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Role of the lattice energy from chemical agents in the activation of highly-condensed carbons

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Abstract: Highly condensed carbons from pet-coke were first treated with Na/K hydroxides and carbonates and then with H₂SO₄. The esterification reaction of palmitic acid reached conversions of up to 97 % on the yielded activated carbons. The results evidence the relationship between the efficacy of Na/K hydroxides and carbonates as treatment agents and their lattice potential energy. Moreover, the analysis of carbonaceous solids confirms that both surface area and acidity are primary factors promoting activity in the esterification reaction. Furthermore, the results do not indicate a direct relationship between the activity and the oxidized species (SO_x) arising from the treatment with H₂SO₄. The relatively low melting and decomposition temperature of Na/K hydroxides can improve their effect on the pet-coke matrix, leading to higher surface areas, acidities, and catalytic activities than treatment with carbonates. This supports an affinity between the carboxyl functions of the fatty acid molecules and the polar and catalytically active centers of the hydroxide-treated solid surface.

Keywords: acidity; activated carbon; delayed pet-coke; esterification.

INTRODUCTION

Pet-coke is a petroleum refinement by-product, mostly composed of highly condensed carbon species. A way to help address the amounts of pet-coke that result from heavy-petroleum refinement consists in their conversion into environmentally-friendly products with a higher aggregate value, as activated carbons. The activated carbons have been extensively studied because of their catalytic and adsorptive properties.^{1–4} Moreover, their acid modifications have good activity in acid-catalyzed reactions^{5,6} such as the hydrolysis of the cellulose⁵ or the esterification of free fatty acids.⁶

In the industries of cosmetology, solvents, polymers, and alternative fuels, among others, esters play an important role. They mainly come from the trances-

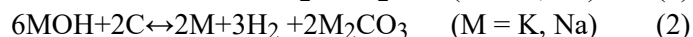
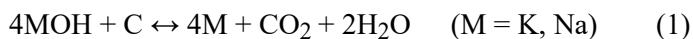
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terification⁷ of triglycerides contained in vegetable oil and animal fats in the presence of homogeneous catalysts, such as metal hydroxides or (less frequently) inorganic acids. Likewise, in Fisher's esterification of fatty acids, inorganic acids are commonly used.

Special attention has been directed to the use of waste oils from industrial and domestic sources to avoid the use of alimentary resources. However, the high presence of fatty acids in these sources limits the efficacy of base-catalyzed transesterification because of the formation of soaps. To overcome this problem, prior esterification of fatty acids is applied in the presence of an alcohol and strongly acidic homogeneous catalysts, such as H₂SO₄ and HF, followed by transesterification.⁸ Conversely, their corrosive nature and difficulties in separation from the reaction product mixture have driven the search for heterogeneous catalysts of a less corrosive nature and relatively easy separation and reutilization.⁸ In this sense, several alternatives were analyzed, such as ion exchange resins,⁹ superacids, mesoporous aluminosilicates, microporous solids, such as zeolites¹⁰ and activated carbons.¹⁻⁴ Activated carbons, for example, have remarkable properties as catalysts and adsorbents.¹⁻⁴ These could be obtained by thermal treating (also called "physical treatment") between 873 and 1073 K, of organic precursors, such as sugar, wood, charcoal or asphalt, among others, in the presence of CO₂, steam, noble gases or N₂,¹¹ and/or by treatment with chemical reagents of diverse character.^{12,13}

Among the different agents for the chemical treatment of carbonous precursors, K and Na hydroxides have gained increasing attention. Zeng *et al.*² reported the use of activated carbon (achieved by step treatment with KOH and H₂SO₄ of Chinese pet-coke) in oleic acid esterification with methanol. The resulting activated carbons had stronger acidity than that of SO₄²⁻/ZrO₂ solids but were slightly weaker than pure H₂SO₄. Furthermore, their catalytic performance was close to 72 %. Lee and Choi³ treated high sulfur petroleum coke with K and Na hydroxides between 673 and 873 K. Their investigation revealed that KOH was a more effective activating agent, leading to a surface area of 1980 m² g⁻¹ with a metal hydroxide to coke mass ratio of 4. Similar observations were first made by Ehrburger *et al.*,¹⁴ who reported that much more CO₂ was yielded from coal treated with KOH than with NaOH.

