The Determination of Active Filter Aid Adsorption Sites by Temperature-Programmed Desorption

Z.Y. Zhu[a], **R.A. Yates**[b,*] and **J.D. Caldwell**[b]
[a]Concordia College, Moorhead, Minnesota and [b]The Dallas Group of America, Jeffersonville, Indiana 40210

Temperature programmed desorption (TPD) was used to evaluate the active sites of several filter aids that have been promoted for use by the deep-frying industry: activated carbon, aluminas, bleaching earths, diatomaceous earth, silica and synthetic magnesium silicate. TPD analysis determines both the total surface concentration of the active sites and the details of their intensity distribution. A correlation analysis was made between the adsorbents' oil treatment performance and the observed acidic/basic sites. For some of the adsorbents, the adsorption of free fatty acids and the percent change in the color of the oil was shown to relate to the total basic sites and acid sites, respectively. The study also showed that other factors might affect these adsorptivities.

KEY WORDS: Acidic active site, adsorbent, adsorption, basic active site, color adsorption, free fatty acid, temperature-programmed desorption, used frying oil.

Filtration has long been used in the deep-frying industry for removal of particulates from the used oil. Recently, various adsorbents have been promoted as active filter aids for used frying oils. Adsorbents not only remove particulates, but also remove soluble impurities that are the products of triglyceride degradation during the frying process. Most of these degradation products are polar compounds, which are expected to be adsorbed on a polar adsorbent according to adsorption theory (1). Several papers have been published to identify and quantify the chemical degradation products of triglyceride during the frying process (2–4) and the adsorption performance of the active filter aids used in the deep frying industry (5,6). Laboratory research is continuing to improve the efficiency of the current filter aids.

It is thought that several characteristics of the adsorbents are responsible for adsorption of the impurities from the triglyceride oil. These factors include relative polarity, surface active sites, surface area and porosity, particle size, the pH value in water and the moisture content. These chemical and physical factors depend on the chemical composition and physical structure of the adsorbents and are related to the thermodynamics, mass transfer and sorption kinetics in the adsorption process. How these factors affect the performance of the adsorbents has been broadly studied in the triglyceride oil-refining process (7,8). However, in comparison to the research done in refining oil, little has been reported on the study of adsorption factors in used frying oil (5,6). The physical and chemical properties that determine adsorbent efficiency in used frying oil are still poorly understood.

A profound understanding of the adsorption mechanisms in the filtration of used frying oil, the identification of the chemical and physical factors and the determination of their relative impact on adsorbent performance are essential for the design of improved adsorbent systems in frying oil. Of these chemical and physical factors, the surface-active sites, *i.e.*, the acidic and basic sites, are expected to play an important role in the adsorption of polar compounds from used frying oil. No study of the behavior of these active sites, neither acidic nor basic sites, in used frying oil has been reported yet. Several works that study the function of acidic sites have been reported in triglyceride oil refining (9–13). It is expected that the basic sites will also play some role in the filtration of used frying oil.

Generally, there are two classes of acidic species—those that can act as proton donors to basic molecules and those that can accept electron pairs from basic molecules to form coordination bonds. The former are known as Brønsted acids; the latter are known as Lewis acids. Similarly, the Brønsted base is a proton accepter and the Lewis base is an electron pair donor. The total surface acidic (or basic) sites per gram of adsorbent (in units of mM/g) is defined as the corresponding total surface concentration of the active sites. The intensity of the acidity (or basicity) on individual active sites varies from one site to another. The dependence of the site density ($\Delta n/\Delta I$, where ΔI is the intensity range and Δn is the number of sites within this intensity range) on the site intensity is defined as the intensity distribution of the active sites. Both the total surface concentration and its intensity distribution are significant in adsorption (9).

