

Step by Step Modeling of Superbasic Catalysts of the EDA Complex Type

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A range of catalysts was synthesized; these catalysts contained species analogous to the structures appearing during the various elementary steps in the hydrogenation of alkenes over catalysts of extremely strong one-electron donor centers. The primary catalytic system, γ -Al₂O₃-metallic potassium, was modified by naphthalene, anthracene, and perylene vapors to form surface electron donor-acceptor (EDA) complexes. The specific EDA complexes were also prepared by the immobilization of potassium naphthenide on a γ -Al₂O₃ surface in amounts relative to the number of surface hydroxyls. The investigated catalysts were tested in the isomerization of 1-pentene and 1-hexene and in the hydrogenation of ethene and propene. The catalytic importance of ion radical species of alkenes formed during their isomerization and hydrogenation over superbasic systems was demonstrated.

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INTRODUCTION

In previous work we described the properties and activities of superbasic catalysts of the oxide-alkali metal type and demonstrated that they have extremely strong one-electron donor properties (1-8). These catalysts were able to ionize molecules with electron affinity values in the range of 0.2 eV and exhibited high activity in the selective hydrogenation of various alkenes (e.g., ethene, propene, cyclohexene, styrene, isoprene (4, 5)) or carbon monoxide (6, 8). Surface color centers of F_s⁺ character (formed as a result of the alkali metal vapor reaction with anionic vacancies on oxide surfaces) were identified as the strongest one-electron donor sites (3, 4, 6). The results of reactions carried out over the catalysts with the one-electron donor sites, suppressed by the adsorbed poison (3), and the correlation between the one-electron donor site concentration and their hydrogenation activity indicated that the extremely strong electron donor centers were responsible for the initiation of the reaction (6). Nevertheless, it should be emphasized that the very active centers of H₂ molecule activation were secondary centers of an anion radical type which originated from an alkene or CO adsorption on surface F_s⁺ centers (5, 6). Dihydrogen homolytic splitting was expected to occur as a result of the H₂ reaction with an alkene anion radical leading to the formation of a semi-hydrogenated state, similar to the hydrogenation reactions

catalyzed by anion radicals of polycyclic aromatic hydrocarbons as reported by Tamaru (9).

The conception of this work was the synthesis of catalysts containing species analogous to the structures appearing during the various elementary steps in the hydrogenation of alkenes over our superbasic catalysts and over electron donor-acceptor (EDA) complexes of polycyclic aromatic hydrocarbons described by Tamaru (9). To provide evidence for the analogy between the above catalytic systems we investigated the following heterogeneous catalysts with an EDA complex character: (i) containing F_s⁺ centers formed by reaction of alkali metal (potassium) atoms with anionic vacancies on the oxide surface (γ -Al₂O₃); (ii) synthesized by the adsorption of polycyclic aromatic hydrocarbons (naphthalene, anthracene, or phenanthrene) on the surface of γ -Al₂O₃-potassium system rich in F_s⁺ centers; (iii) prepared by the chemical immobilization of naphthalene anion radical salt (potassium naphthenide) on γ -alumina surface. Catalyst (i) is a specific type of EDA complex formed between alkali metal atoms and electron-deficient sites on a solid surface. It catalyzes the hydrogenation of olefins by means of the formation of an anion radical complex with adsorbed alkene; this further activates the homolytic decay of H₂ molecule. Catalyst (ii) is an analogue to the EDA complexes of Tamaru. In contrast to the classical EDA complex, it possesses the donor component of the secondary character, exhibiting a much higher donor power than the initial alkali metal (10-12). Catalyst (iii) is also an analogue to Tamaru EDA complexes, but in this case the typical interaction of the alkali metal atom with the polycyclic aromatic molecule is weakened by the deposition of the complex on electron-deficient centers of the γ -Al₂O₃ surface.

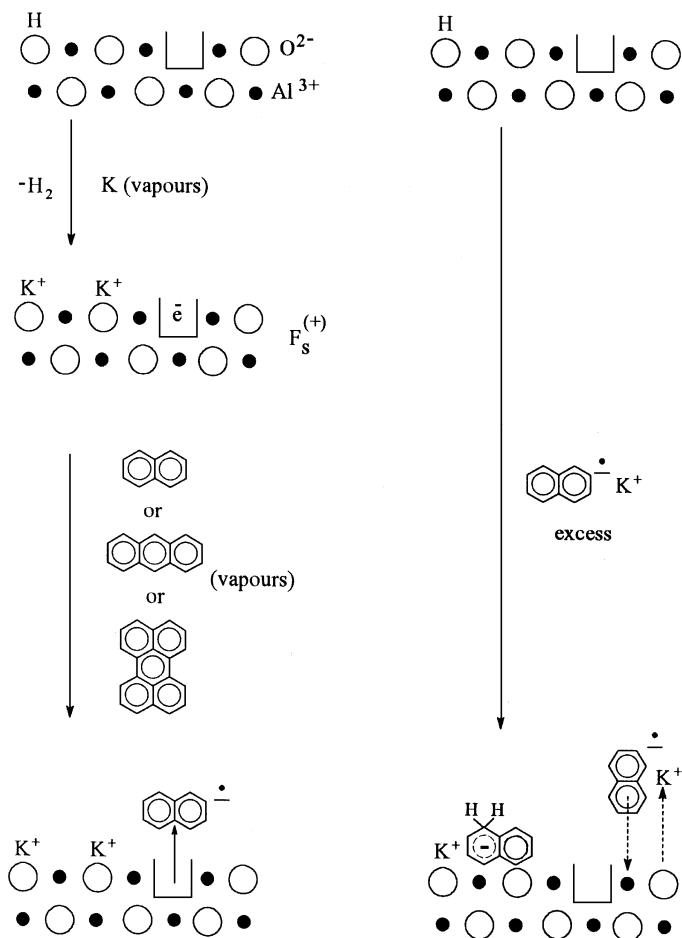
The reactions of the synthesis of the particular catalytic systems are depicted on Scheme 1.

The activity of the studied catalysts was investigated in 1-pentene and 1-hexene isomerization and in ethene and propene hydrogenation.

