The Nature and Catalytic Influence of Coke Formed on Alumina: Oxidative Dehydrogenation of Ethylbenzene

R. FIEDOROW, W. PRZYSTAJKO, AND M. SOPA

Institute of Chemistry, A. Mickiewicz University, Poznan, Poland

AND

I. G. DALLA LANA

Department of Chemical Engineering, University of Alberta, Edmonton, Alberta, Canada

Catalytic properties of alumina doped with 0.1 to 1.0 wt% NaOH, as well as that of pure alumina, were studied for the oxidative dehydrogenation of ethylbenzene and for some acid-catalyzed model reactions. The largest contribution to the formation of coke catalytically active for styrene formation was found to come from sites of moderate and weak acid strengths. Stronger acid centers produce cokes lower in hydrogen content, whereas weaker centers form cokes of a more saturated chemical nature. On very very weak centers, cokes with the ratio of C/H < 1 are formed and such cokes show low catalytic activity for oxidative dehydrogenation. Based on ESR measurements, it has been suggested that paramagnetic centers are the active sites for styrene formation in the process of ethylbenzene oxidative dehydrogenation.

INTRODUCTION

Alumina, a typical catalyst for acid–base reactions, has been reported (*1–3*) to be an active catalyst for oxidative dehydrogenation of ethylbenzene and other alkylbenzenes. This activity for formation of styrene from ethylbenzene and oxygen was interpreted (*4, 12*) on the basis of a two-center mechanism involving adjacent electron-acceptor and electron-donor sites. Subsequently (*5*), Alkhazov and Lisovskii limited this explanation to being applicable to the early course of the reaction, prior to formation of so-called "coke" on the surface of alumina. This monolayer of coke was then considered to be responsible for subsequent catalytic oxidative dehydrogenation of benzene. In this explanation, both alumina and coke are considered to display activity for oxidative dehydrogenation of ethylbenzene with coke being the more active catalyst of the two. Similar studies using SO_2 in place of oxygen (from

air) (*13*) produced a coke differing in composition and of much lower activity for oxidative dehydrogenation than the former coke or the γ-Al_2O_3. More recently, Fiedorow *et al.* (*6*) have questioned the validity of Alkhazov's scheme at any stage of the dehydrogenation. They chose to believe that the role of alumina is limited to providing coke-forming centers, the surface coke alone providing active centers for oxidative dehydrogenation. By introducing the feed in pulses, Lisovskii *et al.* (*7*) were able to show that the initial pulses produced neither styrene nor carbon dioxide and only with subsequent pulses, did styrene appear in the eluted product stream. This additional evidence corroborates the view that coke is initially formed and with increasing extent of "coke centers" on the surface of the alumina, the catalytic activity for oxidative dehydrogenation increases significantly. Notwithstanding the above conflicting views, the formation of a coke with such unusual catalytic activity

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presents a novel and interesting situation; unexpected in that coke formation during catalytic cracking results in deactivation of the catalyst.

The catalytic activity of γ-alumina initially increases with a rise in coke coverage and then stabilizes (*1*) to what has been termed (*7*) quasi-stationary activity. The latter term reflects the view that the chemical composition of this oxygen-rich coke is also a factor in the activity exhibited (*13*). In this paper, the genesis and some properties of such cokes are investigated.

EXPERIMENTAL BASIS

1. Catalysts

The alumina catalysts were produced by hydrolysis of aluminum isopropoxide to aluminum hydroxide (*8*). The obtained precipitate was dried at 110°C for 24 h and then calcined at 800°C for 6 h. Interpretation of X-ray analyses of the resulting alumina, based on Lippens and Steggerda (*9*), showed the alumina to be mixtures of the phases χ-, δ-, and θ-Al_2O_3. Portions of the above preparation were doped with sodium hydroxide in the amounts, 0.1, 0.3, 0.5, and 1.0 wt% NaOH, in the manner reported earlier (*10, 11*); i.e., the alumina was mixed with aqueous solution of NaOH to form a paste and then dried at 110°C for 24 h with occasional remixing. The pure and doped aluminas were labeled 0.0S, 0.1S, 0.3S, 0.5S, and 1.0S, respectively.

