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Activated Carbons for Hydrothermal Decarboxylation of Fatty Acids

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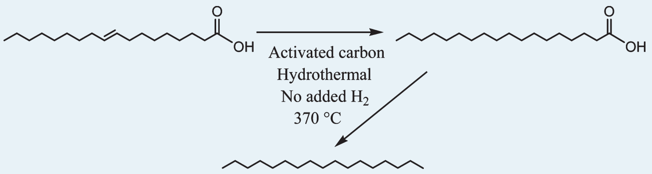
ABSTRACT: We converted palmitic and oleic acids to fuel range hydrocarbons using two activated carbons in near- and supercritical water with no H_2 added. The main products from palmitic acid were C_8-C_{15} *n*-alkanes. The major products from oleic acid were $C_{12}-C_{17}$ *n*-alkanes and some C_{17} olefins. The pseudo-first-order rate constants displayed Arrhenius behavior. The apparent activation energy of 125 kJ/mol for palmitic acid decarboxylation is higher than that observed with a 5% Pt/C catalyst. Nevertheless, these results show that activated carbons possess catalytic activity for the hydrothermal decarboxylation of fatty acids.



KEYWORDS: supercritical, kinetics, cracking, biofuel

INTRODUCTION

Fatty acids are produced from the hydrolysis of triglycerides in animal fats and plant oils, and they constitute an important renewable fuel feedstock. Removing oxygen from these fatty acids leads to hydrocarbons that can potentially serve as or be converted to drop-in replacements for the liquid transportation fuels in use today. There have been many recent reports of heterogeneous catalytic decarboxylation of fatty acids, and good overviews are available.[1,2] Typically, the most active heterogeneous catalysts are noble metals (Pt, Pd) on a high-surface area support.[3,4] Aside from two recent articles from our lab[5,6] and a pioneering study by Watanabe et al.,[7] all of the published work on heterogeneous catalytic decarboxylation of fatty acids has been done without solvent or in hydrocarbon solvents (e.g., dodecane, mesitylene). There is growing potential for using water as the medium for catalytic decarboxylation since there are several biofuel production schemes that produce aqueous streams containing free fatty acids.[8−13] One can reasonably expect catalytic materials and catalytic reactions to behave differently in water than in organic liquids, so there is a need for research on hydrothermal catalytic decarboxylation of fatty acids.

Watanabe et al.[7] reported that NaOH and KOH in supercritical water (SCW) at 400 °C produced the C_{17} alkane decarboxylation product from stearic acid. Metal oxides such as CeO_2, Y_2O_3, and ZrO_2 were also tested. ZrO_2, when present in equal amounts (by mass) with the stearic acid reactant at 400 °C for 30 min, led to the highest conversion reported (68%). Fu et al.[5,6] showed that Pt/C and Pd/C catalysts are highly active for hydrothermal decarboxylation of different saturated and unsaturated fatty acids. A single background experiment with just the carbon support revealed some modest activity for decarboxylation from the support alone (without the expensive Pt or Pd crystallites). These results motivated this present investigation of whether activated carbon alone could be an effective catalyst for hydrothermal decarboxylation of fatty acids.

There are reports of the use of charcoals and activated carbons as catalysts for gasification[14,15] and oxidation[16−19] reactions in supercritical water. Modified carbons also catalyzed the oxidative decarboxylation of *N*-phosphonomethyliminodi-acetic acid at 95 °C in an aqueous phase.[20,21] To the best of our knowledge, however, apart from our single experiment,[5] there has been no report on the use of activated carbons for decarboxylation of fatty acids in hydrothermal media. If sufficiently active, these materials could be attractive as low-cost catalysts for this transformation. In this article, we investigate the use of two different commercial activated carbons (Darco and Norit RO 0.8) for the catalytic conversion of a saturated (palmitic) and an unsaturated (oleic) fatty acid to fuel-range hydrocarbons in near- or supercritical water, without added H_2.