EXPERIMENTAL

Catalysts

γ -Alumina was obtained by hydrolyzing aluminum triisopropoxide (Fluka, pract. dest. ≥98% Al), previously pu-



SCHEME 1. Synthesis of ion radical species on γ -alumina surface.

rified by distillation under reduced pressure (b.p. 140°C, 1.07 kPa). The hydrolysis procedure has been described elsewhere (17). The obtained $\text{Al}(\text{OH})_3$ was dried at 40, 80, and 120°C for 24 h at each temperature. Before potassium evaporation or impregnation with potassium naphthenide solution, aluminum hydroxide was calcined, first in air at 550°C for 1 h and then in the stream of water-free and deoxygenated nitrogen for 5 h at the same temperature. Grains, 0.5–1.0 mm in diameter, were used for the evaporation and impregnation.

The number of OH groups on $\gamma\text{-Al}_2\text{O}_3$ was determined by means of the potassium naphthenide titration method (14) and the pulse chromatographic method using $\text{Zn}(\text{CH}_3)_2$ as a titrant according to Nondek (13).

Metallic potassium (Fluka, purum, $\geq 98\%$) was deposited onto γ -alumina surfaces by evaporation under vacuum (1.3 Pa) at 300°C. After evaporation the catalysts were evacuated at 350°C and then cooled in a stream of water-free, deoxygenated nitrogen.

γ -Alumina was impregnated with a 0.1 N solution of potassium naphthenide in THF obtained by a method anal-

ogous to that proposed by Scott *et al.* (18). THF (Loba Chemie, for chromatography) was purified by distillation from the benzophenone–potassium system. Naphthalene (Koch–Light, puriss) was purified by sublimation. The titration of a known amount of water (5 μl) in dry THF with the prepared solution was used for the control of the titer (14). Titration ended with the appearance of the characteristic green coloration. The impregnation was performed according to the following procedure: the freshly calcined $\gamma\text{-Al}_2\text{O}_3$ grains were poured into the reactor with 0.1 N potassium naphthenide solution in THF in an amount equimolar to the number of OH groups, two or three times greater than the quantity of hydroxyls. All operations were done in a water- and oxygen-free atmosphere. After 1 h of stirring at room temperature THF was evacuated. The prepared catalysts were dried at 60°C for 2 h and at 100°C for 2 h in a stream of dry deoxygenated nitrogen.

The evaporation of naphthalene (Koch–Light, puriss), phenanthrene, and perylene (both Fluka AG, puriss) onto the $\gamma\text{-Al}_2\text{O}_3\text{-K}$ catalyst surface was performed under vacuum (1.3 Pa) at 250°C. An excess of polycyclic hydrocarbon was evacuated for 1 h at 300°C.

All operations with the studied catalysts were performed in an atmosphere of dry deoxygenated nitrogen.

Reactions

Isomerization of 1-pentene (Fluka, puriss.) and 1-hexene (Fluka, puriss.) were carried out at 20°C in the batch-type setup containing the thermostated 20-cm³ glass reactor, equipped with a stirrer, and connected to a system providing vacuum (1.3 Pa) and deoxygenated dry nitrogen. Before each reaction the reactor was evacuated and filled with purified nitrogen. The reactant and catalyst were introduced under nitrogen. The following standard amounts of reactants and catalysts were used: 3 g of 1-pentene per 100 mg of the catalyst and 2 g of 1-hexene per 100 mg of the catalyst. Reaction products were analyzed by GC using a 50-m capillary Squalane column at room temperature.

Hydrogenation of ethene and propene (both Aldrich, chrom. $\geq 99\%$) was performed in the thermostated batch-type glass reactor of 300 cm³ volume at 100°C under normal pressure at the H_2 : alkene partial pressure ratio equal to 1. In each reaction run, 0.2 g of ethene or 0.3 g of propene per 80 mg of catalysts was used. The reaction products were analyzed by GC using a 30-m capillary Carbowax 20 M column.

Base Properties

The strength of basic sites on the studied catalyst surfaces was determined using the following Hammett indicators: aniline (Fluka, puriss., $pK_a = 27$), triphenylmethane (Fluka, purum, $pK_a = 33$), and diphenylmethane (Fluka, purum, $pK_a = 35$). Indicators were adsorbed from dry

deoxygenated benzene solutions in a water- and oxygen-free atmosphere.

One-Electron Donor Properties

The one-electron donor properties of the catalysts were determined by adsorbing of nitrobenzene from 0.1 M solution and recording the ESR signal of the resulting anion radical. The concentrations of ion radicals were determined by comparing their ESR signal intensities with the intensities of DPPH standards.

ESR Measurements

The ESR spectra were registered at room temperature using a Jeol JES-MC-3X spectrometer. γ -Al₂O₃-K sample with 1-pentene, preadsorbed at room temperature, was examined at -100°C .

Poisoning of the Active Sites

The poisoning of active centers was performed according to a procedure discussed elsewhere (3, 19-21).

The catalyst was suspended in benzene solution of diphenylmethane, the amount of which was stoichiometric or equal to 10% with respect to the number of superbasic sites on the catalyst surface. The suspension was stirred for 4 h at room temperature. Benzene was then distilled off under a vacuum of 1.3 Pa, and dry deoxidized nitrogen was admitted to the flask containing the catalyst.

RESULTS AND DISCUSSION

Surface Anion Radicals Prepared from F_s⁺ Sites

The evaporation of metallic potassium onto alumina surfaces resulted in the formation of surface F_s⁺ centers. The colorless catalyst became dark blue, typical of color centers, and exhibited strong paramagnetic properties. The characteristic narrow signal of $g=2.0018$ and $\Delta H_{\max}=1.5$ Gs was recorded by ESR. The total consumption of potassium during the evaporation was 0.62 mmol per 1 g of γ -Al₂O₃. The intensity of the signal corresponded to the concentration 1.6×10^{17} spin \cdot g⁻¹. In addition to the reaction with anionic vacancies leading to color center formation, metallic potassium underwent reactions with other types of surface electron acceptor centers, which were the holes trapped on oxygen anions near the cationic vacancies and surface hydroxyl groups (4):

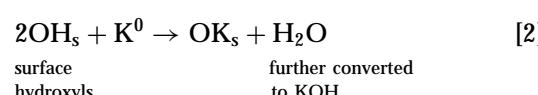
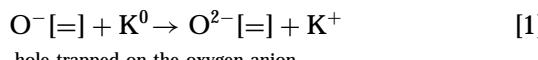
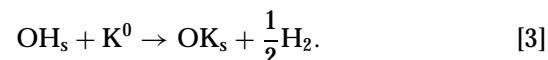


TABLE 1
Properties of γ -Al₂O₃-K-Polyaromatic Hydrocarbon Catalytic Systems

Catalytic system	Color	Paramagnetic properties
Al ₂ O ₃ -K	Dark blue	F _s ⁺ , $g=2.0018$
Al ₂ O ₃ -K : 1Knph ^a	Yellow	None
Al ₂ O ₃ -K : 2Knph	Brick red	None
Al ₂ O ₃ -K : 3Knph	Gray green	$g=2.0038$
Al ₂ O ₃ -K : naphthalene	Yellow	$g=2.0036$
Al ₂ O ₃ -K : anthracene	Red	$g=2.0034$
Al ₂ O ₃ -K : Perylene	Blue	$g=2.0034$

^a Knph, potassium naphthenide.