Another alumina sample labeled 0.1 B/Al was promoted by adding orthoboric acid (H_3BO_3) in a similar way to yield a boric acid/alumina (B/Al) ratio of 0.1. The procedure differed in that after drying at 110°C for 24 h, the 0.1 B/Al was calcined at 600°C for 6 h.

2. Apparatus and Procedure

The catalytic activities of the various aluminas for oxidative dehydrogenation of ethylbenzene were measured in a flow reactor as described earlier (*6*). The standardized reaction conditions used 0.25 g catalyst, 500°C, NTP space velocity of 3333 h^{-1} and an ethylbenzene-to-air feed ratio of 1 : 4.4. The analyses of reaction products listed in Table 1 were obtained after 7 h, i.e., after the quasi-stationary activity was attained. The catalyst was then removed from the reactor and examined in various ways.

About 0.015 g of such catalysts was subjected to 1.33 × 10^{-3} Pa and 350°C for 2 h to remove unreacted ethylbenzene and liquid products. No further volatile matter evolved from the catalyst sample when heated to 350°C in a mass spectrometer (JMS-D-100, JEOL, Tokyo). Such coke samples were detached from the vacuum line and stored in a sealed ampoule until analyzed on a Perkin–Elmer Elemental Analyzer Model 240.

ESR measurement of the coke-covered catalysts were obtained at room tempera-

TABLE 1

Conversion of Ethylbenzene and Selectivity of the Process for Oxidative Dehydrogenation Using Sodium Hydroxide-Poisoned Aluminas (Expressed as Percentage)

Catalyst	Yield of				Total conversion	Selectivity to			
	CO	CO_2	C_6H_6	Styrene		CO	CO_2	C_6H_6	Styrene
0.1 B/Al	3.8	4.7	0.5	68.0	77.0	4.9	6.1	0.7	88.3
0.0S	2.4	5.8	0.3	50.2	58.7	4.1	9.9	0.4	85.6
0.1S	3.4	6.3	0.3	48.4	58.4	5.8	10.8	0.5	82.9
0.3S	3.0	5.9	0.1	36.7	45.7	6.5	12.9	0.1	80.5
0.5S	1.6	2.7	0.1	11.8	16.2	9.9	16.7	0.6	72.8
1.0S	1.3	1.9	Trace	5.8	9.0	14.4	21.1	—	64.5

ture (JES-3BX/JEOL, Tokyo) at klystron frequency of 9.4 GHz and a magnetic field modulation of 100 kHz. An ultramarine sample with spin concentration of 1.5 × 10^{16} was used as a standard for estimating the concentration of unpaired electrons in a catalyst sample. The acid strength of catalysts was estimated by determining their relative catalytic activities for different acid-catalyzed reactions. The activities were measured using pulsed flows through a Perkin–Elmer Model 154-0502 microreactor gas chromatographic accessory. The model reactions which were used included:

(a) *Skeletal isomerization of cyclohexene.*
Reaction temperature = 370°C; catalyst weight = 0.3 g; volume/pulse cyclohexene (liquid) = 0.3 μl; flow-rate helium carrier = 23 cm^3/min; GC column, 2 m propylene carbonate at 30°C.

(b) *Isomerization of 1-butene.*
Reaction temperature = 200°C; catalyst weight = 0.1 g; volume/pulse 1-butene (gas) = 0.5 cm^3; flow-rate helium carrier = 30 cm^3/min; GC column, 8 m propylene carbonate at 0°C.

(c) *Decomposition of 2-propanol.*
Reaction temperature = 300°C; catalyst weight = 0.01 g; volume/pulse isopropanol (liquid) = 0.1 μl; flow-rate helium carrier = 25 cm^3/min; GC column, 1 m Emulphor O at 50°C.

