

CONDENSATION OF OLEFINS ON CLAYS. GAS-SOLID SYSTEMS. PART II: SPECTROSCOPIC METHODS

EDUARDO CHOREN, ALEXANDER MORONTA, ARNEDO ARTEAGA AND JORGE SÁNCHEZ

Centro de Superficies y Catálisis, Facultad de Ingeniería, Universidad del Zulia,
Apartado 15251, Maracaibo 4003A, Venezuela

Abstract—The adsorption of olefins at 25 °C in gas- or vapor-solid systems on 4 clays dried at 120 °C, was studied by infrared spectroscopy. Products of condensation have the spectra of paraffinic oligomers. Paraffins are adsorbed onto the same structural surface hydroxyls that adsorb olefins, confirming the physical unspecific character of this adsorption. These hydroxyls do not participate in the condensation reaction. The reappearance of these hydroxyl bands after evacuation suggests that product molecules are not adsorbed onto the surface but remain on it because of its low vapor pressure. The reversible adsorption sites participate in feeding the condensation sites. Double-bond isomerization of olefins was not observed, at room temperature, on clays, alumina and silicas dried at 120 °C. When the gas-phase is evacuated or swept with inert gas, reaction does not proceed with a new monomer. Paraffins are only physically adsorbed.

Key Words—Adsorption, Infrared Spectra, Interlayer, Montmorillonite, Olefins, Paraffins, Polymerization.

INTRODUCTION

In Choren et al. (1997), a gravimetric study of adsorption and condensation of light olefins in the gas- or vapor-phase on 7 adsorbents, some preliminary remarks were drawn. Although gravimetry allows the visualization of some aspects of the whole process, spectroscopic methods are valuable for understanding aspects that do not depend upon mass or mass changes. In this work, infrared (IR) spectroscopy is applied to obtain a more complete picture of the olefin adsorption-condensation process. “Condensation”, in this work, includes all of the reactions that generate products of higher molecular weight, such as etherifications and oligomerizations.

EXPERIMENTAL

Materials

The adsorbents and adsorbates were described in Choren et al. (1997).

The deuteration of clays was carried out according to the following procedure: approximately 300 mg of clay and 1 mL of D₂O were placed in a small stainless steel autoclave lined with polytetrafluorethylene (PTFE), heated in an oven at 150 °C for 1 h. The vessel was then cooled to room temperature, opened and reheated to evaporate the remaining D₂O. The procedure was repeated twice.

A Fourier transform infrared (FTIR) spectrometer was used. The single-ray, computerized Perkin Elmer 1710 model was equipped with an MTC detector of 1 cm⁻¹ resolution, cooled with liquid nitrogen. The method of taking the IR spectra was the object of a preliminary study described as follows. The KBr pellets with a few milligrams of clay permitted the ob-

servation of the low wave number region but excluded bands—in particular, the important 4730 cm⁻¹ band, which disappeared totally. The use of compressed sheets presents the possible inconvenience of blocking the access of hydrocarbons to the internal surface. In preparing compressed wafers, one must take 2 variables into account: the pressure applied and the compression time. To evaluate their effects, a set of 5 pressures between 140 kg/cm² and 700 kg/cm² and times of 15 s and 2 min were tested by adsorption of 1-butene. The only difference found was a small loss in the intensity of hydrocarbon bands in the wafers prepared at higher pressure and longer time, but the toughness makes them less frail and more suitable to handling. Consequently, the following procedure was finally adopted: 15–20 mg of adsorbent were compressed in a cylindrical die of 30 mm diameter, with a load of 700 kg/cm², for 15 s. The wafer cut to a 1 cm × 2 cm rectangle was placed in a sample holder at the end of a thin glass rod that permitted the displacement of the sample between the pretreatment zone and the cell in a 20-mm borosilicate glass tube by means of an external magnet. The cell body is made of stainless steel with NaCl windows. The usual procedure was as follows: the wafer was dried for 2 h at 120 °C with a flow of 30 SPT mL/min of Ar. The sample was placed in the cell and the first spectrum taken. The Ar was then replaced by 1-butene. Another spectrum was taken immediately after the equilibration of a butene pressure of 2.5 kPa. This spectrum was designated “initial adsorption”. After 1.5 h, the olefin was swept with Ar for 10 min and a final spectrum was taken, called “irreversible adsorption”. All of the spectra are the result of 100 scans. As the spectrometer is a single-ray type, it was first necessary to take a