There are several well-developed methods to determine the total surface concentration and the intensity distribution of active adsorption sites. One procedure is the titration of a suspension of the adsorbents in a nonaqueous solvent with a probe solution. An organic base, such as *n*-butylamine or pyridine, is used as a probing chemical for acidic sites; a solution of organic acid, such as trifluoroacetic acid or trichloroacetic acid, is used as a probing chemical for basic sites. In this titration procedure, a series of indicators can be used, and the Hammett acidity distribution will be obtained (10). Similarly, a microcalorimeter can be used to monitor the temperature change during the titration to determine both the total surface concentration and the intensity distribution of the active sites (14). This titration method has been applied to explore the active sites of adsorbents applied to edible oil filtration (9,11,12).

Because the results obtained from this titration method depend considerably on the titration conditions, there are significant limitations. One of the most important limitations is the temperature. In frying oil filtration, the operating temperature is about 423°K. However, in the titration method, the sample is evaluated only at ambient temperature, about 298°K. Another limitation is that the assumption of equilibrium in the titrated solution is questionable.

In the 1970s, a new procedure was developed to determine the active sites, *i.e.*, temperature-programmed desorption (TPD). In this method, the solid adsorbent is loaded into an empty gas chromatography (GC) column (15) or into specially designed TPD instruments (17–19). After the active sites on the surface of the adsorbent are saturated by a probing chemical, a temperature program is applied to desorb the adsorbed chemical. The desorption from sites of different intensity will occur at different temperature ranges. The desorption from weak sites occurs at lower temperature ranges, and the desorption from strong sites occurs at higher temperature ranges. Therefore, from the desorption chromatogram, not only the total active sites can be obtained

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*To whom correspondence should be addressed at 1402 Fabricon Blvd., Jeffersonville, IN 47130.

from the total integrated area, but the intensity distribution can also be obtained from the fine structures of the chromatogram. This method has the advantage of providing information about the acidities (or basicities) under the application conditions, such as the high temperature of frying oil. The application of the Hammett acidity determination method in oil chemistry research has been reported (9–12). However, the TPD method for both acidic and basic site determination has not yet been introduced into this field.

In the present study, we address these issues as part of our efforts to more fully understand the fundamental properties of the surface activity as they relate to the adsorption capacity in frying oil. Several adsorbent materials, commonly used in frying oil filtration, were investigated for their acidic/basic active sites. The new method, TPD, has been evaluated in this frying oil study.

MATERIALS AND METHODS

Adsorbent materials. The adsorbent materials tested and their common physical and chemical properties are listed in Table 1. The pH is that of a 5% (by weight) suspension in deionized water. Surface area was determined by nitrogen adsorption (19) with a Model 2200 high-speed surface area analyzer (Micromeritics Instrument Corp., Norcross, GA). All these materials were tested without any further treatment except for degassing at 200°C for 60 min immediately before the loading of the probing chemicals.

Probing chemicals. n-Butylamine $CH_3(CH_2)_3NH_2$, 99% (Aldrich Chemical Co., Milwaukee, WI) and trifluoroacetic acid CF_3COOH, 99% (Kodak, Rochester, NY) were used directly as received without any further treatment.

TPD instrumentation. A Varian 3700 gas chromatograph (Varian Associates, Sugarland, TX) was used to carry out the TPD procedure. A flame-ionization detector (FID) was used to monitor the eluted probe chemicals. An empty glass column (Supelco Inc., Bellefonte, PA) of 60 cm length and 1/4″ diameter was used for packing of the adsorbents tested. N_2 was used as the carrier gas at a flow rate of 40 mL/min. The flow rates of air and hydrogen were adjusted to 300 mL and 30 mL/min, respectively. The temperatures of the injector and detector were set at 150 and 300°C, respectively. A personal computer-based chromatography chemstation (Galactic Industries Corp., Salem, NH) was used for data collection and for further treatment of the data.