Only the color center exhibited very strong one-electron donor and paramagnetic properties (Table 1).

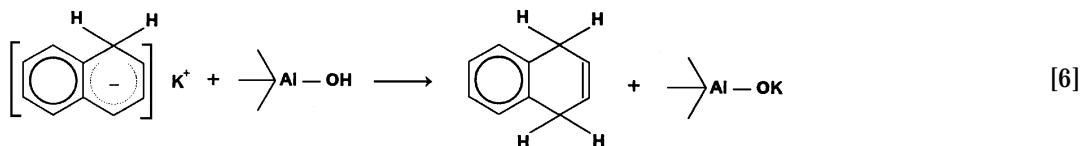
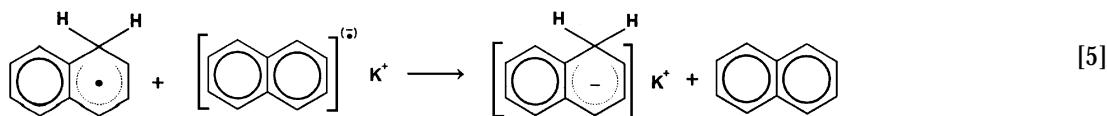
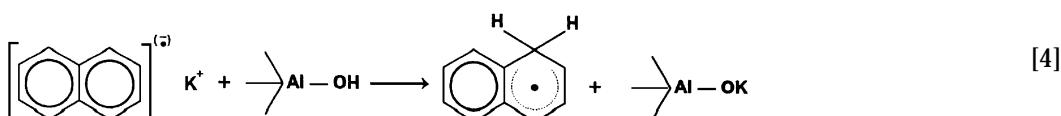
The concentration of strong one-electron donor centers measured by nitrobenzene adsorption was 1.9×10^{17} spin \cdot g⁻¹; i.e., it was eight times higher than in the case of pure γ -alumina (2.4×10^{16} spin \cdot g⁻¹). The resulting catalyst also exhibited extremely high basicity ($\text{H}_- \geq 35$).

The introduction of polyaromatic hydrocarbon onto the surface of the Al₂O₃-K system resulted in an immediate change in the color of the polyaromatic anion radical (Table 1). The intensity values of anion radical ESR signals were close to the value of the intensity measured for the signal of F_s⁺ centers. This indicated that the surface color sites were strong enough to transfer a single electron to all the studied polyaromatic molecules independent of their electron affinities.

γ -Alumina Modified with Anion Radical Salt

Three types of catalysts were obtained by the depositing of various amounts of potassium naphthenide on γ -alumina surfaces calcined at 550°C . The quantities of the deposited anion radical salt were in the ratio 1 : 1, 2 : 1, and 3 : 1 relative to the number of surface hydroxyls detected on γ -Al₂O₃. The concentrations of surface OH groups on γ -alumina, determined using the pulse chromatographic method (13) and by the titration with potassium naphthenide (14), were 0.30 and 0.29 mmol g⁻¹, respectively. The number of surface hydroxyls evaluated by both methods were in good agreement. For the other calculations the higher value of the two determinations, i.e., 0.30 mmol g⁻¹, was taken into consideration.

Reaction of OH groups with the equimolar amount of potassium naphthenide. The anion radical salt was used in the amount of 0.30 mmol per 1 g of γ -Al₂O₃. The surface reaction proceeded according to the equations (4-6).



The resulting preparations (A type) were yellow and did not exhibit any paramagnetic properties. No additional OH groups active toward potassium naphthenide existed on their surfaces; all protons were exchanged for potassium cations.

Reaction of surface hydroxyls with twice as much potassium naphthenide relative to the number of surface hydroxyls. The anion radical salt was used in the amount of 0.60 mmol per 1 g of γ -Al₂O₃. The simultaneous introduction of the whole amount of anion radical salt solution caused the process to stop at the stage of the reaction (5). Hydronaphthenide anion (0.3 mmol per 1 g of oxide) remained in the solution. The evacuation of the solvent led to anion deposition on γ -Al₂O₃ surface and its coordination by Lewis acidic sites (Scheme 1). The preparations (B type) were brick red (characteristic of hydronaphthenide anion) and were nonparamagnetic. Potassium cations (0.6 mmol per 1 g γ -Al₂O₃) remained on the catalyst surface.

Reaction of surface hydroxyls with three times the amount of potassium naphthenide relative to the number of surface hydroxyls. Potassium naphthenide was deposited in the amount of 0.90 mmol per 1 g of γ -Al₂O₃. The obtained preparations (C type) possessed surface species the same as those prepared using the double amount of sodium naphthenide in relation to the surface hydroxyls and the additionally coordinated excess (0.3 mmol per 1 g) of the anion radical salt (Scheme 1). They were gray-green and paramagnetic. The adsorbed anion radicals were stable. When the catalyst was kept in a water- and oxygen-free atmosphere, its ESR spectra did not differ from those recorded immediately after catalysts preparation, even after 2 weeks.

Isomerization of Alkenes

The isomerization of 1-pentene and 1-hexene was studied at 20°C (Tables 2 and 3). Under these mild

conditions, pure γ -alumina did not exhibit any activity. Therefore, the observed transformations can be ascribed to the action of catalytic centers, newly formed on γ -Al₂O₃ surfaces during the catalyst preparation procedures. These centers were F_s⁺ centers, their complexes with polycyclic aromatic hydrocarbons, hydronaphthenide anions, and potassium naphthenide deposits interacting with oxide surface.

Activity and Regioselectivity of F_s⁺ Centers and Their Complexes with Evaporated Polycyclic Aromatic Hydrocarbons

The γ -Al₂O₃-K system catalyzed the double bond shift in 1-pentene leading to E-2-pentene as a prevailing product (Fig. 1).