Lillo and coworkers⁴ proposed that K and Na hydroxides are reduced by the carbon, producing a metallic element during the heat treatment:



However, there is increasing interest in the use of less aggressive or corrosives chemical activating agents. Na₂CO₃ and K₂CO₃ offer a possible alternative. In addition to their lower aggressiveness, CO₃²⁺ were proposed as central parti-

cipants in the reaction mechanisms that lead to activated carbons.¹⁵ In this sense, various researchers have proposed¹⁶ that carbonates could react with carbon directly by reactions (3) and (4), yielding the associated metallic element and their oxide during the heat treatment:



Moreover, the derived metallic oxide can also be a key participant in the reaction mechanisms that lead to activated carbons:



However, these reactions do not offer a direct explanation for the development of an acidic character in some resulting activated carbons.

Inorganic acids, such as H_3PO_4 , H_2SO_4 , HCl and HNO_3 , were early employed¹⁷ for the synthesis of activated carbons. Between them, H_2SO_4 has considerable use^{2,5,6} as a sulfonation agent.¹⁸ The incorporation of sulfuric acid into the interior carbonous matrix promotes sulfonation¹⁸ of aromatic structures that constitute the coke and results in stable carbon structures with a higher density of $-\text{SO}_3\text{H}$ groups. In this regard, various research groups^{5,6} have reported the preparation of activated carbons bearing $-\text{SO}_3\text{H}$ functions by treating several organic species with concentrated sulfuric acid.

Carbons with $-\text{SO}_3\text{H}$ groups are known for their considerable acidity, showing good activity in acid-catalyzed^{5,6} reactions, such as the hydrolysis of cellulose⁵ or the esterification of free fatty acids with methanol.⁶

The lattice potential energy¹⁹ (LPE) is usually expressed in kJ mol^{-1} and defined in some textbooks as the energy required for the endothermic breaking apart of an ionic solid and the conversion of its component atoms into gaseous ions, giving positive values. Another definition explains it as the reverse process, giving negative values. The direct experimental determination of lattice potential energy is difficult. Nevertheless, LPE can be calculated from other measurable energy quantities through the Born–Fajans–Haber thermochemical cycle.²⁰ Moreover, there are theoretical models for the calculation of lattice energies of ionic crystals based on the Born–Mayer equation²¹ using the Madelung constant²² or more approximately through the Kapustinskii equation.²³

The LPE can be taken into account as an indicator of the relative stabilities of the treatment agents and their propensity to transformation in the chemical species that effectively perform the chemical activation of carbons. In this sense, it could be valuable to estimate the relative proneness of the activation.

Although there is substantial knowledge about the aforementioned features, the understanding of their action on issues such as acidity, substrate adsorption, or catalytic activity remains incomplete. Consequently, the present work addresses these aspects through the study of KOH , NaOH , K_2CO_3 and Na_2CO_3 acti-

vating action and the subsequent treatment with sulfuric acid on the physico-chemical properties and catalytic performance in the esterification of palmitic acid; of highly condensed carbons obtained from Venezuelan delayed pet-coke.

EXPERIMENTAL

Synthesis and characterization of activated carbons

Venezuelan delayed pet-coke from the upgrader complex “José Antonio Anzoátegui”, ground and sieved to particles of about 53–500 μm , was used as the raw material. KOH, NaOH, Na_2CO_3 and K_2CO_3 were used as activating agents. To prepare each sample, 8 g of each activating agent and 2 g of pet-coke (mass ratio of 4:1) were thoroughly mixed. The samples were loaded in alumina crucibles into a horizontal tubular electric furnace under argon flow, heated at 1073 K for 30 min, and left cool down to room temperature. Alternately, the resulting materials were washed (by vacuum filtration) with a 5 % HCl solution and distilled water until reaching a neutral pH. Then solids were dried for 24 h at 343 K. The resulting four carbonaceous solids were labeled ActKOH, ActNaOH, Act K_2CO_3 and Act Na_2CO_3 , according to the activating agent. Half of each dry sample was stirred with 50 vol. % H_2SO_4 , using a ratio of 100 mL per gram of solid at 363 K for 3 h. Then, each resultant solid was washed with deionized water by vacuum filtration until reaching a neutral pH value and dried for 24 h at 343 K. These solids were treated with H_2SO_4 and labeled ActKOH_Su, ActNaOH_Su, Act K_2CO_3 _Su and Act Na_2CO_3 _Su.