TPD. Approximately 0.2 g of the adsorbent to be tested were placed in the glass GC column through a powder funnel and held in place by a plug of glass wool. The column and adsorbent were weighed to the nearest 0.1 mg. The column was shaped like a "W", and this was enough material to approximately fill one side of the column. To minimize dead volume problems, the packed end of the column was placed directly into the detector. The other end of the column was adapted to the injector. The empty space inside the column allowed the probing chemicals to reach thermal equilibrium with the oven before reaching the packed adsorbent (Fig. 1). The adsorbent in the packed column was degassed and activated at 200°C for 1 h with N_2 flowing through the column. After degassing, the column was cooled to 80°C, and the FID detector was turned on. With a chromatography syringe, known volumes of the probing chemical were injected into the column. Usually, the detector gave no response to the first several injections, because almost all the molecules of the probing chemical were completely adsorbed by the active sites on the surface of the adsorbent tested. After several injections, a signal emerged, and subsequent signals increased as more injections were applied. Eventually, the detector gave an almost constant signal for each injection (Fig. 2). At this point, the active sites on the surface of the adsorbent were regarded as saturated, and equilibrium was established. This is described by Lowell and Shields (20) and Ghosh and Curthoys (21). Ten minutes to several hours were required for the carrier gas to evacuate the excess probing chemicals from the column and to allow the signal to return to the baseline. The temperature program could be initiated as soon as the signal reached the baseline.

The temperature program started at 80°C, ended at 420°C and stayed at 420°C for about 15 min. (The maximum temperature allowed for the GC oven was 420°C.) The temperature rate was 10°C/min, and the time axis in the chromatogram can thus be converted to a temperature

TABLE 1

Common Physical and Chemical Properties of the Materials Tested

Material	Trade name	pH	% LOD[a]	% LOI[b]	Surface area (m^2/g)
Activated carbon	Darco T-88[c]	8.0	4.8	90.6	824
Acidic alumina	Brockmann I[d]	4.30	<1.0	2.8	167
Neutral alumina	ABA 6000[e]	6.55	11.5	18.1	312
Basic alumina	A-2[f]	9.55	0.1	7.7	787
Bleaching earth #1	Filtrol 105[g]	3.80	15.2	5.6	311
Bleaching earth #2	Tonsil Supreme[h]	3.55	12.3	4.9	400
Diatomaceous earth	FW-18[i]	9.60	0.1	0.2	<10
Magnesium silicate	Magnesol XL[j]	8.50	10.8	10.9	619
Silica	TriSyl[k]	2.75	65.6	3.9	955

[a]LOD, percent weight loss on drying at 105°C for 2 h.

[b]LOI, additional loss on ignition at 900°C for 1.5 h (% of dry basis by weight).

[c]American Norit Co. (Jacksonville, FL), [d]Aldrich Chemical Co. (Milwaukee, WI), [e]Selecto Inc. (Kennesaw, GA), [f]LaRoche Chemicals (Baton Rouge, LA), [g]Harshaw Filtrol (Cleveland, OH), [h]LA Saloman (Port Washington, NY), [i]Eagle Picher (Reno, NV), [j]Dallas Group of America Inc. (Liberty Corner, NJ) and [k]WR Grace & Co. (Baltimore, MD).

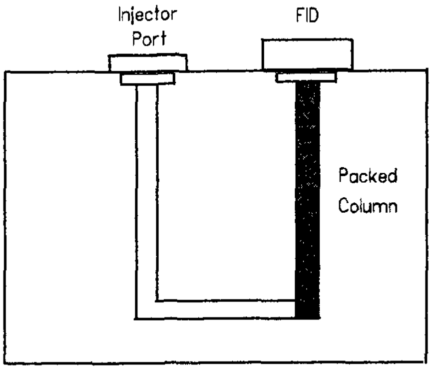

FIG. 1. The instrumentation of temperature-programmed desorption by gas chromatography.