One-electron donor centers behaved in the reaction according to the mechanism (2), depicted by Eqs. [7]–[9].

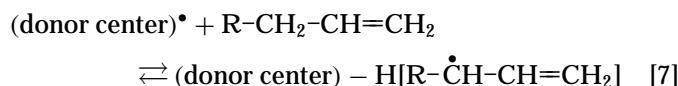


TABLE 2

The Initial Rate (r_0) of the Double Bond Shift in 1-Pentene and Z/E Ratio of 2-Pentene at 20°C over Studied Catalysts

Catalyst	r_0 , mol/g · min	$(Z/E)_0^a$	$(Z/E)_2$
γ -Al ₂ O ₃ -K	0.430	0.5	0.50
γ -Al ₂ O ₃ -K: naphthalene	0.060	4.1	1.75
γ -Al ₂ O ₃ -K: anthracene	0.075	3.8	1.73
γ -Al ₂ O ₃ -K: perylene	0.129	2.1	1.56
γ -Al ₂ O ₃ -K: 1Knph ^b	0	—	—
γ -Al ₂ O ₃ -K: 2Knph	0.061	7.1	1.67
γ -Al ₂ O ₃ -K: 3Knph	0.189	1.5	0.44

^a $(Z/E)_0$, initial Z/E ratio; $(Z/E)_2$, Z/E ratio after 2 h.

^b Knph, potassium naphthenide.

TABLE 3

The Initial Rate (r_0) of the Double Bond Shift in 1-Hexene and the Z/E Ratio of 2-Hexene at 20°C over γ -Al₂O₃-K Catalyst Modified with Polyaromatic Hydrocarbons

Catalyst	r_0 mol/g · min	(Z/E) ₀ ^a
γ -Al ₂ O ₃ -K	0.231	2.0
γ -Al ₂ O ₃ -K : naphthalene	0.077	4.7
γ -Al ₂ O ₃ -K : anthracene	0.127	3.0
γ -Al ₂ O ₃ -K : perylene	0.176	2.5

^a Negligible amounts of E-3-hexene appeared in the products mixture only over the Al₂O₃-K catalyst.



Such a mechanism is supported by the high affinity of the F_s^+ center toward atomic hydrogen, exhibited, for example, in the previously studied dehydrogenation of alkylaromatics (2-4). ESR studies of 1-pentene adsorbed on an the γ -Al₂O₃-K system revealed the presence of an organic anion radical ($g \approx 2.0020$) similar to the one recorded earlier for the MgO-K system which confirmed the suggestion about the radical character of the reaction.

The activity of the series of Al₂O₃-K catalysts, modified with polyaromatics, decreased in the sequence perylene > anthracene > naphthalene. The initial Z/E ratio changed in the opposite order. Exactly the same regularity was noted during the isomerization of 1-hexene (Table 3). The polyaromatic anion radicals acted as donor centers in this case. Doubtless, the one-electron donor character determined the activity of the studied catalysts. Therefore, the mechanism described by Eqs. [7]-[9] is also postulated for the alkene isomerization carried out over γ -Al₂O₃-K catalysts doped with vapors of various polyaromatic hydrocarbons. The intermediary formed hydroanion of polyaromatic hydrocarbon (Eq. [10]) is in close contact with the alkene radical species and cannot act as a basic center toward the next alkene molecule.

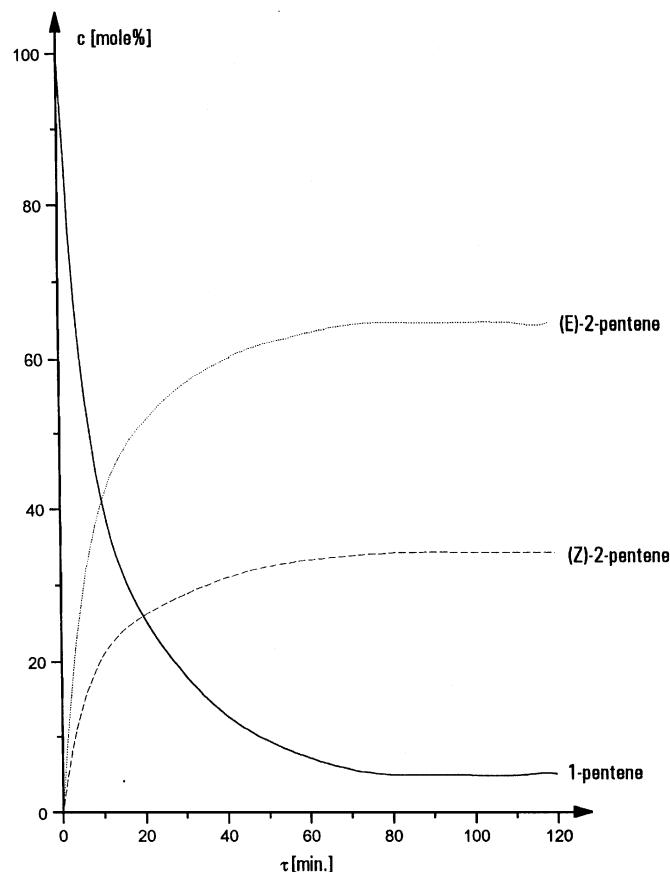
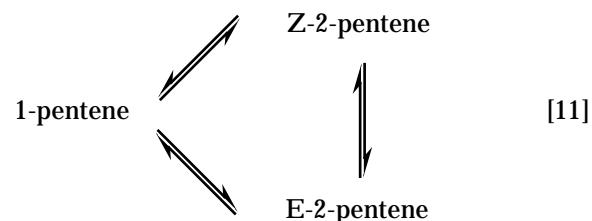
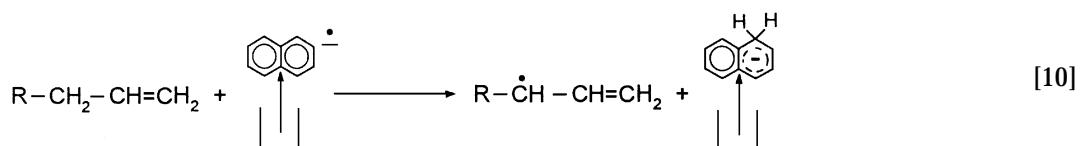


FIG. 1. Isomerization of 1-pentene over F_s^+ centers as active sites. Catalyst, γ -Al₂O₃-K; temp., 20°C.

