% Cl	1.87	0.73
Al_2O_3 0.2% K	0.54	0.45
Al_2O_3 0.6% K	0.15	0.10

TABLE 6

Effect of Coke Deposits on the Acidity of Catalysts Coked at 793 K

Catalyst	Acidity (meq H^+/g) × 10^2
Al_2O_3	44.1
coked Al_2O_3	42.4
Al_2O_3 1.0% Cl	57.8
coked Al_2O_3 1.0% Cl	53.5
SiO_2–Al_2O_3 75–25	82.7
coked SiO_2–Al_2O_3 75–25	60.2

Remaining Acidity of Catalysts after the Coking Reaction

We chose to determine acidity after the coking reaction at 793 K, a temperature at which the amount of coke deposited per square meter (%C/m^2) is comparable on Al_2O_3 and SiO_2–Al_2O_3 75–25 (Fig. 6). The values recorded in Table 6 show that the acidity measured by ammonia desorption up to 773 K is slightly inhibited on alumina after the coking reaction, while it strongly decreases on silica–alumina. Figure 7, which illustrates the curves of the amount of de-

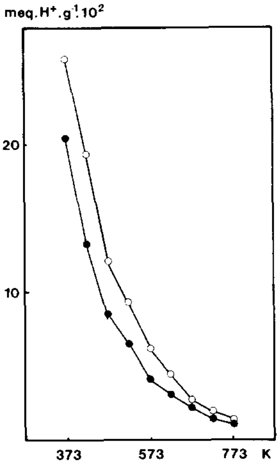

FIG. 7. Acidity distribution determined by NH_3 thermodesorption on: (○) fresh SiO_2–Al_2O_3 75–25; (●) SiO_2–Al_2O_3 75–25 coked at 793 K.

sorbed ammonia versus desorption temperature on fresh and coked silica–alumina 75–25 shows that on such catalysts all acidic sites are inhibited by carbon deposits, whatever their strength.

DISCUSSION

The measure of acidity by ammonia desorption has shown the modifications induced by chloride and potassium on the acidic properties of alumina. The substitution of OH^- or O^{2-} surface anions by Cl^- increases the acidity of the alumina, while in an opposite way, addition of a low amount of potassium inhibits medium and strong acidic sites.

On silica–aluminas, the density of acidic sites per unit surface area decreases as the silica content increases. However, it is known that the nature of the acidic sites varies with the silica–alumina composition (*13*). Indeed, Brønsted acidity, which is very low on alumina, increases with the silica content up to a composition akin to 40 wt% alumina and 60 wt% silica. Furthermore, it decreases to zero on pure silica. On the other hand, Lewis acidity decreases from pure alumina to pure silica.

The coking reaction with anthracene under hydrogen flow depends on the acidity and the nature of the catalyst. At low temperature (lower than 840 K), the addition of chloride to alumina leads to greater amounts of deposited coke, the higher the chlorine content and therefore the higher the acidity. An isokinetic temperature appears at about 840 K, whereas the amount of coke is the same on all the alumina catalysts, whatever their chloride content. At higher temperatures, the more acidic catalysts would lead to the lower coke deposits. Such a result can be explained by assuming that coke deposition is a complex reaction which results partly from the polymerization of dehydrogenated species on the acidic sites and on the other hand from their destruction by cracking or methanation. As the apparent activation energies of these latter reactions are higher than that of polymerization reactions, destruction reactions prevail over polymerization reactions at high temperatures.

Competition between polymerization and destruction of coke precursors is still more obvious on silica–alumina catalysts. For such high cracking activity catalysts, the apparent activation energy of the coking reaction with anthracene is negative for temperatures ranging from 673 to 793 K. The change of the amounts of coke deposited per unit surface area versus the silica content of the silica–alumina catalysts has shown an isokinetic point for a silica content akin to 10–15% by weight. For a lower silica content the amount of coke would increase with temperature, while for high silica contents it would decrease by an increasing temperature.

The inhibition of the acidic sites of alumina by adsorption of ammonia at 323 K and desorption at different temperatures shows that coke precursors polymerize mainly on acidic sites which desorb ammonia at temperatures higher than 673 K. This result explains why the acidity, measured by ammonia desorption up to 773 K, is slightly inhibited by coke deposits. Addition of chloride increases the number of these acidic sites, whereas they are poisoned by potassium.

On the other hand, in the case of the silica–alumina 75—25 catalyst, it appears that the coking reaction with anthracene occurs on acidic sites which desorb ammonia at temperatures lower than 723 K. Consequently, the acidity is strongly inhibited by coke deposits. This difference between aluminas and silicas–aluminas agrees with the measures of the acidity made by Yori *et al.* (*15*) who pointed out that acidic sites with the same acid strength (H_0) desorb ammonia at a lower temperature on silica–aluminas than on aluminas. Such a difference can be explained by assuming that silica–aluminas show mainly an acidity of the Brønsted type, whereas aluminas have an acidity of the Lewis type. These results indicate that the strength as well as the nature of the acidic sites (Lewis or Brønsted) plays an important role in the competition of polymerization and destruction reactions and therefore for the coking reaction.

In conclusion, acidic sites of aluminas and silica–aluminas are responsible for the polymerization of dehydrogenated species which lead to coke deposits. On aluminas, the coking reaction occurs mainly on strong Lewis acidic sites which desorb ammonia at temperatures higher than 673 K. On the other hand, in the case of silica–aluminas, Brønsted acidic sites, which desorb ammonia at temperatures lower than 773 K, are responsible for coke deposition. Finally, although they have a higher cracking activity than Lewis acidic sites, Brønsted acidic sites lead to higher coke deposits in the temperature range studied in this work.

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