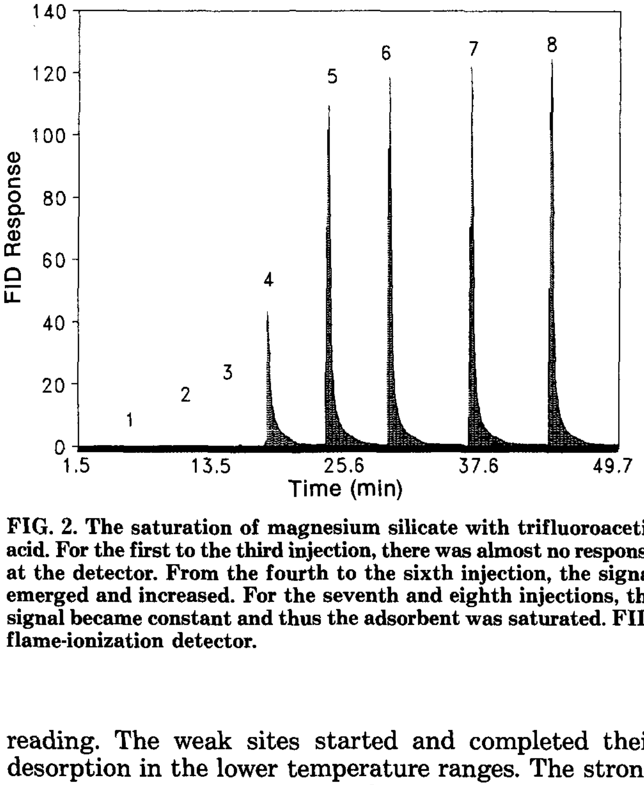

FIG. 2. The saturation of magnesium silicate with trifluoroacetic acid. For the first to the third injection, there was almost no response at the detector. From the fourth to the sixth injection, the signal emerged and increased. For the seventh and eighth injections, the signal became constant and thus the adsorbent was saturated. FID, flame-ionization detector.

reading. The weak sites started and completed their desorption in the lower temperature ranges. The strong active sites kept the probing molecules adsorbed until the temperature was high enough for desorption to occur. Therefore, the TPD chromatogram usually consisted of several bands. The bands at lower temperature range correspond to the weak active sites, whereas those bands that emerge at higher temperature ranges correspond to strong active sites. The integration of the total area covered by the chromatogram corresponds to the total surface-active sites, which is the summation of weak sites and strong sites, and the individual area covered by the individual band corresponds to the intensity distribution.

After one run is completed, the column and sample were weighed again to determine the moisture content lost during TPD, and thus the concentration of the surface-active sites can be calculated on a dry basis. Several runs were carried out for each material, and the mean value was taken. In each duplicate run, the column must be emptied and repacked with fresh sample.

To examine the adsorption process of n-butylamine, an experiment of partial adsorption is also carried out. That is, the injected amount of the probing chemical was attentively less than that needed for saturation, and thus the adsorbent was not saturated. The TPD was initiated to explore on which sites the molecules of probing chemical start to adsorb and on which sites the molecules of the probing chemical subsequently adsorb.

Oil treatment performance test. The oil treatment performance of each of the adsorbents tested was evaluated. A used frying oil was treated with 1% by weight of each of the adsorbents for 5 min at 150°C. The initial and the treated oils were evaluated for the free fatty acid (FFA) concentration and the photometric color according to AOCS standard methods (Ca 5a-40 and Cc 13c-50, respectively) (22).

The FFA adsorbed in mg per g of adsorbent, was calculated by the equation:

$$\text{FFA Ads.} = (\text{initial }\%\text{FFA} - \text{final }\%\text{FFA}) \times 1000\ \text{mg/g/1\%} \quad [1]$$

The percent change in the photometric color was calculated by the equation:

$$\%\ \text{photometric color change} = (\text{initial} - \text{final}) \times 100\%/\text{initial} \quad [2]$$

RESULTS AND DISCUSSION

The experimental results were reproducible. Both the total surface concentration and the intensity distribution of the active sites were obtained as expected. The TPD chromatograms showed fine structures at individual temperature ranges, and usually these fine structures had good reproducibility. Different adsorbents showed different TPD chromatograms with characteristic bands, which, in fact, can be used to identify an individual adsorbent if a series of standard TPD chromatograms is available in the library. Several TPD chromatograms are shown as samples (Figs. 3 and 4 for basic sites, Figs. 5 and 6 for acidic sites).