EXPERIMENTAL SECTION

Palmitic and oleic acid and the activated carbons were purchased from Sigma-Aldrich. We denote the two granular activated carbons as AC-1 (Darco) and AC-2 (Norit RO 0.8). AC-1 is an activated charcoal made via washing with phosphoric acid. AC-2 was made from peat and was steam activated. Both carbons were ground and sieved to particle sizes <150 μm before use. We denote AC-1 pretreated at 600 °C and ambient pressure for 6 h with 100 mL min^{-1} g^{-1} of either H_2 or N_2 as AC-1H and AC-1N, respectively. N_2 or H_2 pretreatment can remove any acids, bases, or organic compounds that might be on the surface of the carbon from its manufacture and storage. Such surface impurities could affect the decarboxylation process. These pretreated catalysts were transferred to a glovebox, and special care was taken to avoid their exposure to air.

Surface areas and pore size distributions for AC-1 and AC-2 were determined from N_2 physisorption isotherms collected at

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77 K using an ASAP 2010 BET analyzer (Micromeritics). The catalysts were degassed at 120 °C to 5×10^{-4} kPa for more than 4 h before the measurements. The total surface areas were calculated using the Brunauer—Emmett—Teller (BET) method. The pore size distributions were determined using the methods of Horvath—Kawazoe for slit-shaped pores. X-ray diffraction (XRD) patterns of samples were measured between 5 and 90° (2θ) at a scan rate of 4 deg/min (40 kV, 40 mA) using a Miniflex II (Rigaku).

We conducted the isothermal reaction experiments in stainless steel batch reactors (1.67 cm^3 volume) assembled from 3/8-in. Swagelok tube fittings. Unless stated otherwise, the reactors were loaded with 0.195 mmol of fatty acid, 0.25—0.72 cm^3 of water, and 15 mg of carbon. Loaded reactors were immersed in a fluidized sand bath set at the desired reaction temperature. Product analysis was done using capillary column gas chromatography with flame ionization (FID) and mass spectrometric detection. To quantify compounds for which we had no authentic standards, we made the reasonable assumption that the FID response was proportional to the number of carbon atoms in the eluting molecule. Our earlier articles provide additional details.[5,6] Product yields were calculated as the moles of product formed divided by the initial moles of reactant. The selectivity was calculated as the number of moles of a given product formed divided by the number of moles of fatty acid that had reacted. Experiments were carried out in triplicate. The uncertainties reported are the experimental standard deviations from these runs.

RESULTS AND DISCUSSION

This section presents information about the structure of the carbon catalysts, the products observed from the hydrothermal reactions of a saturated and an unsaturated fatty acid, and the kinetics for palmitic acid decarboxylation.

Structural and Compositional Properties. The BET surface areas for fresh AC-1 and AC-2 carbons were 600 ± 20 m^2/g and 730 ± 20 m^2/g, respectively. Figure 1 shows the pore size distributions. The AC-2 carbon had a slightly narrower pore size distribution than did AC-1.

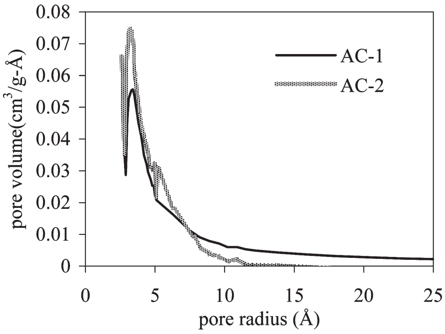

Figure 1. Pore size distributions for AC-1 and AC-2 carbons.

X-ray diffraction patterns, given in Figure 2 for the AC-1 and AC-2 carbons, indicated that these materials were amorphous, but a detectable amount of SiO_2 was present in the AC-1 carbon. There was no evidence for the presence of metals or metal oxides in the AC-1 or AC-2 carbons.

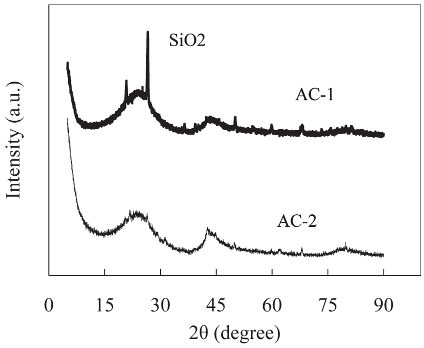

Figure 2. X-ray diffraction patterns for AC-1 and AC-2.