BET areas were calculated for the catalysts based upon N_2 adsorption at −195°C. The addition of NaOH or H_3BO_3 to alumina, within the range of amounts added, appeared to have little effect on the BET areas, which ranged from 121 m^2/g for the

0.1 B/Al to 130 to 133 for the pure and NaOH-doped catalysts.

RESULTS AND DISCUSSION

1. Influence of Acidity (NaOH Doping)

Figure 1 demonstrates that decreasing the acidity of alumina, i.e., increasing the NaOH content of the catalysts, reduces both the total conversion of ethylbenzene and the styrene yield. The styrene yield decreases markedly from 50.2% on the 0.0S alumina to 5.8% on the 1.0S doped alumina. Since minor additions of NaOH (0.1S) affect the activity for oxidative dehydrogenation of ethylbenzene only slightly relative to that of the 0.0S alumina, one may infer that the strongest acid centers are not as important catalytic sites as the moderate and weaker acid centers. Increasing the NaOH beyond the 0.1S level rapidly poisons the activity because moderate and weaker acid sites are being eliminated.

Since alumina is known to change from an inactive catalyst to an increasingly active catalyst for alcohol dehydrogenation with increased extent of NaOH doping (*10, 14*), the possibility that the NaOH-doped aluminas used in this work also may catalyze nonoxidative dehydrogenation was checked. If both oxidative and nonoxida-
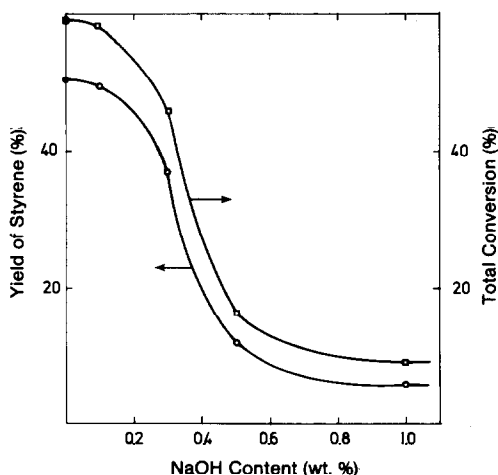

FIG. 1. The effect of poisoning with NaOH on the total conversion of ethylbenzene and on the yield of styrene.

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TABLE 2

Results of Elemental Analysis of the Coke Deposited
on Catalysts Used in the Process of Oxidative
Dehydrogenation

Catalyst	Coke content (wt%)	Elemental composition (wt%)			Empirical formula	C/H ratio
		C	H	O		
0.1 B/Al	25.0	82.0	2.4	15.6	$C_{7.0}H_{2.5}O$	2.80
0.0S	16.1	80.1	3.1	16.8	$C_{6.4}H_{3.1}O$	2.06
0.1S	13.2	78.8	3.0	18.2	$C_{5.8}H_{3.0}O$	1.93
0.3S	10.5	78.1	3.8	18.1	$C_{5.8}H_{3.8}O$	1.53
0.5S	3.0	79.3	6.8	13.9	$C_{8.0}H_{8.1}O$	0.99
1.0S	2.1	76.7	12.4	10.9	$C_{9.4}H_{18.2}O$	0.52

tive dehydrogenation processes occurred simultaneously, the interpretation of the catalytic influence of the coke centers would be seriously limited. In experiments using N_2 flows in place of air flows through the ethylbenzene-containing saturator, non-oxidative dehydrogenation of ethylbenzene was not observed to occur in the range of NaOH concentration used in this study.

The performance of the various catalysts (at the standardized conditions tested earlier) are shown in Table 1. Table 2 shows the coke content of these catalysts and their elemental composition after 7 h of opera-

FIG. 2. C/H ratio and coke content as functions of catalyst acidity as expressed by the wt% of NaOH added to alumina.

tion, a period of time considered sufficient to achieve the so-called quasi-stationary activity (7).