The sites for which the desorption temperature is higher than 300°C can be defined as strong acid sites. The total surface concentration of the acidic sites is the summation of the strong sites and the weak sites. Because the adsorption and evacuation temperature is higher than the boiling point of the probe chemical, and the desorption begins substantially at a temperature much higher than the boiling point, the possibility of physical adsorption can be ruled out.

The results from the partial adsorption TPD give the sequence of the order of the intensity of basic sites and acidic sites on the surface of magnesium silicate (Figs. 3 and 5, respectively). When the surface is only partially saturated with butylamine, the strong acidic sites compete with the weak acidic sites and have the higher priority to adsorb the n-butylamine molecules, leaving the weak acidic sites empty. When the amount of n-butylamine loaded is increased, the basic molecules start to spread over the weak acidic sites after the strong acidic sites are preferentially saturated. Thus, the partial TPD experiment demonstrates that the adsorption process starts at the strongest sites and eventually ends at the weakest sites. Therefore, the strong sites may be of more

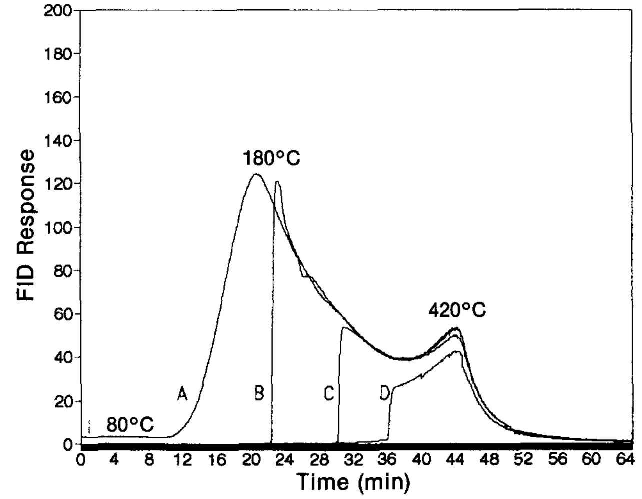

FIG. 3. Temperature-programmed desorption (TPD) chromatograms for the acidic sites of magnesium silicate. A, total TPD after complete saturation; B, TPD after 64% partial saturation; C, TPD after 34% partial saturation; and D, TPD after 18% partial saturation. FID, flame-ionization detector.

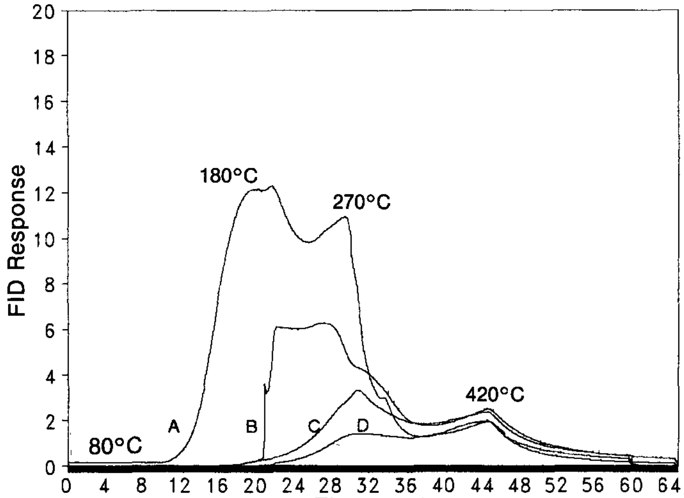

FIG. 5. TPD chromatograms for the basic sites of magnesium silicate. A, total TPD after complete saturation; B, TPD after 50% partial saturation; C, TPD after 33% partial saturation; and D, TPD after 16% partial saturation. Abbreviations as in Figure 3.