Textural properties were acquired from N_2 adsorption isotherms at 77 K on a Micromeritics TriStar 3000 adsorption analyzer, with a vacuum pre-treatment at 423 K for 24 h, following a previously published procedure.²⁴ The surface area (S_{BET}) was acquired by the BET model.²⁵ The microporous volume (V_{μ}) was determined by the “*t*-plot” method²⁵ and the “total porous volume” (V_t) by the “Gurvitsch” rule.²⁵

X-Ray photoelectron spectroscopy (XPS) analysis was performed under high vacuum conditions (10^{-6} Pa) on a Specs–Leybold instrument with a Phoibos 150 electron analyzer and Al X-rays (1486.6 eV/240 W) emission source. The binding energy (BE) of 284.6 eV for the C 1s core level was used as an internal standard.

The superficial acidity was obtained through a wet method,⁸ in which 0.1 g of each solid previously dried at 393 K for 24 h, was introduced into test tubes with airtight screw lids with 10 mL of KOH 0.01 mol L^{-1} . In addition, a blank test with only 10 mL of KOH 0.01 mol L^{-1} was prepared. Then, the mixtures were vigorously stirred every 8 h for 3 days and centrifuged for 10 min at 4000 min^{-1} . Four milliliters from each tube were titrated with 0.01 mol L^{-1} HCl using phenolphthalein as the indicator. After this, 2 mL of HCl were added and a back-titration with KOH 0.01 mol/L was performed. The acidity was estimated in mmol g^{-1} :

$$A = \frac{[(V_{\text{oHCl}} + 2)N_{\text{HCl}} - (V_{\text{oKOH}}N_{\text{KOH}})] - [(V_{\text{iHCl}} + 2)N_{\text{HCl}} - (V_{\text{iKOH}}N_{\text{KOH}})]}{0.4m} \quad (6)$$

where m is the mass in grams of catalyst, N_{KOH} and N_{HCl} are the concentrations of KOH and HCl in mol L^{-1} , respectively, V_{oHCl} and V_{iHCl} are the milliliters of HCl required to titrate the blank test and each particular sample, V_{oKOH} and V_{iKOH} are the milliliters of KOH required for the back titration of the blank test and each particular sample.

Catalytic activity evaluation

The catalytic behavior of each studied solid was evaluated through the Fisher esterification reaction for 24 h, using 0.150 g of catalyst and 0.500 g of palmitic acid (98 %) dissolved

in 50 mL of ethanol (99 %) in a 100 mL PARR 4593 batch reactor with a Teflon liner connected to a 4848 controller unit. A lateral port allowed syringe extraction of 3 mL aliquots from the stirred reaction mixture at programmed reaction times, at 403 K. The syringe was frozen before each extraction, and the aliquots were kept in refrigerated test tubes with airtight screw lids, to freeze the reaction and prevent evaporation. Then all test tubes were allowed to reach room temperature and centrifuged for 15 min at 4000 min⁻¹. The fatty acid concentration was determined by titration of 2 mL of the transparent supernatant solution of each test tube with ethanolic 0.02 mol L⁻¹ KOH using phenolphthalein as indicator, and the conversion (X) in each reaction time was calculated by the Eq. (7):

$$X = (M_0 - M) / M_0 \quad (7)$$

where M_0 is the initial concentration in mol L⁻¹ and M is the concentration for each reaction time.

