Diffuse Reflectance Fourier Transform Infrared Spectroscopy of Triacylglycerol and Oleic Acid Adsorption on Synthetic Magnesium Silicate

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ABSTRACT: Diffuse reflectance Fourier transform infrared (FTIR) was used to observe adsorption complexes of triacylglycerol and oleic acid on silica gel and synthetic magnesium silicate. The spectra provide evidence of the nature of the surface interaction. Triacylglycerol was shown to be physically adsorbed to both adsorbents. Oleic acid was physically adsorbed to the silica gel, but both physically and chemically adsorbed to the magnesium silicate. The FTIR spectrum of magnesium silicate that was used to treat a degraded frying oil was similar to that of oleic acid adsorbed on magnesium silicate.

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KEY WORDS: Adsorption, FTIR spectroscopy, magnesium silicate, oleic acid, triacylglycerol.

Magnesol® XL (The Dallas Group of America, Inc., Jeffersonville, IN) is a food-grade synthetic magnesium silicate for active filtration of used frying oils. Previous studies have shown this material to have high adsorptive capacity for free fatty acids and other polar compounds that result from triacylglycerol degradation (1,2). Temperature-programmed desorption has shown this product to have a unique adsorbent surface in terms of the number and strength of adsorbent sites (3). In a study of rat liver enzyme activity, Lamboni (4) showed that adsorption of impurities from a degraded frying oil by Magnesol® improved its nutritional value.

Recently, Proctor *et al.* used diffuse reflectance Fourier transform infrared (FTIR) spectroscopy to study the adsorption complexes of triacylglycerol (TAG) and oleic acid (OA) on silicic acid (5,6) and rice hull ash (7). The former studies showed that TAG and OA were physically adsorbed to silicic acid *via* hydrogen bonding of the carbonyl group (C=O) to silanol groups (Si–O–H) on the surface of the silicic acid. The latter study showed that some OA was also chemically adsorbed (chemisorbed) to rice hull ash *via* ionic adsorption between a carboxylate ion ($RCOO^-$) and metal oxide on the surface of the rice hull ash.

The objectives of this study were to apply the method of Proctor *et al.* (5–7) to investigate adsorption of TAG and OA to the surface of synthetic magnesium silicate and determine the nature of the bond(s).

MATERIALS AND METHODS

Lipid, solvents, and adsorbent. OA (NF, Mallinckrodt Specialty Chemicals, Paris, KY), hexane (Analytical Reagent, Mallinckrodt Specialty Chemicals), olive oil (Progresso Quality Foods Co., St. Louis, MO), Silica Gel 60A (column chromatography grade, 70–230 mesh; Baxter Scientific Products, Chicago, IL), and synthetic magnesium silicate (Magnesol® XL) were used. This silica gel is of the type specified in AOCS Method Cd 20-91, Polar Compounds in Frying Fats (8). Table 1 presents a comparison of some of the physical and chemical properties of the two adsorbents.

FTIR spectra. FTIR spectra were obtained with an Impact Model 410 FTIR instrument (Nicolet, Madison, WI) equipped with a Model 0001-395 baseline diffuse reflectance kit (Spectra-Tech, Shelton, CT). Spectra were obtained by co-adding 100 interferograms at a resolution of 4 cm^{-1} with Happ-Genzel apodization and no correction. Spectra were originally recorded by using Nicolet's OMNIC software and saved in the J-CAMP format for later manipulation with GRAMS 386 software (Galactic Industries, Salem, NH).

The FTIR spectra of TAG and OA were obtained by direct transmission of the infrared beam through a film of the pure material on a salt window.

The baseline FTIR spectra of the silica gel and magnesium silicate after exposure to hexane were obtained by adding 0.5

TABLE 1
Properties of Absorbents Used

Material	pH[a]	LOD[b] (%)	LOI[c] (%)	Surface area[d] (m^2/g)
Silica gel 60A	6.50	7.0	2.8	430
Magnesium silicate	8.50	10.8	9.9	619

[a]pH of a 5% suspension in deionized water.
[b]Percentage weight lost on drying at 105°C for 2 h.
[c]Percentage additional weight lost on ignition at 900°C for 1.5 h (percentage of dry basis weight).
[d]Nitrogen adsorption (BET) method.