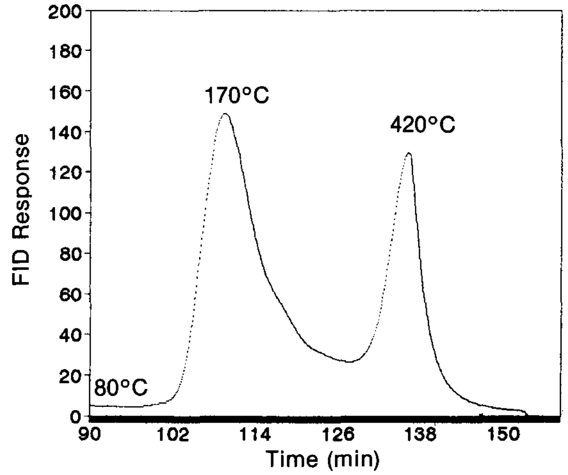

FIG. 4. TPD chromatogram for the acidic sites of bleaching earth. Abbreviations as in Figure 3.

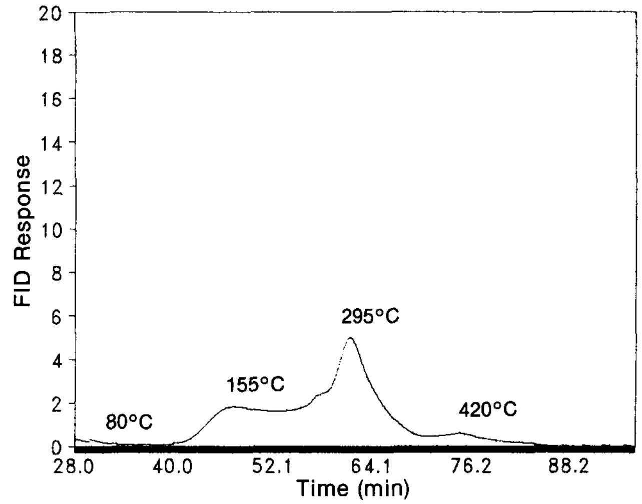

FIG. 6. TPD chromatogram for the basic sites of alumina (neutral). Abbreviations as in Figure 3.

significance than the weak sites in the adsorption. The situation is the same for basic sites, as shown in Figure 5.

The total surface concentration and intensity distribution of acidic active sites are presented in Figure 7. The total height of the stacked bars stands for the total surface concentration of the acidic active sites in mM per gram. The individual parts of the stacked bar correspond to the intensity distribution. These data indicate that magnesium silicate has the highest value of total acidic sites, *i.e.*, 1.8 mM/g. In silica, bleaching earth and activated carbon, the values are in the range of 0.7–1.1 mM/g. In activated alumina, the total acidic sites are about 0.3–0.5 mM/g. Diatomaceous earth has less than 0.1 mM/g acidic sites. These data also show that the intensity distributions of the acidic active sites are of significance. For example, although the concentration of the total acidic sites is relatively high in silica, most are weak sites. For magnesium silicate, bleaching earth and activated carbon, the concentration of strong sites is high. Here, the relative intensity of the sites is simply expressed by the desorption temperature range. The stronger the attraction between the sites and the adsorbate molecules, the higher the necessary desorption temperature. For further quantitative study of the intensity of the sites, the enthalpy of adsorption should be determined.

The total surface concentration and the intensity distribution of the basic active sites of the tested adsorbents are shown in Figure 8. Among the adsorbents studied, magnesium silicate had the highest number of basic sites, reaching as high as 2.3 mM/g. The other materials studied have values in the range of 0.3–0.6 mM, and activated carbon has a value of 1.3 mM/g. In magnesium silicate, aluminas, bleaching earth and activated carbon, the weak basic sites (below 300°C) predominate over strong sites.