Adsorption isotherms of stearic acid

The adsorption isotherms of stearic acid at 305 K were obtained through a reported methodology,⁸ in which 0.1 g of each solid was shaken with 5 mL of stearic acid 10⁻³ mol L⁻¹ in hexane in sealed test tubes. After 24 h, all test tubes were centrifuged and 3 mL samples the clear supernatant solution were taken and titrated with 2-propanolic KOH 2×10⁻³ mol L⁻¹. The amount in mg of stearic acid adsorbed per gram of adsorbent after equilibrium (Q_{e_0}), in the point P_0 of the isotherm was calculated:

$$Q_{e_0} = 5M_{SA}(C_0 - C_{e_0})/m \quad (8)$$

where C_0 and C_{e_0} are the concentrations in mol L⁻¹ of stearic acid before and after the equilibrium, M_{SA} is the molar mass in g mol⁻¹ of stearic acid, and m is the mass in g of the adsorbent. Every new point P_i ($i > 0$) of the isotherm was obtained after the addition of 3 mL of stearic acid with a increasing concentration (C_{a_i}) from 2×10⁻³ to 10⁻² mol L⁻¹, and repetition of the cycle (shaking, 24 h of waiting and titration) to calculate the next concentrations (C_i) and adsorbed amount in equilibrium (Q_{e_i}):

$$C_i = (0.4 C_{e_{i-1}} + 0.6 C_{a_i}) \quad (9)$$

$$Q_{e_i} = Q_{e_{i-1}} + 5 M_{SA}(C_i - C_{e_i})/m \quad (10)$$

Eq. (11) represents the data of the isotherms fitted to the Langmuir model, where K_L is a constant and Q_m / mg g⁻¹ is the Langmuir monolayer capacity.

$$\frac{C_e}{Q_e} = \frac{C_e}{Q_m} + \frac{1}{K_L Q_m} \quad (11)$$

RESULTS AND DISCUSSION

The data in Table I (columns 3–5) confirm that the solids treated with hydroxides (ActKOH, ActNaOH, ActKOH_Su and ActNaOH_Su) developed higher values of BET specific surface area, total V_t , and microporous V_μ volumes than those treated with carbonates (ActK₂CO₃, ActNa₂CO₃, ActK₂CO₃_Su and ActNa₂CO₃_Su). Additionally, KOH had higher effects over these textural properties than NaOH, K₂CO₃ and Na₂CO₃. Moreover, the Na/K hydroxide-treated solids suffered slight reductions of their superficial areas after H₂SO₄ treatment (3.43 and 14.18 %) unlike Na/K carbonate-treated solids (66.8 and 56.3 %). This

behavior indicates the persistence of Na/K carbonate clusters after HCl washing during treatment.

TABLE I. Catalytic performance, acidity, and textural properties of the studied solids; S_{BET} = surface area through BET model; V_t = total porous volume, estimated by the Gurvitsch rule; V_{μ} = microporous volume, estimated by the t -plot method; X = maximum conversion of palmitic acid; k = rate constant; Q_m is the Langmuir monolayer capacity

Sample	Acidity mmol g ⁻¹	S_{BET} m ² g ⁻¹	V_t cm ³ g ⁻¹	V_{μ} cm ³ g ⁻¹	X %	k h ⁻¹	Q_m mg g ⁻¹
ActKOH	0.81	2713	1.2915	0.8044	96	0.777	416.7
ActKOH_Su	0.96	2620	1.2432	0.7659	97	0.361	434.8
ActNaOH	0.62	1456	0.7907	0.3988	97	0.496	238.1
ActNaOH_Su	0.86	1250	0.6958	0.3445	95	0.710	238.1
ActK ₂ CO ₃	0.28	268	0.1238	0.0881	28	0.0272	–
ActK ₂ CO ₃ _Su	0.93	89	0.0445	0.0262	67	0.211	–
ActNa ₂ CO ₃	-0.14	32	0.0180	0.0026	28	0.114	–
ActNa ₂ CO ₃ _Su	0.12	14	0.0079	0.0017	2.2	0.001	–
Pet-coke	0.15	18	0.0124	0.0011	19	0.0356	–
Self-catalyzed	–	–	–	–	9.7	0.007	–