During the buildup of activity to the quasi-stationary level, it is believed that both the amounts and the chemical nature of the coke being formed may change. The observed conversions and yields stabilized only after a 7-h preliminary period of reaction. Presumably, some balance between these two factors could account for the quasi-stationary activity. It is not known whether the pore structure of the alumina has been altered by coke deposition on the surface or whether a new pore structure within a coke layer has evolved. The BET areas do not vary significantly.

2. Nature of the Catalytically Active Coke

Figure 2 shows that both the coke content and its C/H ratio diminish with a decrease in number of acid centers, the result of poisoning with sodium hydroxide. On the other hand, Table 2 also reveals that an increase in acidity (catalyst 0.1 B/Al) increases both the coke content and its C/H ratio. Thus, one may conclude that the more unsaturated coke is formed on stronger acid centers, whereas the coke being formed on weaker acid centers becomes richer in hydrogen.

The coke formed during oxidative dehydrogenation reaction conditions is seen to contain substantial oxygen, with corresponding empirical formulas changing considerably with increasing hydrogen content. No single empirical formula appears applicable to all cokes but up to 0.3 wt% NaOH the formulas do not change drastically. Coke from this reaction has been suggested (5) to contain fragments corresponding to the structure of polynaphthoquinone. Additionally, polynaphthoquinone, both alone and supported on alumina, has been demonstrated to catalyze the oxidative dehydrogenation of ethylbenzene at 200°C with 100% selectivity (15). Comparisons between the elemental com-
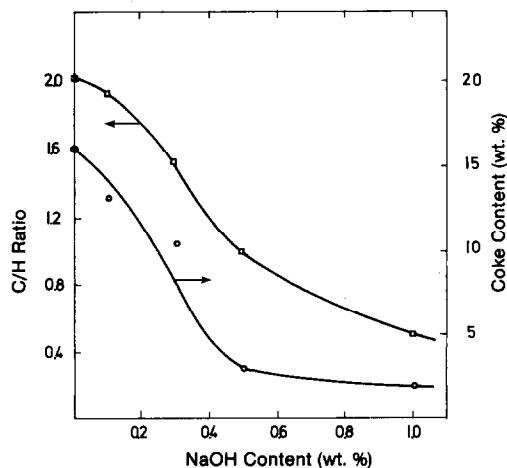
position of polynaphthoquinone, 76.9% C, 2.6% H, and 20.5% O, and the empirical formulas in Table 2 show that the differences are minor for cokes with high catalytic activity. Since the coke formed on the most active catalyst, 0.1 B/Al, deviates from the composition of polynaphthoquinone more than the cokes deposited on less active catalysts, 0.0S and 0.1S, it may be expected that other compounds with lower oxygen contents or different functional groups than those of polynaphthoquinone are also catalytically active. The cokes on catalysts with low activity (0.5S and 1.0S) have a considerably higher hydrogen content than the more active cokes and deviate substantially from the composition of polynaphthoquinone.

3. Acidity and Activity

With increased NaOH content in the aluminas, the C/H ratio of the cokes decreased and the catalyst activity for oxidative dehydrogenation also decreased. Figure 3 shows this effect and also that the selectivity for styrene correspondingly diminishes. As already mentioned, the strongest acid sites do not appear to play an
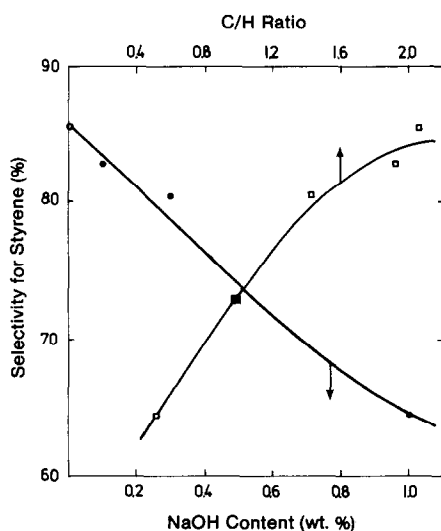
TABLE 3

Activity of Alumina Poisoned with Increasing Amounts of Sodium Hydroxide for Skeletal Isomerization of Cyclohexene