The performance of these adsorbents, relating to the adsorption of FFA and color, has also been measured

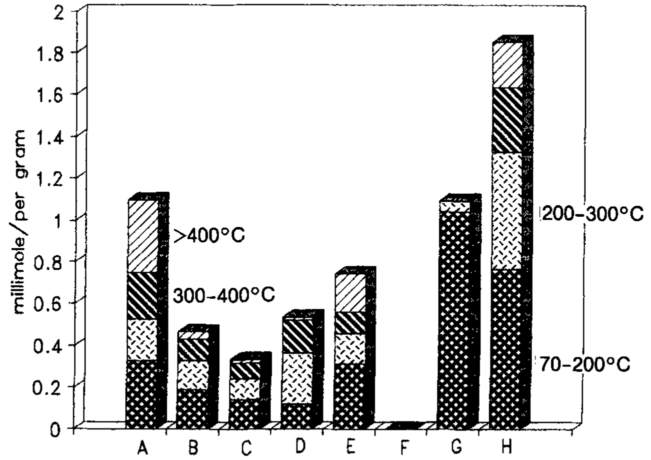

FIG. 7. Surface concentrations and their intensity distributions for the acidic sites of adsorbents used in frying oil. A, activated carbon; B, alumina (basic); C, alumina (neutral); D, alumina (acidic); E, bleaching earth; F, diatomaceous earth; G, silica; and H, magnesium silicate.

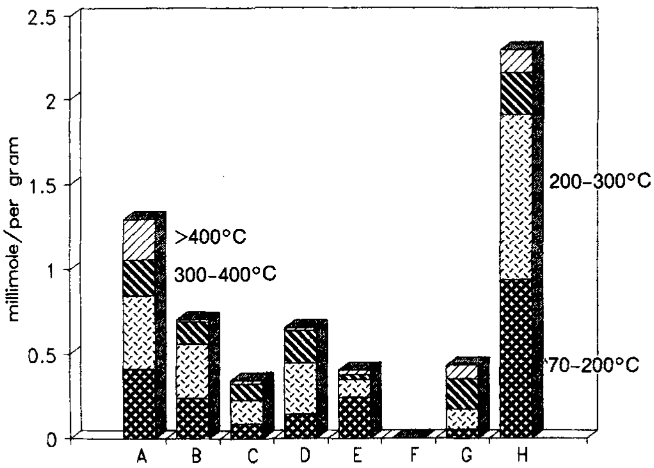

FIG. 8. Surface concentrations and their intensity distributions for the basic sites of adsorbents used in frying oil. A, activated carbon; B, alumina (basic); C, alumina (neutral); D, alumina(acidic); E, bleaching earth; F, diatomaceous earth; G, silica; and H, magnesium silicate.

separately. Figure 9 shows the adsorption of FFA as a function of the total basic active sites. The adsorptivity increases as the surface concentration of basic sites increases in some of the adsorbents, *e.g.*, in the sequence from diatomaceous earth to silica, aluminas and magnesium silicate. But alumina (neutral), bleaching earth and activated carbon deviate from this trend. This complexity demonstrates that not only the basic active sites, but other factors as well, affect the adsorption of FFA. For example, the pore size distribution might unequally limit the impact of the basic active sites to the adsorption of FFA molecules. Edible oil bleaching studies (7,11) have shown that the pore size distribution disturbs the role of the acidic sites. Also, some of the adsorption might be partially due to nonspecific adsorption.