The XPS spectra of the S 2p core levels for the studied solids are shown in Fig. 1. The signal near 164.04 eV could be associated with sulfur species of thiophene compounds²⁶ that remained as so-called refractory thiophene^{27,28} after achievement of the parental delayed pet-coke. This signal tends to decay after chemical treatment at 1073 K, as a possible result of an early decomposition (some authors mention higher temperatures²⁷) with the removal of the residual volatile sulfur products. Moreover, initial studies²⁹ suggest that at high temperatures, Na or K hydroxides and carbonates can react with thiophene compounds, leading to M₂S salts (M = Na or K), that would dissolve during the subsequent HCl washing. Additionally, in the solids treated with H₂SO₄, a signal close to

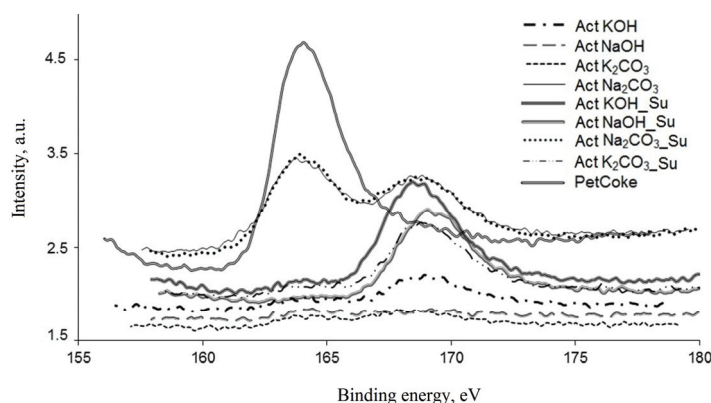


Fig. 1. XPS spectra of the S 2p region for the studied solids.

168.90 eV³⁰ associated with SO_x groups, indicates sulfonation²⁹ of the aromatic structures that constitute the coke matrix.

Treatment of pet-coke with hydroxides led to significant acidity (Table I, column 2), KOH being more effective than NaOH. However, treatment with carbonates led to poorly acidic solids, except for the ActK₂CO₃_Su, the acidity of which was similar to hydroxide-treated solids. The results also evidenced some enhancing effect of H₂SO₄ treatment over the acidity. Nevertheless, this behavior does not yield a constant increase in the activity in the esterification reaction (Table I, columns 2, 6 and 7). The low-accessibility of the fatty acid molecules to the catalytically active SO_x groups could cause this behavior.

A possible reaction between alkali metal hydroxides and halogen-substituted aromatic species³¹ present in the coke matrix under the intense conditions applied in this work would explain the acidic properties of resulting solids before treatment with H₂SO₄ (Fig. 2).

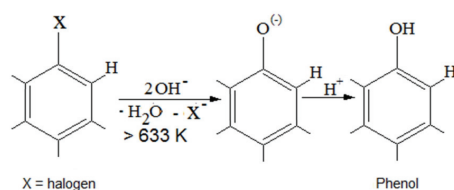


Fig. 2. The possible reaction between NaOH or KOH and halogen-substituted aromatic species during the activation process.

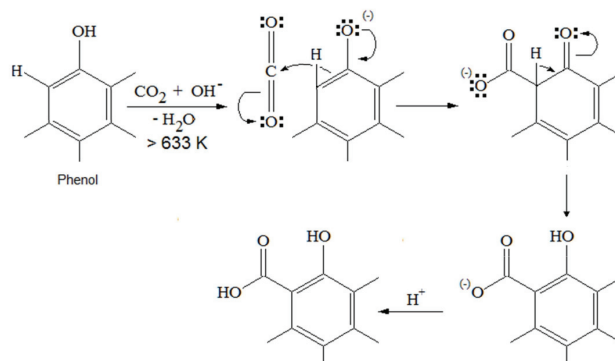


Fig. 3. The possible reaction between phenols and CO₂ generated during the activation process, leading to carboxylic groups.