Products from Hydrothermal Decarboxylation. We did a control experiment with palmitic acid and 6.3 mg SiO_2 (but with no activated carbon) to determine whether this material, which is an impurity in AC-1, might influence the hydrothermal decarboxylation reaction. The experiment (370 °C, 3 h) produced no measurable yield of pentadecane. Thus SiO_2 has no measurable activity for hydrothermal decarboxylation at the reaction conditions investigated here.

Table 1 summarizes key results for the hydrothermal decarboxylation of palmitic and oleic acids at 370 °C for 3 h over the as-received and pretreated carbons. For palmitic acid, the major product of the reaction was always pentadecane, the C_{15} *n*-alkane arising directly from decarboxylation. Pretreating the AC-1 material did not alter its activity for decarboxylation. Regardless of whether the experiment was done with AC-1, AC-1N, or AC-1H, the palmitic acid conversion was 20—24%, the pentadecane molar yield was 9—10%, and the selectivity to pentadecane was about 40—50%. These results are essentially the same given the experimental uncertainty. This outcome indicates that pretreatment of this activated carbon did not significantly affect the hydrothermal catalytic decarboxylation of palmitic acid. The selectivities in Table 1 are all much lower than the values of around 90% obtained from hydrothermal decarboxylation of palmitic acid using Pt/C or Pd/C catalysts.[5]

Table 1 shows that the AC-2 carbon produced a higher pentadecane yield (19%) than did the AC-1 carbon. This result suggests that carbons arising from different sources and/or produced via different processes might have different hydrothermal decarboxylation activities. Of course, additional work with more materials is required to test this hypothesis. The mass balance ranged from 93—96% for these experiments with palmitic acid.

The final row in Table 1 shows results from the hydrothermal decarboxylation of oleic acid, a monounsaturated fatty acid, over AC-1. The main decarboxylation product of this reaction was heptadecane, an alkane, rather than heptadecene even though the C_{18} fatty acid contains a double bond. This result indicates that the activated carbon has activity for hydrogenation and not just decarboxylation alone. The mass balance was 77% in this sole oleic acid experiment. We suspect that the presence of the double bond in oleic acid makes oligomerization paths available for this compound. These paths would produce higher-molecular-weight material that does not elute from the GC.

Table 2 shows the yields and identities of the minor products from palmitic acid. These products are C_8—C_{14} alkanes and 2-heptanone. Their yields were very similar for both of the carbons, which suggests that the activity for reactions such as cracking was about the same for the two materials.

Table 3 provides the identities and yields of reaction products from oleic acid over AC-1. The major product is stearic acid, formed in about 24% yield, presumably via hydrogenation of

Table 1. Conversion and Decarboxylation Product Yield and Selectivity after 3 h at 370 °C

catalyst	reactant	decarboxylation product	conversion (%)	molar yield (%)	selectivity (%)
none[a][5]	palmitic	pentadecane		0.7 ± 0.2	
AC-1N	palmitic	pentadecane	20 ± 4	10 ± 2	52 ± 5
AC-1H	palmitic	pentadecane	21 ± 2	10 ± 2	48 ± 6
AC-1	palmitic	pentadecane	24 ± 3	9 ± 2	38 ± 6
AC-2	palmitic	pentadecane	33 ± 13	19 ± 6	58 ± 4
AC-1	oleic	heptadecane	80 ± 4	6 ± 1	7 ± 1

[a] The batch holding time without catalyst was 17 h.

Table 2. Identities and Molar Yields of Minor Products from Palmitic Acid after 3 h at 370 °C

product	molar yield (%)	
	AC-1	AC-2
octane	0.47 ± 0.05	0.4 ± 0.3
nonane	0.50 ± 0.05	0.4 ± 0.3
decane	0.52 ± 0.03	0.4 ± 0.3
undecane	0.47 ± 0.04	0.4 ± 0.2
dodecane	0.64 ± 0.05	0.7 ± 0.3
tridecane	0.86 ± 0.06	0.9 ± 0.4
tetradecane	1.4 ± 0.1	1.4 ± 0.6
2-heptanone	1.9 ± 0.1	0.96 ± 0.01