Catalyst	Composition of reaction products (%)			
	MCPan	CHan	MCPen	CHen
0.0S	Trace	19.6	40.0	40.4
0.1S	0.0	0.9	1.4	97.7
0.3S	0.0	0.05	0.05	99.9
0.5S	0.0	0.0	0.0	100.0

Note: MCPan—methylcyclopentane; CHan—cyclohexane; MCPen—methylcyclopentene; CHen—cyclohexene. Cyclohexane and methylcyclopentane are the products of the concomitant reaction of hydrogen disproportionation.

important part in the formation of coke which is active for styrene production because relatively high styrene yields were obtained on the 0.1S and the 0.3S catalysts, where the strong acid centers should be largely poisoned by these amounts of NaOH added to the alumina.

Model reactions whose progress has been related to known strengths of catalytic acid centers may be used to evaluate the presence of strong acid centers on the various aluminas.

(i) Skeletal isomerization of cyclohexene. Table 3 shows the influence of NaOH poisoning of alumina upon its catalytic activity for cyclohexene isomerization, a reaction known to require strong acid centers (16). The rapid decline of activity at NaOH contents of 0.1 NaOH and above verifies the dependence of the skeletal isomerization rate upon strong acid centers, whose presence may be largely eliminated from the 0.1S catalyst.

(ii) Isomerization of n-butene. The isomerization of n butene also depends upon strong acid centers (17) as shown in the results in Table 4.

(iii) Use of 0.1 B/Al. The most active of the catalysts tested, 0.1 B/Al, possesses predominantly acid sites of moderate

FIG. 3. The effect of C/H ratio and the wt% of NaOH introduced on the selectivity for styrene.

TABLE 4

Activity of Alumina Catalysts for Double-Bond and *cis–trans* Isomerizations of Butenes

Catalyst	Composition of reaction products (%)			Ratio of *cis*-2-butene to *trans*-2-butene
	1-butene	*cis*-2-butene	*trans*-2-butene	
0.0S	61.0	25.9	13.1	1.98
0.1S	94.6	3.6	1.8	2.05
0.3S	~100	Trace	Trace	—
0.5S	100	0.0	0.0	—
1.0S	100	0.0	0.0	—

strength, capable of converting triphenyl-methanol ($pK_{R^+} = -6.63$) into colored carbonium ion (*18*).

On the basis of the above, it appears that when the level of NaOH content increases, the poisoning initially affects strong acid centers, then moderate-strength acid centers, and gradually the weaker sites, until only the weakest sites remain. Cokes formed on the latter sites are those with lower C/H ratios which exhibit poor activity for styrene formation. All cokes formed on the acid centers will undergo combustion to CO and CO_2, the more so the poorer their selectivity for styrene.

(*iv*) *Dehydration of 2-propanol.* This reaction, contrary to the isomerization model reactions, does not require strong acid centers and may even proceed on weak acid centers. Table 5 presents the activities of the various catalysts toward dehydration of

2-propanol; indicating that up to 0.3 wt% NaOH, the dehydration activity remains very high (more thn 95% reacted alcohol). Only at 0.5 wt% NaOH does the activity of the catalyst change, decreasing for production of the olefin but, at the same time, starting to produce ketone. Indicator tests using *p*-dimethylaminoazobenxene show the absence of centers with acid strengths corresponding to the pK_a of the above indicator, 3.3. Thus, the acid strength of the remaining sites on the alumina surface after reaching 0.5 wt% NaOH is very very low.