Moreover, phenols could react²⁹ with the CO₂ generated during the activation process, yielding carboxylic groups (Fig. 3). Such a possibility concurs with the similarity in the order of magnitude between the superficial chlorine concentration (by XPS Cl 2p 207 eV, Fig. 4) in pet-coke (0.75 mmol g⁻¹) and the average density of acid sites after treatment with KOH and NaOH (Table I, col-

umn 2). The combination of these acidic structures, with an adequate porosity, would act as active sites during the esterification of fatty acids. The characteristic behavior of ActK₂CO₃_Su with respect the other carbonate treated solids could originate from the smaller modulus of the lattice potential energy¹⁹ of K₂CO₃ with respect Na₂CO₃, which promotes further thermal decomposition of K₂CO₃ and prepares the available surface of pet-coke for the subsequent action of H₂SO₄.

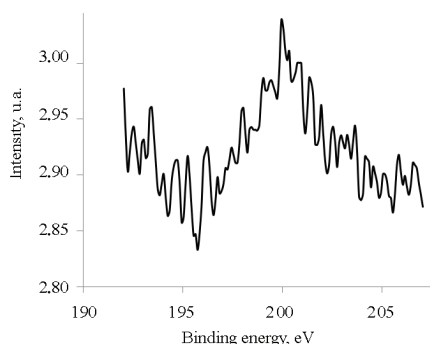


Fig. 4. XPS spectrum of the Cl 2p region of the parental delayed pet-coke.

The moderately negative acidity of ActNa₂CO₃ indicates the persistence of alkaline Na₂CO₃ clusters after HCl washing during treatment.

The adsorption isotherms of stearic acid (Fig. 5) can be separated into the A and B groups, related respectively to the hydroxide treated solids (with higher Q_e values), and pet-coke along with the carbonate-treated solids (with lower Q_e values).

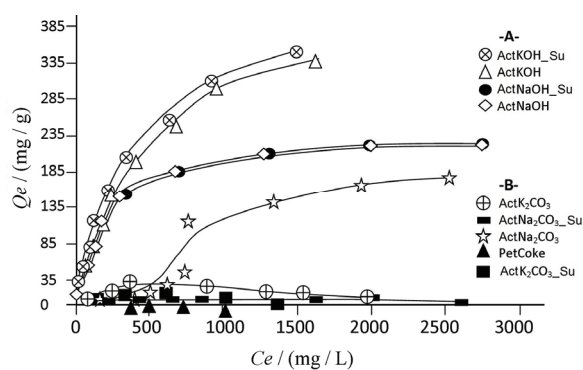


Fig. 5. Adsorption isotherms at 305 K of stearic acid on the studied solids.

The isotherms of the solids from group A fit with the linearized Langmuir model (Fig. 6), providing monolayer capacities Q_m between 238 and 435 mg g⁻¹ (Table I, column 8).

Although studies of fatty acids adsorption isotherms on activated carbons are scarce, a comparison with published values for diverse adsorbents^{8,32-34} reveals

a good affinity between fatty acid molecules and the surface of the hydroxide-treated solids. Additionally, these results evidence that KOH yields activated carbons with higher Q_m values than NaOH. On the other hand, pet-coke and group B solids do not show good agreement with this adsorption model (not displayed), probably because of the low affinity of stearic acid for their surfaces.