Table 3. Identities and Molar Yields of Products from Oleic Acid over AC-1 after 3 h at 370 °C

product	molar yield (%)
dodecane	0.72 ± 0.03
tridecane	0.17 ± 0.09
tetradecane	0.22 ± 0.04
pentadecane	0.25 ± 0.05
hexdecane	0.47 ± 0.15
2-heptanone	0.83 ± 0.17
2-pentanone	0.23 ± 0.05
heptadecane	5.8 ± 1.1
heptadecenes	4.7 ± 0.3
decylcyclopentane	0.39 ± 0.05
undecylcyclohexane	0.64 ± 0.07
nonanoic acid	0.33 ± 0.07
decanoic acid	0.30 ± 0.04
undecanoic acid	0.17 ± 0.05
dodecanoic acid	0.17 ± 0.05
tridecanoic acid	0.16 ± 0.04
stearic acid	24 ± 1
2(3H)-furanone-dihydro-5-tetradecyl	1.1 ± 0.3

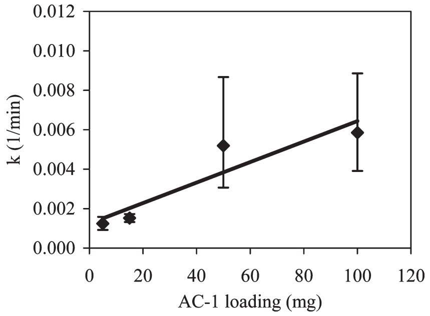

Figure 3. Effect of catalyst loading on the pseudo-first-order rate constant.

oleic acid. The combined yield of C_{17} alkanes and alkenes was 10.5%, which is less than half that of the hydrogenation product. Thus, hydrogenation of the double bond in oleic acid appears to be faster than its decarboxylation to form C_{17} hydrocarbons. A similar preference for hydrogenation over decarboxylation was noted for Pt/C-catalyzed reactions of unsaturated fatty acids both in hydrothermal[6] and organic reaction media.[22] Since no H_2 was added to the reactor in our experiments, the H atoms used to saturate the double bonds must have arisen from either the solvent (water) or a different oleic acid molecule. It is possible that a small portion of the oleic acid was gasified, especially since activated carbons have seen previous use as hydrothermal gasification catalysts,[14] though at temperatures much higher than those used here. It is also possible that water reacted with the carbon catalyst to form CO + H_2. Of course, the CO could react further to form more H_2 via the water gas shift reaction. We expect carbon gasification, if it occurs, to be much slower than gasification of the fatty acid, however.[14,15] Although the reaction pathway and mechanism for hydrogen formation is not clear at present, the present results from oleic acid show that neither added H_2 nor a noble metal is required for the hydrogenation path to proceed more rapidly than the decarboxylation path for unsaturated fatty acids in a hydrothermal environment. Table 3 also shows that several $C_{12}-C_{16}$ alkanes and C_9-C_{13} fatty acids were among the products. The presence of these products indicates that C−C bond cracking reactions occurred during this hydrothermal process.

Kinetics of Palmitic Acid Decarboxylation. The decarboxylation of palmitic acid was investigated over AC-1 at catalyst loadings ranging from 5 to 100 mg. The same batch holding time (3 h), palmitic acid loading (0.195 mmol), and reaction temperature (370 °C) were used in experiments. We calculated the pseudo-first-order rate constant (k) from the palmitic acid conversion (X) measured at each of the different catalyst loadings. Figure 3 shows that this rate constant increases linearly with the catalyst loading, which indicates that the reaction is first-order in the AC-1 carbon catalyst.

The decarboxylation of palmitic acid was next investigated over AC-1 at 330, 350, 370, and 385 °C. The same batch holding time (3 h), palmitic acid loading (0.195 mmol), and catalyst loading (15 mg) were used in all of the experiments. The mass balance was always around 95%.