Additional correspondence between yields of propylene from dehydration of isopropanol and yields of styrene plus car-

TABLE 5

Activity of Alumina Catalysts for 2-Propanol Decomposition

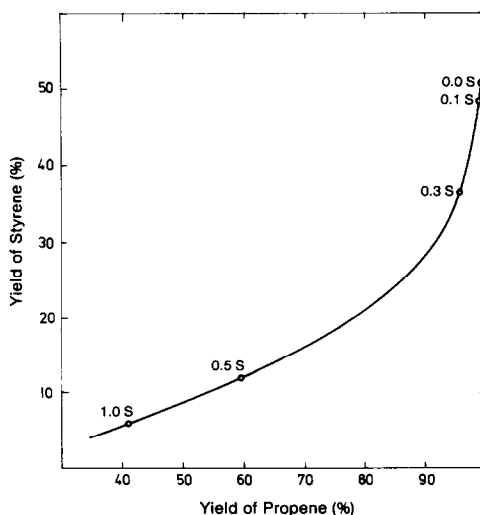| Catalyst	Composition of reaction products (%)		
	Propene	Acetone	Unreacted alcohol
0.0S	99.7	0.0	.3
0.1S	98.9	0.0	1.1
0.3S	95.4	0.0	4.6
0.5S	59.5	0.8	39.7
1.0S	40.7	2.5	56.8

FIG. 4. Dependence between activity for isopropanol dehydration and activity for formation of styrene.

bon oxides from mild and deep, respectively, oxidation of ethylbenzene, is indicated by Fig. 4. Plotting of the isomerization reaction yields on the same basis would reveal essentially no correlation between the two yields. The good correlation between dehydration and styrene formation yields appears to confirm the earlier expectation that weaker acid centers, active for propanol dehydration, are also important to the catalytic oxidative dehydrogenation of ethylbenzene in the sense of roles as coke-forming centers. On the other hand, the very very weak acid centers catalyzing alcohol dehydration with yields of 40 to 60% (see Table 5) are of little importance to the process of oxidative dehydrogenation of ethylbenzene because the coke formed on these centers catalyzes conversion of ethylbenzene into styrene with only 5.8 to 11.8% yields. Since the cokes formed on the acid centers on alumina surface are believed to be the active agents for catalytic oxidative dehydrogenation, the cokes corresponding to the weaker acid centers (but not the weakest ones)

would be expected to be the preferred ones for styrene formation.

4. Catalytic Nature of Active Coke Centers

The preceding discussion has attempted to relate the oxidative dehydrogenation catalytic reaction to particular, even unique, chemical forms of coke, and to suggest that these more catalytically active cokes form preferably on weak acid sites of the alumina surface. Questions concerning the catalytic nature of the coke itself have not been examined. ESR studies were used to study the coke-covered catalysts.

Figure 5 suggests that correlations exist between the concentration of unpaired electrons and both coke content and styrene yields; the latter dependence implying that paramagnetic centers could be the active sites for styrene formation on the coke catalyst. Conceivably, such paramagnetic centers could result from the rupture of carbon–carbon bonds, a not unlikely situation for catalytic surfaces. The presence of such ruptured bonds in coke may also be argued by the correlations observed (19–26) between both chemisorptive and catalytic abilities of active carbons and their paramagnetic properties.

Table 6 summarizes the ESR measurements. The exceptional activity for oxidative dehydrogenation of the 0.1 B/Al cata-
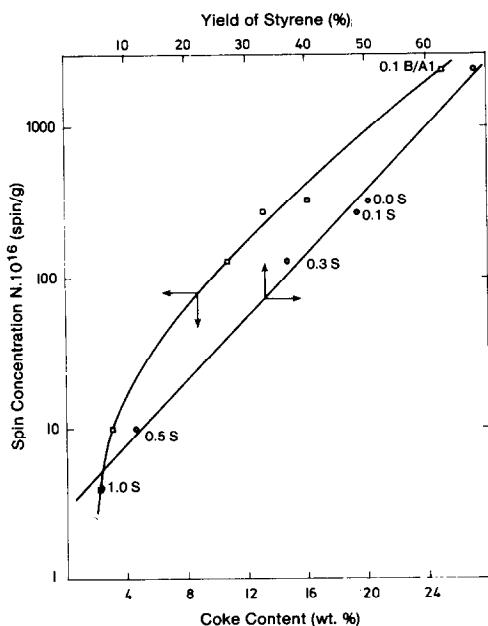

Fig. 5. Dependence of spin concentration on coke content and yield of styrene.