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g of the adsorbent to 100 mL hexane in a sealed flask and mixing for 15 min. The adsorbents were recovered and dried under air flow in a fume hood for 15 min prior to FTIR analysis as described above. These spectra were subtracted from subsequent spectra following lipid adsorption to isolate the spectra of the adsorbed lipid.

TAG and OA adsorption. A 100-mL volume of 0.05 M TAG in hexane was stirred with 0.5 g adsorbent for 15 min. The adsorbents were recovered by gravity filtration through Whatman #1 filter paper and dried under air flow in a fume hood. The dried adsorbents were analyzed by FTIR as described above. This procedure was repeated with 0.05 M OA in hexane for each adsorbent.

Treatment of used frying oil. A partially hydrogenated soybean oil, used to fry potatoes, was obtained from a local fast food restaurant. This oil had an initial free fatty acid concentration over 5% when analyzed by AOCS Method Ca 5a-40 (8). The oil was filtered to remove food debris and other particulates prior to adsorbent treatment. To simulate a typical food-service application, 1% by weight magnesium silicate was added to the used oil at 150°C. The hot mixture was stirred for 5 min, then filtered through Whatman #41 filter paper under vacuum. The filter cake was washed with hexane to remove the absorbed oil. The hexane was removed by drying under air flow in a fume hood, and the dried adsorbent was analyzed by FTIR as described above.

RESULTS AND DISCUSSION

Adsorbent spectra. Figures 1 and 2 show the FTIR spectra of hexane-washed silica gel and hexane-washed magnesium silicate, respectively. The spectra of the adsorbents are similar. Both show a broad band at about 2800 to 3750 cm^{-1} due to the OH stretch of surface hydroxyl groups (O-H) and water undergoing hydrogen-bonding to these groups. The H–OH bending peak is at 1627 cm^{-1} for the silica and at 1641 cm^{-1} for the magnesium silicate.

The literature describes a peak or shoulder for silica gel at 3740 cm^{-1} due to nonhydrogen-bonded surface hydroxyl (OH) groups (9). This shoulder appears in the silica gel spectrum, but it does not appear in the magnesium silicate spectrum. Hydroxyl groups bonded to silica (Si–O–H) are also known as silanol groups.

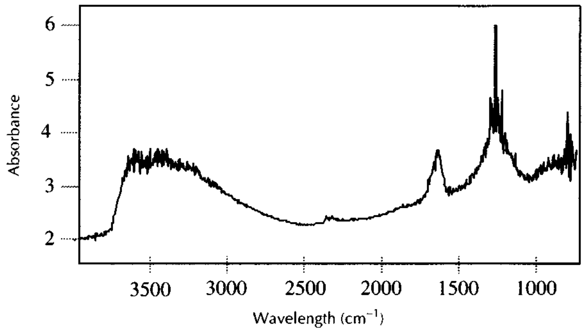

FIG. 2. The diffuse reflectance Fourier transform infrared spectrum of hexane-washed synthetic magnesium silicate.

An intense structural siloxane band (Si-O-Si) is found in the silica gel spectrum from about 1250 to 1400 cm^{-1}. A similar band, but much broader and more complex, is found in the spectrum of the magnesium silicate. This broadening is likely due to the random presence of magnesium in the structure (9). The silica gel spectrum includes broad bands around 1970 cm^{-1} and 1864 cm^{-1} due to structural vibrations. There are no corresponding bands in the magnesium silicate spectrum.

TAG spectrum. The FTIR spectrum of pure TAG is shown in Figure 3. The peak at 3002 cm^{-1} is the C–H stretch alpha to the double bond [R–C=C(H)R′] of an esterified unsaturated fatty acid. The peaks at 2926 and 2851 cm^{-1} are the asymmetric and symmetric stretching vibrations of methylene (CH$_2$) groups. The carbonyl (C=O) stretch is at 1744 cm^{-1}, and methylene "wag" is shown by the peak at 1460 cm^{-1} (10).