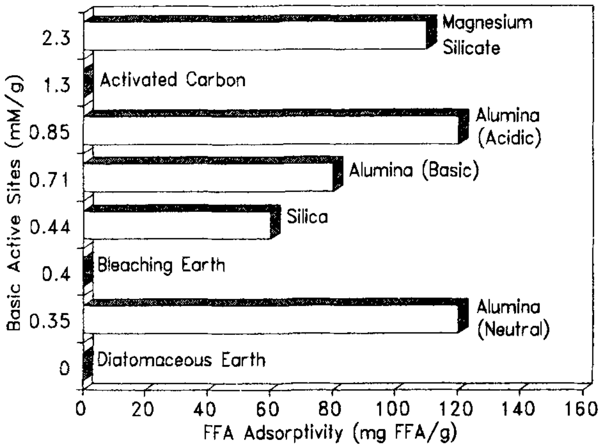

FIG. 9. Bar graph of the concentrations of basic sites against the adsorptivities of free fatty acid (FFA).

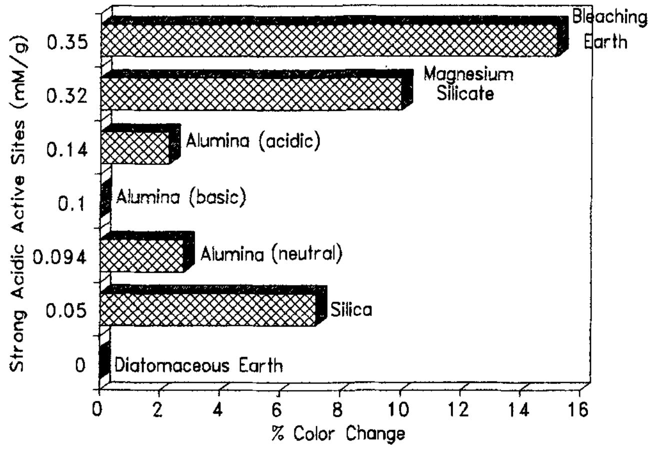

FIG. 10. Bar graph of the concentrations of the strong acidic sites against percent color adsorption.

The acid site distribution of bleaching earth is particularly striking. From the TPD chromatogram of bleaching earth (Fig. 6), two almost completely separated peaks can be identified. One peak at about 170°C can be assigned to weak acid sites, and the other at about 420°C can be assigned to strong acid sites. The volumes of these two peaks are comparable. Two commercial brands of bleaching earth, Tonsil Supreme and Filtrol, were tested by this TPD method. The resulting TPD chromatograms are similar to each other. Only the TPD chromatogram of magnesium silicate is similar to that of bleaching earth. In the TPD chromatogram of magnesium silicate, there are also two bands of peaks. The first peak has a T_m value, defined as the temperature corresponding to the maximum peak height, of 180°C. The second peak has a T_m value of 420°C. These two T_m values match with the T_m values in bleaching earth, which are 170 and 420°C, respectively.

The difference between the bleaching earth and magnesium silicate TPD chromatograms is that the band of weak sites is broader for magnesium silicate than for bleaching earth. Therefore, the volume of the weak sites predominates over the strong sites in magnesium silicate rather than having an equal volume, as is the case with bleaching earth. Because bleaching earth has superior color removal over magnesium silicate and because both are superior over the other materials tested, it is assumed that only the strong acidic active sites are responsible for color removal. Figure 10, in which the percent color change is plotted against the strong acidic active sites, shows that for some of the adsorbents tested, *e.g.*, from bleaching earth, magnesium silicate and alumina down to diatomaceous earth, the color removal decreases as the surface concentration of strong acidic active sites decreases. There are some exceptions, *i.e.*, alumina (neutral) and silica. The deviations from the expectation can also be explained in terms of the contribution of pore size distribution, nonspecific adsorption etc. Further studies need to be completed to distinguish the specific and nonspecific adsorption on these adsorbents.

This study demonstrated that the surface concentration and the intensity distribution of the active sites vary among the active adsorbents used in frying oil. The adsorptivity of these active adsorbents toward the degradation products of triglyceride may depend on several possible factors, among which the active sites (acidic and/or basic) play an important role. This study also demonstrated that the TPD method is convenient and accurate, and that it has great potential in the surface characterization of active adsorbents used in frying oil.

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