TABLE 6

Linewidth and Spin Concentration of Coke-Covered Catalysts as Measured by ESR Spectroscopy

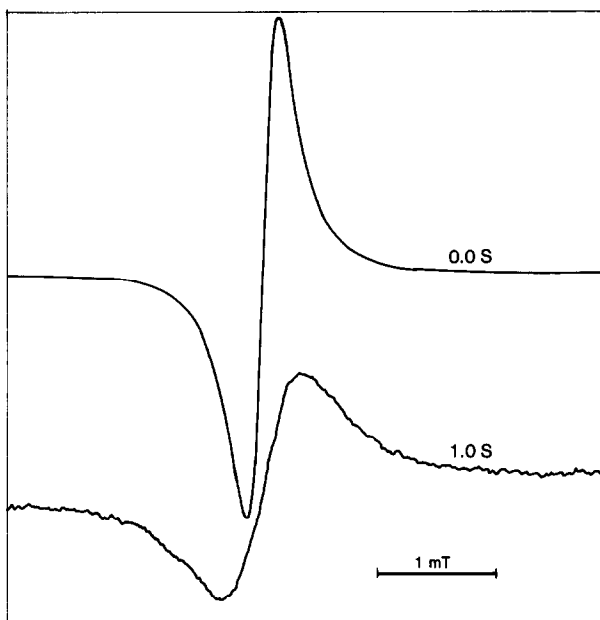| Catalyst	Linewidth $2\Delta B$ (mT)	Number of spins N per g of catalyst ($\times 10^{17}$)	Spin concentration in relation to 0.0S catalyst
0.1 B/Al	0.12	234.6	11.01
0.0S	0.26	32.3	1.00
0.1S	0.25	27.1	0.95
0.3S	0.33	13.0	0.61
0.5S	0.64	1.0	0.05
1.0S	0.74	0.4	0.02

FIG. 6. ESB spectra of coke-covered catalysts.

lyst may be related to its exceptionally high spin concentration, an order of magnitude larger than the highest spin concentration on any non-boron-containing catalyst. Another interesting dependence between linewidth and spin concentration is evident. The linewidth decreases with an increase in radical concentration, whereas for dipolar interactions (between spins of electrons, as well as interactions between spins of electrons and spins of nuclei) a linear increase in linewidth would be expected for increasing concentration of paramagnetic centers. This observed opposite dependence frequently occurs in the case of high concentrations of radicals attributed to so-called exchange narrowing caused by exchange interaction between radicals. It shows that the concentration of paramagnetic defects in the investigated coke is sufficiently large even in catalysts partially poisoned using NaOH. The narrowing is more visible in Fig. 6, where the first derivatives of ESR spectra are contrasted; i.e., 0.0S catalyst with a spin concentration of 32.3×10^{17} exhibits a narrow symmetrical single line, whereas 1.0S catalyst with a spin concen-tration of 4×10^{16} exhibits a considerably wider spectral line.

CONCLUSIONS

1. In the process of formation of catalytically active coke for ethylbenzene oxidative dehydrogenation, centers of different acid strength on alumina surface are involved. The evidence suggests no specified threshold of acid strength for centers participating in the formation of this unusual oxygen-rich coke, but the decisive role is played by moderate- and weak-acid-strength centers, whereas very strong and very very weak acid centers are of much lesser importance.

2. Increased poisoning of alumina by increasing the NaOH content results in decreasing C/H ratio in the cokes. Thus, stronger acid centers produce coke of more unsaturated character, whereas weaker acid sites form cokes richer in hydrogen. Cokes with the ratio of C/H less than unity exhibit low catalytic activity for styrene formation.

3. The catalytic activity of alumina for oxidative dehydrogenation of ethylbenzene

is promoted considerably by the addition of H_3BO_3 to the ratio, $B/Al = 0.1$.

4. Active sites for styrene formation over coke-covered catalysts are, most likely, paramagnetic centers formed as a result of chemical bond ruptures in the defective coke structure.

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