TAG adsorption from hexane. Figures 4 and 5 are the FTIR spectra of TAG adsorbed on silica gel and magnesium silicate, respectively. The baseline spectra of the hexane-washed adsorbents have been subtracted to better observe the key features of the bound lipid.

The C–H stretching and deformation mode bands at 3008, 2926, 2860, and 1464 cm^{-1} are only slightly shifted from those of pure TAG, thus indicating the adsorption of TAG in

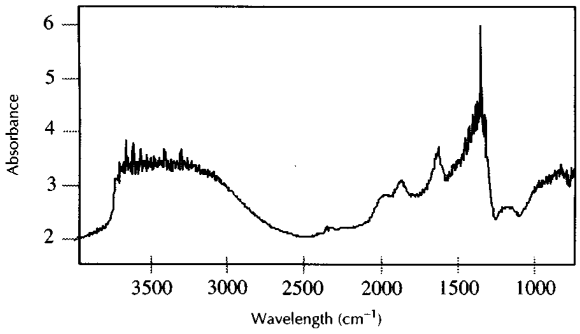

FIG. 1. The diffuse reflectance Fourier transform infrared spectrum of hexane-washed silica gel.

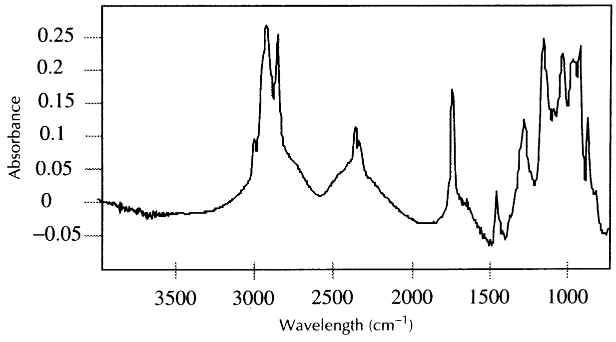

FIG. 3. The Fourier transform infrared spectrum of olive oil on a salt window.

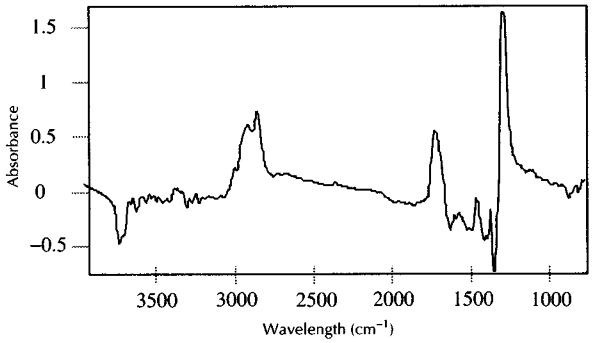

FIG. 4. The diffuse reflectance Fourier transform infrared (FTIR) spectrum of olive oil adsorbed on silica gel; the FTIR spectrum of hexane-washed silica gel (see Fig. 1) has been subtracted.

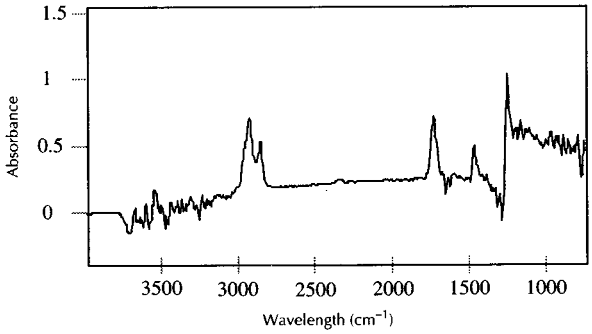

FIG. 6. The FTIR spectrum of oleic acid on a salt window. See Figure 4 for abbreviation.

a relatively unchanged form. The broadening and shifting of the carbonyl stretch at 1726 cm^{-1} relative to that of the free lipid (Fig. 3) indicates that the carbonyl group of the TAG is hydrogen-bonded to the adsorbent (9).