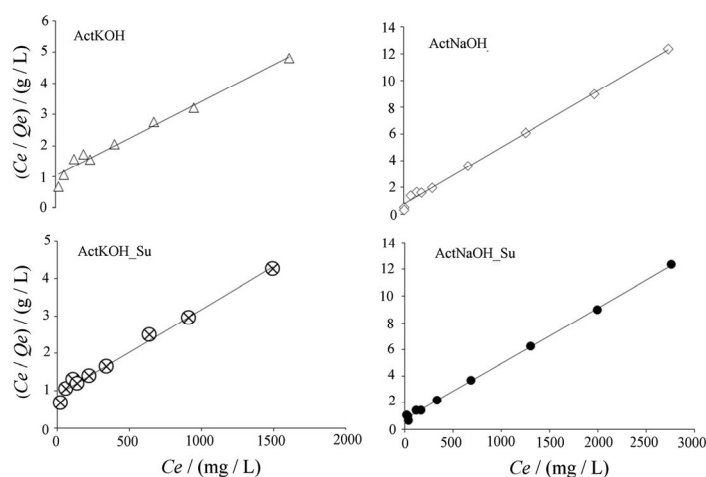


Fig. 6. Fitting of the stearic acid adsorption isotherms on the hydroxide treated solids to the linearized Langmuir model.

Moreover, treatment with H_2SO_4 did not lead to a significant increase in the Q_m values for stearic acid adsorption, as a possible consequence of the low accessibility of the fatty acid molecules to the acidic SO_x groups. Results evidence the overall trend where solids with higher acidity and activity in the esterification reaction also show a higher affinity between their surface and fatty acid molecules (Table I, columns 2, 6–8). This suggests adsorption of fatty acid molecules with their carboxyl functions oriented to the superficial polar and catalytically active centers. The nature of the superficial polar groups is not clear. However, it would be related to carboxylic and phenolic functions resulting from the action of hydroxide over substituted aromatic rings of the carbonous matrix. Interaction with fatty acid molecules could be through hydrogen bonding, as shown in Fig. 7. The sample Act K_2CO_3 _Su represents an exception. It has significant activity in the esterification reaction (Table I, columns 6 and 7), but it pertains to group B (with lower Q_e values, Fig. 5). This suggests a more complex interaction between fatty acid molecules and the superficial active sites of this solid.

The linearized representation of $\ln(1-X)$ as a function of the reaction time, t , from the data of the esterification of palmitic acid is shown in Fig. 8, which is compatible with a pseudo-first-order kinetic model:

$$\ln(1-X) = -kt \quad (12)$$

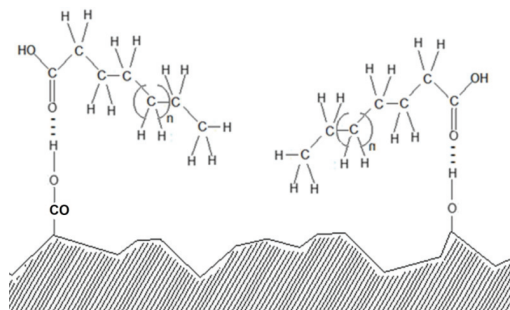


Fig. 7. Possible interaction of the superficial polar groups with the fatty acid molecules through hydrogen-bonding.

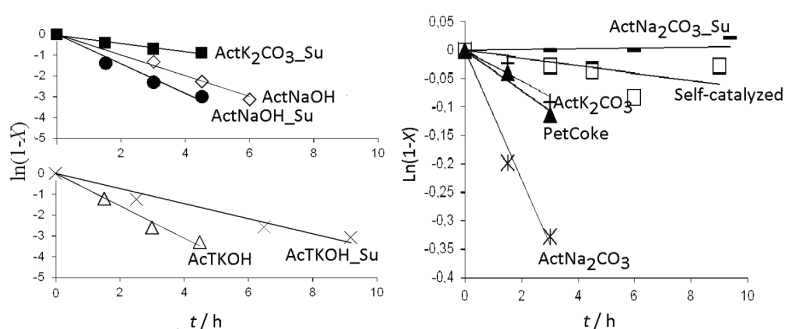


Fig. 8. Fitting of the data of the palmitic acid esterification to a pseudo-first-order kinetic model.

Then, the values of the rate constant k (Table I, column 7) reveal that hydroxide-treated catalysts are more active than their carbonate-treated counterparts, agreeing with the overall trend of both superficial area and acidity (columns 2 and 3). This behavior corroborates the fundamental role of the acid sites as catalytically active centers and the surface area.

The superior performance of hydroxides as treatment agents might be caused by the lower melting temperatures of K and Na hydroxides (591 and 683 K, respectively)³⁵ than their carbonate counterparts (1124 and 1178 K, respectively)⁴ favoring the action of hydroxides on the pet-coke.