It is noteworthy that the discussed mechanism explains the occurrence of the double bond shift in an alkene molecule. The studied isomerization reaction is of a complex parallel-consecutive nature (Eq. [11]). Therefore, its regioselectivity cannot be inferred from the above mechanism (Eq. [7]-[9]).



As was stated above under *Surface Anion Radicals Prepared from F_s^+ sites* the surface concentrations of the studied polyaromatic complexes with F_s^+ centers on γ -Al₂O₃-K



catalysts were practically identical and close to the concentration of F_s^+ sites. Therefore, the observed differentiation of the investigated catalyst activity (measured by the initial reaction rate) and the differences in the reaction regioselectivity are the result of the nature of the active centers and are not connected with their number. It should be emphasized that there is an optimum range for the electron affinity of acceptor compounds with respect to the electron donor and catalytic properties of the resulting surface EDA complex. We have observed many times (3, 5, 19–21) that the adsorption of strong electron acceptors, such as tetracyanoethene ($E_A = 2.56$ eV (22)), *m*-dinitrobenzene ($E_A = 1.85$ eV (22)), and moderate as nitrobenzene ($E_A = 1.3$ eV (22)), on F_s^+ centers or even on weaker one-electron donor sites led to the complete (or almost complete) poisoning of their donor properties and catalytic activity. In contrast, the EDA complexes of F_s^+ sites with the weaker acceptors such as perylene ($E_A = 1.12$ eV (22)) anthracene ($E_A = 0.64$ eV (22)), and naphthalene ($E_A = -0.02$ eV (22)) exhibited remarkable activity in the studied transformations. Their activity in the isomerization and hydrogenation of alkenes diminished with the decrease in the electron affinity value of the deposited hydrocarbon (Tables 2–4). Thus, it could be ascertained that, taking into account the activity of the formed EDA complex, the E_A value of an electron acceptor has to be lower than 1.3 eV (for E_A values ≥ 1.3 eV the availability of a single electron for any acceptor reactant was completely suppressed) but higher than 0.64 eV (the complex with perylene exhibited remarkably higher activity than the one with anthracene). We assumed that the E_A value of the acceptor was the decisive parameter for the EDA complex activity. It is also noteworthy that the activity of all prepared EDA complexes was significantly lower than the activity of the starting F_s^+ centers on the $\gamma\text{-Al}_2\text{O}_3\text{-K}$ surface.

The differentiation of the studied catalysts properties was also reflected in the regioselectivity of the catalyzed isomerization reactions (Tables 2 and 3 and Figs. 2 and 5). In contrast to the color centers, their EDA complexes favored the

TABLE 4

The Initial Rate (r_0) of the Ethene and Propene Hydrogenation over Studied Catalysts

Catalyst	$r_0 \text{ % min}^{-1}\text{g}^{-1}$	
	Ethylene	Propylene
$\gamma\text{-Al}_2\text{O}_3\text{-K}$	17.0	11.0
$\gamma\text{-Al}_2\text{O}_3\text{-K: naphthalene}$	5.0	3.8
$\gamma\text{-Al}_2\text{O}_3\text{-K: anthracene}$	8.0	5.8
$\gamma\text{-Al}_2\text{O}_3\text{-K: perylene}$	12.2	7.4
$\gamma\text{-Al}_2\text{O}_3\text{: 3Knph}$	3.25*	4.4

* Product composition at the total ethene conversion: 88 mol% ethane; 6 mol% butane; 4 mol% 2-butene; 2 mol% 1-butene.

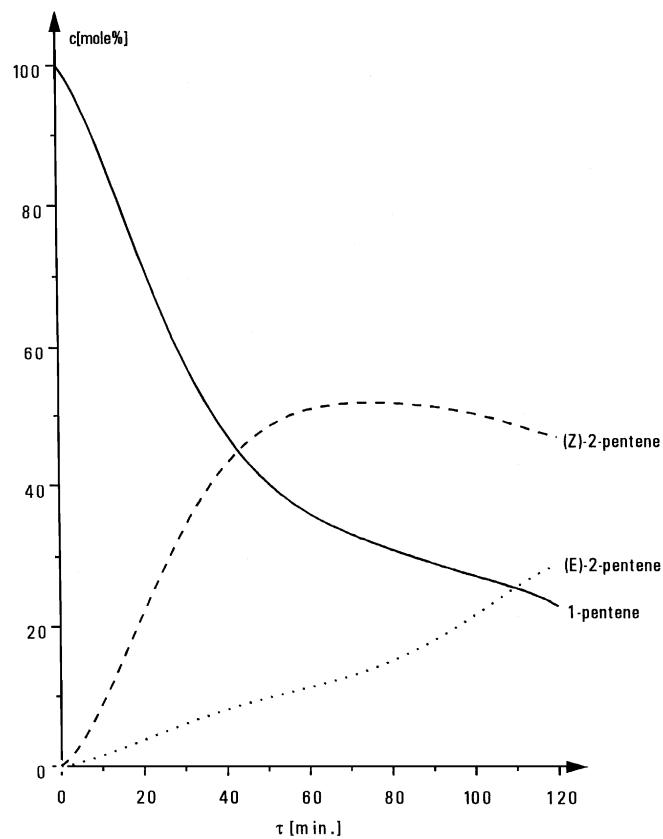


FIG. 2. Isomerization of 1-pentene over $\gamma\text{-Al}_2\text{O}_3$ with immobilized hydronaphthenide anion. Catalyst, $\gamma\text{-Al}_2\text{O}_3$ + twofold excess of potassium naphthenide; temp., 20°C.

formation of Z-2 pentene. The complex with naphthalene exhibited the highest selectivity toward Z isomer, while the complex with perylene was of the lowest selectivity toward Z-2-pentene. The regioselectivity vs 1-pentene conversion profiles, determined for the naphthalene and anthracene complexes, were similar and differed remarkably from the regioselectivity profile of the perylene complex. However, all of them converged at the Z/E of the range of 1.55–1.75 at 1-pentene conversion higher than 90%. The final Z/E ratio, much higher than the equilibrium value ($Z/E \approx 0.5$), was evidence of the low activity of the surface polyaromatic complexes in the consecutive isomerization of Z-2-pentene to the E isomer (Eq. [11]). The regioselectivity profile noted for F_s^+ centers was indicative of the thermodynamic composition of the isomerization products already at the step of the double bond shift (Eq. [11]).