In the spectra of TAG adsorbed on silica gel (not shown), adsorption shifts the large Si–O–Si band at about 1300 cm^{-1} to a lower frequency. Subtraction of the hexane washed silica gel spectrum produces the negative and positive peaks in this region (9). This shift of structural bands occurs for the TAG adsorption on magnesium silicate as well.

The subtraction process also produced negative peaks between 2800 and 3800 cm^{-1} for both adsorbents. Proctor *et al.* reported a single narrow negative peak at about 3750 cm^{-1} that was attributed to the absence of the peak for unbonded silanols in the spectra of adsorbed lipids (5–7) and subsequent subtraction of the hexane-washed adsorbent spectrum. While more complex, these negative absorption bands also appear in the spectra for both silica gel and magnesium silicate. Hence, the absence of unbonded silanols in these absorption spectra is further evidence of hydrogen bonding at these sites.

OA spectrum. The FTIR spectrum of pure OA is shown in Figure 6. The important features of this spectrum are the C–H stretch for an R–CH=CH–R′ group at 3003 cm^{-1}, the asymmetric and symmetric C–H stretching vibration of a CH_2 group at 2930 and 2857 cm^{-1}, and the CH_2 deformation band at 1460 cm^{-1}. Other significant peaks are the carbonyl stretch at 1709 cm^{-1} and the peaks at 1284 and 954 cm^{-1} due to skeletal vibrations (10).

OA adsorption on silica gel. The FTIR spectrum of OA adsorbed on silica gel is shown in Figure 7. The adsorbent spectrum has been subtracted to better observe the key features of the bound lipid.

As with TAG adsorption on silica gel, the C–H stretching and deformation bands at 3003, 2930, 2857, and 1460 cm^{-1} are only slightly shifted from those of pure OA, thus indicating the adsorption of OA in a relatively unchanged form. The broadening and shifting of the carbonyl stretch (1716 cm^{-1}) relative to that of the pure material (Fig. 6) is evidence that the carbonyl group of the OA is hydrogen-bonded to the adsorbent (9) and is further supported by the negative band about 3740.

OA adsorption on magnesium silicate. The FTIR spectrum of OA adsorbed on magnesium silicate is shown in Figure 8. The adsorbent spectrum has been subtracted to better observe the key features of the bound lipid.

As with OA adsorption on silica gel, the C–H stretching

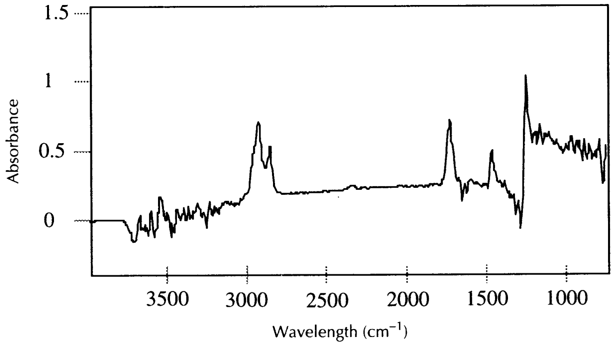

FIG. 5. The diffuse reflectance FTIR spectrum of olive oil adsorbed on magnesium silicate; the FTIR spectrum of hexane-washed magnesium silicate (see Fig. 2) has been subtracted. See Figure 4 for abbreviation.

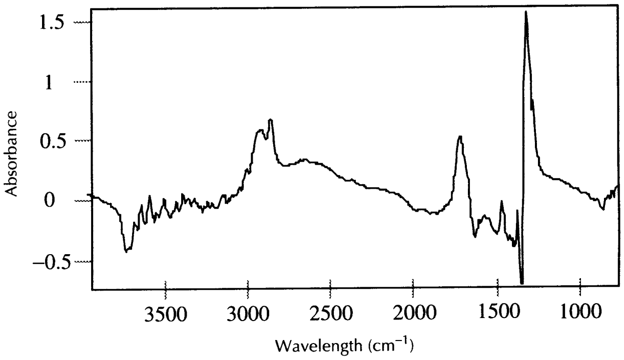

FIG. 7. The diffuse reflectance FTIR spectrum of oleic acid adsorbed on silica gel; the FTIR spectrum of hexane-washed silica gel (see Fig. 1) has been subtracted. See Figure 4 for abbreviation.