Finally, the results evidence a relationship between the modulus of the lattice potential energy¹⁹ (LPE) of Na/K hydroxides and carbonates and their efficacy as treatment agents: The increase of the mean values of the properties from the derived activated carbons (resulting from the treatment with each agent) with the reduction of the LPE values are given in Table II. In this way, a lower LPE implies an easier thermal-decomposition of the treatment agents into the chemical species that perform pet-coke activation. The impact of the LPE would explain the superior efficacy of the potassium-based treatment agents in comparison with

their sodium-based counterparts, also agreeing with previous findings¹⁴ that mention the superior effectiveness of KOH over NaOH as an activating agent.

TABLE II. Mean values of the properties from the derived activated carbons and the modulus of the lattice potential energy (LPE) of the chemical treatment agents. Mean: before and after H₂SO₄ treatment. LPE: The values¹⁹ correspond to the “Born–Fajans Haber thermochemical cycle”

Treatment agent	Acidity mmol/g	S_{BET} m ² g ⁻¹	V_t cm ³ g ⁻¹	V_{μ} cm ³ g ⁻¹	X %	k h ⁻¹	Q_m mg g ⁻¹	Modulus of LPE kJ mol ⁻¹
Na ₂ CO ₃	-0.01	23.00	0.01295	0.00215	15.1	0.0575	–	2030
K ₂ CO ₃	0.605	178.5	0.08415	0.05715	47.5	0.1191	–	1858
NaOH	0.740	1353	0.74325	0.37165	96.0	0.6030	238.1	900
KOH	0.885	2667	1.26735	0.78515	96.5	0.5690	425.8	804

CONCLUSIONS

Activated carbons of high surface acidity, obtained by treatment with K and Na hydroxides and sulfuric acid on highly condensed carbons from Venezuelan delayed pet-coke, were active in the esterification reaction of palmitic acid, reaching conversion values of up to 97 %. The analysis of the carbonaceous solids confirms that both surface area and acidity are primary factors that promote the activity in the esterification reaction. Moreover, the results do not indicate a direct relationship between oxidized (SO_x) species and activity. The relatively low melting and decomposition temperature of Na/K hydroxides could improve their effect on the pet-coke matrix, leading to higher surface areas, acidities, and catalytic activities than treatment with carbonates. This behavior matches with the affinity of the carboxyl functions of fatty acid molecules to the polar and catalytically active centers of hydroxide treated surface of solids. Likewise, the results reveal the relationship between the lattice potential energy of Na/K hydroxides and carbonates and their efficacy, where a smaller modulus of the LPE promotes their thermal decomposition into the chemical species that perform direct pet-coke activation.

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ИЗВОД

УЛОГА ЕНЕРГИЈЕ РЕШЕТКЕ ХЕМИЈСКИХ АГЕНСА У АКТИВАЦИЈИ ВИСОКО КОНДЕНЗОВАНОГ УГЉЕНИКА

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Високо кондензовани угљеник добијен од петрол кокса је прво тертиран Na/K-хидроксидима или карбонатима, па затим сумпорном киселином. Реакција естерификације палмитинске киселине на угљенику активираним хидроксидима и сумпорном кисе-

лином је достигла степен конверзије 97 %. Резултати показују везу између ефикасности Na/K-хидроксида и карбоната и њихове енергије решетке. Додатно, анализа карбонизованог материјала потврђује да су и специфична површина и киселост примарни фактори који доприносе повећању активности у реакцији естерификације. Резултати не указују на дирекну везу између активности и оксидованих врста (SO_x) које се појављују услед третмана сумпорном киселином. Релативно ниска температура топљења и разградње Na/K-хидроксида може унапредити њихов утицај на матрикс петрол кокса, захваљући повећању специфичне површине, киселости и каталитичке активности у поређењу са третманом карбонатима. Третман хидроксида обезбеђује већи афинит поларних и каталитички активних центара површине угљеника према карбоксилним групама масних киселина.

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