The analogous regioselectivity differentiation was also noted for the 1-hexene reaction (Table 3). However, in this case, even the pure $\gamma\text{-Al}_2\text{O}_3\text{-K}$ catalysts produced preferentially Z-2-hexene at the step of the double bond shift. A more detailed explanation of the prevalence of Z or E alkene isomers after the double bond shift requires calculations of sterical models of surface EDA complexes and models of their interaction with 1-alkenes molecules.

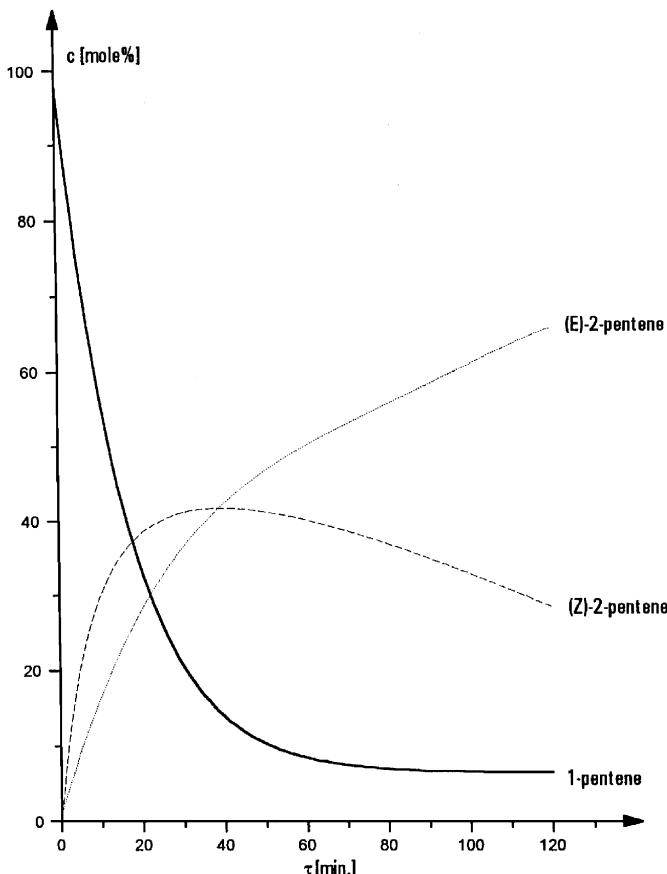


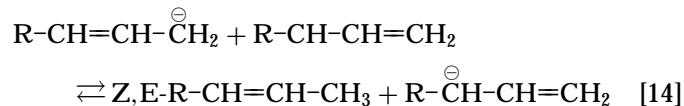
FIG. 3. Isomerization of 1-pentene over γ -Al₂O₃ with immobilized hydronaphthenide anion and potassium naphthenide. Catalyst, γ -Al₂O₃ + threefold excess of potassium naphthenide; temp., 20°C.

Activity and regioselectivity of potassium naphthenide species immobilized on γ -Al₂O₃. The catalyst prepared by the reaction of γ -alumina hydroxyls with an equimolar amount of potassium naphthenide was completely inactive in the transformations of 1-pentene. The B-type system with hydronaphthenide anions immobilized on the surface exhibited remarkable activity in 1-pentene isomerization (Table 2, Fig. 3). The initial Z/E ratio of 2-pentene equal to 7.1 as observed for this catalyst was much higher than the Z/E ratio values determined for the all other studied catalytic systems. The regioselectivity vs. the activity profile determined for the γ -Al₂O₃-K-2Knph system showed its high activity in the consecutive Z-2-pentene \rightarrow E-2-pentene conversion. Simultaneously, the shape of the regioselectivity profile and the fact that the reaction was practically stopped at the relatively low 1-pentene conversion (ca. 80%) indicated catalyst deactivation, perhaps due to the surface polymerization of alkene.

The mentioned catalyst did not possess one-electron donor character. Its activity should be ascribed to the strongly basic hydronaphthenide anion deposited on the surface and exhibiting two-electron donor character. The

basic strength of the γ -Al₂O₃-K-2Knph catalyst evaluated by the Walling method (15) corresponded to $H_{\text{w}} \geq 35$ (colorless diphenylmethane converted to yellow anion).

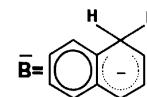
The reaction catalyzed by two-electron donor centers probably proceeded according to the basic mechanism proposed by Pines and Schaap (16):



or



where



The partial poisoning of the strongest two-electron donor (basic) centers on the B system surface realized by the adsorption of diphenylmethane ($pK_a = 35$) in a quantity corresponding to 10 mol% of the amount of the deposited hydronaphthenide anion remarkably retarded the reaction (1-pentene conversion after 2 h did not exceed 20%), while the total coverage of the active centers by diphenylmethane (0.3 mmol per 1 g of catalyst) completely poisoned the catalyst B activity. These observations are evidence of the basic character of the centers active in the studied reaction and confirmed the supposed extremely strong basic properties ($H_- \geq 35$) of the hydronaphthenide anion.

In the case of potassium naphthenide doped γ -alumina of the C type, the hydronaphthenide anion deposited on the surface was accompanied by an equimolar amount of the anion radical salt. The activity exhibited by the catalyst C was therefore a superposition of the activities of one- and two-electron donor centers. The initial Z/E ratio of 2-pentene noted for this system was significantly lower (1.5) than for catalyst B which had very strong two-electron donor centers (Fig. 4). Simultaneously, the activity of the combined system measured by the initial reaction rate was about three times higher.

The shape of its regioselectivity profile (Fig. 5), completely different from that noted for the foregoing catalyst and also different from the profiles determined for the surface EDA complexes on γ -Al₂O₃-K surface catalyst,