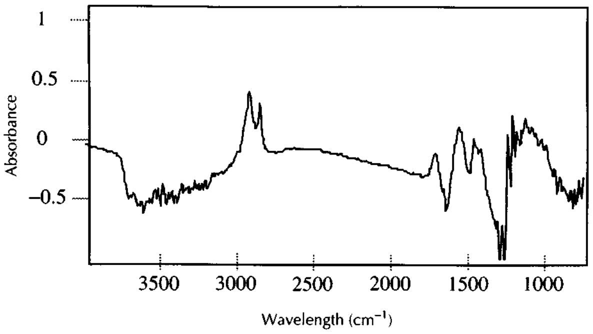

FIG. 8. The diffuse reflectance FTIR spectrum of oleic acid adsorbed on magnesium silicate; the FTIR spectrum of hexane-washed magnesium silicate (see Fig. 2) has been subtracted. See Figure 4 for abbreviation.

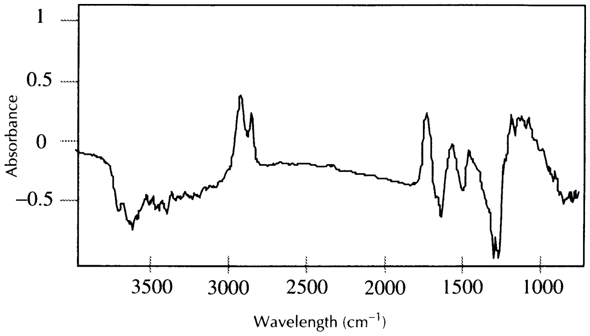

FIG. 9. The diffuse reflectance FTIR spectrum of a hexane-washed magnesium silicate filter cake from treatment of degraded frying oil; the FTIR spectrum of hexane-washed magnesium silicate (see Fig. 2) has been subtracted. See Figure 4 for abbreviation.

and deformation bands at 3006, 2927, 2855, and 1464 cm^{-1} are only slightly shifted from those of pure OA. The broadening and shifting of the carbonyl stretch (1720 cm^{-1}) relative to that of the pure material (Fig. 6) is evidence that the carbonyl group of the OA is hydrogen-bonded to the adsorbent (9).

However, this spectrum includes a peak at 1550 cm^{-1} between the carbonyl stretch and the methylene wag bands, which corresponds to a carboxylate group (RCOO$^-$) (10). The carboxylate is most likely formed by the loss of a hydrogen ion from OA and ionic adsorption to metal oxide on the surface of the magnesium silicate (9). Therefore, this spectrum shows that, in addition to the OA adsorbed by hydrogen bonding, some OA is chemisorbed to the magnesium silicate.

Adsorption of impurites from used frying oil. Figure 9 is the FTIR spectrum of the magnesium silicate that was used to treat degraded frying oil. Residual oil on the surface and between the particles was removed by rinsing with hexane.

Like the spectrum for OA adsorbed on magnesium silicate, this spectrum includes the peak at 1550 cm^{-1}, which indicates the presence of carboxylate groups. This is evidence that the magnesium silicate has chemisorbed carboxylic acids from a used frying oil under conditions of temperature and contact time of a typical food-service filtration.

In summary, FTIR studies show that the structure of synthetic magnesium silicate is similar to that of adsorbent silica. Magnesium silicate physically adsorbs triglyceride and OA through hydrogen-bonding of the carbonyl group to surface silanols as silica does. OA is also chemically adsorbed to the magnesium silicate through formation of a carboxylate ion, which forms an ionic bond with metal oxide on the surface. Chemisorption of fatty acid from a used frying oil by magnesium silicate can occur at temperatures above ambient, and the carboxylate products are tightly bound to the particles.

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