We calculated a pseudo-first-order rate constant from the palmitic acid conversion determined at each temperature. The

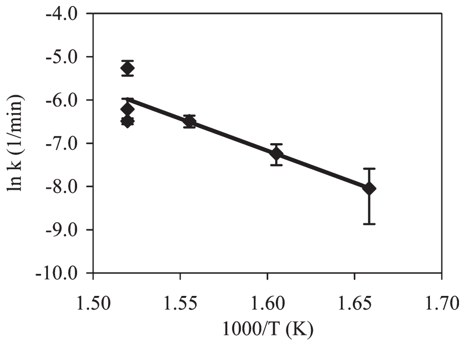

Figure 4. Arrhenius plot for palmitic acid decarboxylation.

activation energy, as determined from linear regression of ln k versus $1/T$ for the runs at subcritical temperatures (T_c = 374 °C), is 125 ± 3 kJ mol^{-1}. Figure 4 shows the Arrhenius plot. This activation energy for the hydrothermal decarboxylation of palmitic acid over AC-1 is about 50% higher than the activation energy of 79 kJ mol^{-1} that was determined for hydrothermal decarboxylation of this compound over Pt/C.[5] This outcome is to be expected since Pt is a better decarboxylation catalyst than is the carbon support alone.

The three left-most data points in Figure 4 are from palmitic acid decarboxylation in supercritical water at 385 °C. These points correspond to experiments done at three different water densities (0.15, 0.31, and 0.50 g cm^{-3}), and hence three different pressures (22, 25, and 30 MPa, respectively, based on the pressure due to the supercritical water). These different densities were achieved experimentally by adding different amounts of water to each reactor. The largest rate constant was obtained at the lowest density, and the rate constants for palmitic acid disappearance were lower at the two higher water densities. Also, the pentadecane yield was 28% at 0.15 g cm^{-3}, which is much higher than the yields of 12% and 13% obtained at the higher water densities of 0.31 and 0.50 g cm^{-3}, respectively. These data suggest that increasing the water density from 0.15 to 0.31 g cm^{-3} at supercritical conditions inhibited the decarboxylation rate for palmitic acid. There are numerous examples in the literature of reaction rates in supercritical fluids being influenced by the fluid density.[23] There are also numerous ways to interpret density-dependent kinetics for reactions in supercritical water.[24] Using the activation volume, $\Delta V^{\ddagger}$, is one such approach. This quantity is the difference in the partial molar volumes of the transition state and the reactant(s). It is generally >0 for bond-breaking reactions such as fatty acid deoxygenation. According to transition state theory, the magnitude and sign of the activation volume controls the influence of pressure on the rate constant. More specifically, for a first-order reaction,

$$\left(\frac{\partial \ln k}{\partial P}\right)_T = -\frac{\Delta V^{\ddagger}}{RT}$$

The decrease in the rate constant as the water density increased from 0.15−0.31 g cm^{-3} indicates that $\Delta V^{\ddagger} > 0$ for palmitic acid decarboxylation (as expected) at these water densities. The data also admit a very rough estimation of the magnitude of $\Delta V^{\ddagger}$ for this reaction at 385 °C as 10^6 cm^3/mol. This estimate is necessarily quite approximate because of the uncertainty in the data and having few data points. The estimate is also very large, but such a result is not unprecedented for reactions performed in highly compressible supercritical fluids near their critical temperatures.[23]

CONCLUSIONS

This study shows that activated carbons can convert saturated and unsaturated fatty acids to fuel-range hydrocarbons in sub- and supercritical water. No additional H_2 is required (at least during the time frame of our experiments) and no noble metal is required. Thus, activated carbons appear promising as inexpensive catalytic materials for converting fatty acids to alkanes.

The products observed in this work are consistent with decarboxylation (removal of O from fatty acids by removing CO_2 from the molecule) being the main pathway for O removal. We did not observe any hexadecane from palmitic acid or octadecane/octadecene from oleic acid, which indicates that hydrodeoxygenation (removal of O as H_2O) was not an important path under the conditions investigated here.

Decarboxylation of both a saturated and a monounsaturated fatty acid produced alkanes as the major products. This absence of unsaturation in the major products indicates that hydrogenation occurred under these reaction conditions. Either water molecules or fatty acid molecules served as the hydrogen donor. Water, of course, is present in high concentration and is known to be reactive at near- and supercritical conditions.

The pseudo-first-order rate constant for activated carbon-catalyzed decarboxylation of palmitic acid displayed an Arrhenius activation energy of 125 kJ/mol, which is higher than the value found for Pt/C-catalyzed decarboxylation. The activation volume was about 10^6 cm^3/mol.

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