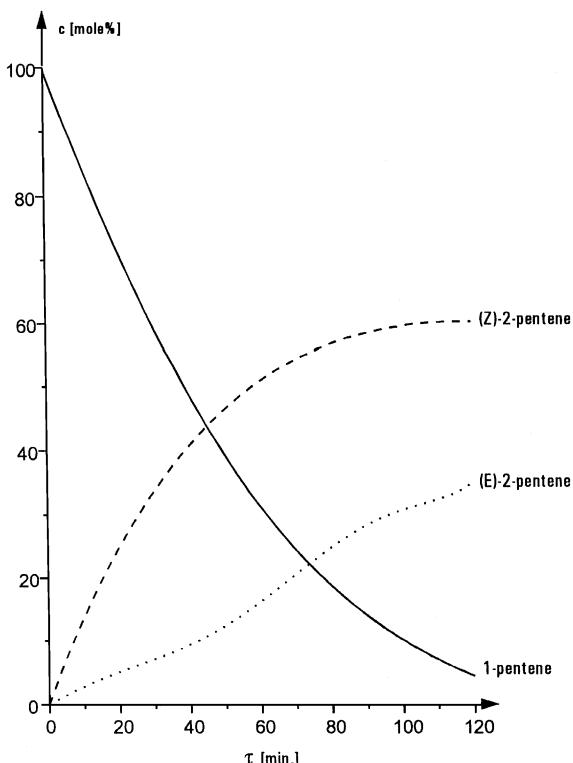


FIG. 4. Isomerization of 1-pentene over γ -Al₂O₃-K system with anion radical from adsorbed naphthalene. Catalyst, γ -Al₂O₃-K-naphthalene; temp., 20°C.

confirmed the participation of both the two-electron donor and the one-electron donor centers in the isomerization of 1-pentene.

The isomerization pathway, analogous to that postulated for the reaction catalyzed by the surface EDA complexes of polyaromatics with F_s⁺ sites, is suggested for the transformations over potassium naphthenide deposited on γ -alumina. Nevertheless, the activity of both kinds of one-electron donor centers could not be considered identical. These centers would differ remarkably in their donor power. The first of them originated during the adsorption of the polyaromatic molecule on F_s⁺ centers possessing extremely high donor strength, while the latter were formed by adsorption of the anion radical salt on electron-deficient sites of γ -alumina surfaces. Irrespective of their origin, the adsorbed ion radical species of polyaromatic hydrocarbons could be regarded as being similar to the ion radicals of 1-pentene or 1-hexene, formed during the isomerization reaction on F_s⁺ centers. However, the last ones exhibit another stereoregularity during the reaction.

Hydrogenation of Alkenes

The γ -Al₂O₃-K catalyst and its preparation, modified with polyaromatic hydrocarbons, exhibited high activity in the hydrogenation of ethene and propene. The sequence of

catalyst activity in both reactions was parallel to the one established in the isomerization of alkenes (Table 4).

From the series of potassium naphthenide supported γ -alumina preparations, only the C-type catalyst was active in the hydrogenation of the studied alkenes. The absence of activity in the hydrogenation of ethene and propene, exhibited by the γ -alumina-potassium naphthenide system of the B type, suggests that the superbasic two-electron donor centers are completely inactive in the hydrogenation of alkenes or that they take part in a complex process in which the cooperation of one-electron donor centers is necessary (the catalyst of C type). Our previous results (2-5) strongly support the first statement. Namely, during the studies of MgO-alkali metals catalysts, differing in the relative concentrations of one- and two-electron donor centers, it was found that the hydrogenating activity strongly depended on the number of the strongest one-electron donor centers. The poisoning of these centers led to the disappearance of catalyst activity. The specificity of the mentioned bifunctional catalysts lay in the fact that the high concentration of the strongest one-electron donor centers was accompanied by the low concentration of the strongest two-electron donor centers and vice versa. Therefore, the observed absence of any positive effect of the two-electron donor centers is particularly meaningful. The higher number of other superbasic catalysts possessing no or negligible amounts of superbasic two-electron donor centers, such as the ZnO-alkali metal series of catalysts, exhibited the high activity found in the hydrogenation of various alkenes (23).

Over the C-type catalysts the products of ethene hydrogenation contained—as well as ethane—butane, 1-butene, and 2-butenes which were formed in the reactant dimerization followed by the consecutive hydrogenation. The dimerization products were not detected when ethene was in contact with the C-type catalyst in the absence of dihydrogen. No change in the gas composition was observed in this case for 2 h. The further introduction of H₂ resulted in the start of the hydrogenation reaction; it was not, however, accompanied by the reactant dimerization. Taking the above into consideration it can be concluded that two types of centers exhibited activity in the presence of dihydrogen. The centers of the first type activated the hydrogenation reaction, and the centers of the second type were responsible for the dimerization of the reactant. The latter were suppressed in contact with alkene only for a long time. The deactivation was probably due to the surface polymerization of olefin.

We observed previously the surface polymerization of ethene over the superbasic catalysts of the MgO (calcined at 550°C) alkali metal type possessing the dominant two-electron donor properties. In contact with alkene above 120°C the catalysts changed in color from dark blue to bright yellow. After evacuation (1.03 Pa) of the gas at room temperature IR spectroscopy revealed the presence of the

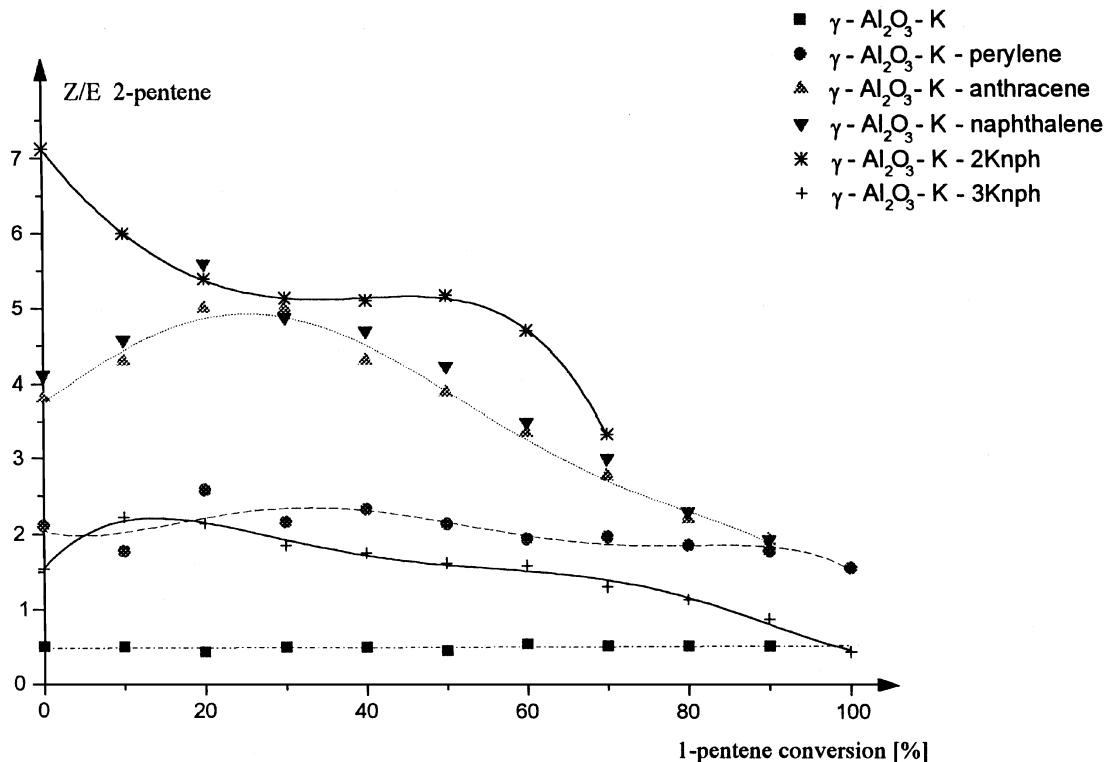


FIG. 5. The Z/E 2-pentene ratio vs the 1-pentene conversion profiles determined for the studied catalysts.

bands at 2935–2830 and 1480–1430 cm^{-1} , characteristic of the methylene group in the hydrocarbon chain. It is noteworthy that the amount of a surface deposit did not increase with time; the intensity of the recorded IR bands remained unchanged for the samples in contact with alkene for more than 2 min. This observation led to the conclusion that the formed polymer rapidly suppressed the activity of the centers initiating the polymerization reaction.

The detailed study of the nature of the polymer residue forming on the surface of γ -alumina preparations with immobilized potassium naphthenide is complicated. The presence of organic deposits related to naphthalene makes it impossible to identify the surface species by IR; the intensities of the bands derived from the adsorbed species of ethene are insignificant in relation to those derived from polyaromatic hydrocarbon (the amount corresponded to 0.6 or 0.9 mmol per 1 g of the catalyst). The use of other techniques, such as TGA-MS, for the characterization of the deposits on the surfaces of the catalysts after use is strongly limited because of the presence of polyaromatic hydrocarbon surface species.

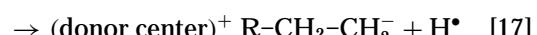
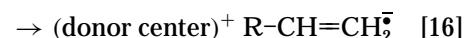
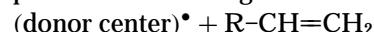
In comparing the results of ethene transformation in the absence/presence of H_2 with the distribution of the active sites on the surfaces of the series of $\gamma\text{-Al}_2\text{O}_3$ -potassium naphthenide catalysts, the surface one-electron donor centers (supported naphthenide ion radical) were found to be active in the hydrogenation. Consecutively, the two-

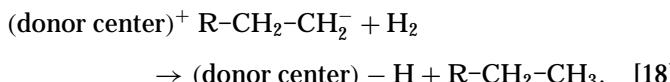
electron donor centers (supported dihydronaphthenide anion) were found to be active in the reactant dimerization. The presence of the one-electron donor centers was necessary to produce hydrogen radicals active in the hydrogenation reaction and most probably in the hydrocracking of polymer chains formed on the catalyst surface which prevented its deactivation due to the formation of polymeric deposits. The activity of two-electron donor centers was related to the polymerization only. Therefore, the catalyst of the B type, possessing only the last type of active centers, did not cause observable changes in the composition of the reacting gases.

The hydrogenation of propene resulted in propane as the only reaction product over C-type catalyst.

The mechanism analogous to the one proposed by Tamari (9) for EDA complexes of polyaromatics with alkali metals was adopted for the hydrogenation of alkenes over the studied catalysts with immobilized polyaromatic ion radicals.

The reaction catalyzed by F_s^+ centers ($\text{Al}_2\text{O}_3\text{-K}$ system) proceeded according similar mechanism (5):





The atomic hydrogen produced in the reaction [17] as well as the hydrogen atom bound to the donor center (Eq. [18]) would immediately take part in the hydrogenation of further alkene molecules.

CONCLUSION

Of all the investigated catalysts of the EDA complex type, i.e., the γ -Al₂O₃-K system containing F_s⁺ centers, the catalysts prepared by the adsorption of polyaromatic hydrocarbons on the surface of γ -Al₂O₃-K catalyst, and the system synthesized by the immobilization of potassium naphthenide in an amount three times as high as that of hydroxyls on the γ -Al₂O₃ surface, exhibit remarkable activity in the isomerization and hydrogenation of alkenes.

The significant differences in the initial rate of the isomerization reactions and their regioselectivity (measured by the Z/E ratio of the produced 2-alkenes) reflect the specificity of the studied types of EDA complexes. The γ -Al₂O₃-K catalyst, possessing one-electron donor centers of primary character (F_s⁺ sites), exhibits the highest activity in the studied transformations and simultaneously the lowest selectivity toward Z-2-alkenes formation. The two other types of catalysts must be considered as one-electron donors of secondary character, the one type because these catalysts originated by the adsorption of the polyaromatic molecules on the primary F_s⁺ centers, the other because these catalysts were formed by the immobilization of the naphthalene radical salt on the electron-deficient sites of γ -Al₂O₃. The mentioned secondary classes of one-electron donor surface centers favor the formation of Z-2-isomers.

The electron affinity of an acceptor in the EDA complex, formed by polyaromatic hydrocarbon with F_s⁺ centers, remarkably influences its activity as well as the regioselectivity in the isomerization of alkenes. The range of the E_A values for the acceptor component, 1.3 eV > E_A > 0.64 eV, is suggested to be the optimum with respect to the electron donor and catalytic properties of the resulting surface EDA complex.

The order of activity of the studied catalysts, possessing the EDA complex type determined for the hydrogenation of ethene and perylene, is analogous to that established for the isomerization reactions.

The specific behavior of γ -alumina, containing twice as much immobilized potassium naphthenide as the number of surface OH, confirms the previously observed (2-5) dif-

ferentiation between one- and two-electron donor centers on superbasic surfaces. This catalyst, possessing only two-electron donor centers of extremum strength (H₋ ≥ 35) and connected with the immobilized hydronaphthenide anion, exhibits very high selectivity toward Z-2-pentene formation and a complete lack of activity in the alkenes hydrogenation. The latter probably resulted from the ability of the catalyst to undergo deactivation by the polymeric forms of an alkenic reactant.

ACKNOWLEDGMENT

This paper is dedicated to Professor Stanisław Malinowski, our inspirer and co-inventor of superbasic catalysts to celebrate 50 years of his great scientific achievements with true appreciations.

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