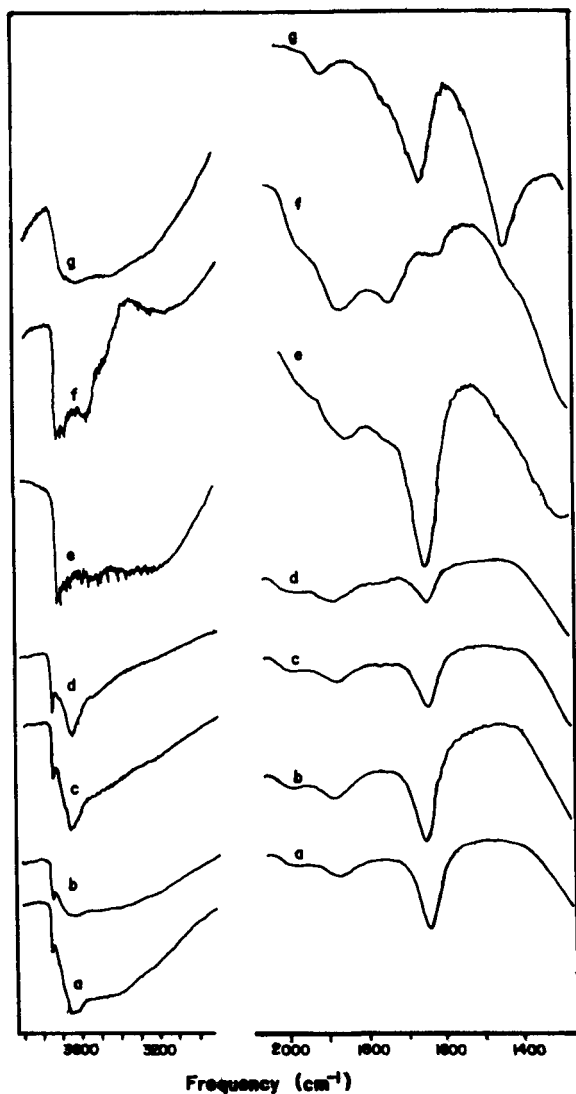


Figure 1. Infrared spectra of: a) F24 clay dried at 120 °C; b) F124 clay dried at 120 °C; c) F24 clay dried at 300 °C; d) F24 clay dried at 450 °C; e) T1 clay dried at 120 °C; f) T1 clay dried at 300 °C and g) T1 clay dehydrated with atmospheric moisture.

“background” spectrum with no wafer. In this case, care was taken, by means of attenuators, to reduce the radiation energy to the values obtained when the wafer is in the optical path. As the compressed clay wafers are not transparent below 1100 cm^{-1} , pellets of KBr were used when the region below this wave number was required.

RESULTS AND DISCUSSION

Infrared Spectra of Clays

The high wave number region of spectra of F24 and F124 clays dried at 120 °C (Figures 1a and 1b) are very similar and can be described as a very broad band

extending from approximately 3800 to about 2600 cm^{-1} . This band corresponds to hydrogen-bonded molecular water because its intensity decreases appreciably when the clay is heated, as can be seen in Figures 1c and 1d. Two bands can be seen enmeshed on it, one sharp at 3743 cm^{-1} assigned to O-H stretching of free Si-O-H groups, and another at 3642 cm^{-1} , usually found at 3630–3620 cm^{-1} , which corresponds to stretching vibrations of montmorillonite hydroxyls (Serratos and Bradley 1958; van der Marel and Beutelspacher 1976). To establish whether the origin of the 3743- cm^{-1} band corresponds to clay or quartz impurities, samples of both clays were pelleted with KBr and the spectra were extended to 400 cm^{-1} . A small band at 798 cm^{-1} was observed, but as noted by van der Marel and Beutelspacher (1976), the absence of a band at 778 cm^{-1} indicates that the quartz content is small.

In the low wave number region, besides 2 overtones and combination structural bands at 1980 and 1870 cm^{-1} , there is a band at 1630 cm^{-1} , usually assigned to bending vibrations of water molecules.

The IR spectra of T1 clay are different from those of the F24 and F124 clays. Figure 1e shows the spectrum of a sample dried at 120 °C. Again, the large noise obscures the instrumental localization of the bands; on the broad water band, 2 stretching bands of structural hydroxyls can be distinguished, about 3700 and 3550 cm^{-1} . The first band appears in the spectra reported by Fripiat and Toussaint (1963) and van der Marel and Beutelspacher (1976), but assigned to kaolinite. The second band is frequently found in spectra of smectites. The spectrum change upon heating T1 at 300 °C is notable (Figure 1f): there is a loss of absorbance around 3300–3400 cm^{-1} , and 4 bands can be seen, the former at 3700 and 3560 cm^{-1} and 2 more bands at 3660 and 3180 cm^{-1} , all of them noisy. In the low wave number region, the former 1632 cm^{-1} band is now very weak, shifted to 1620 cm^{-1} , and accompanied by 2 other bands at 1723 and 1850 cm^{-1} . This sample was equilibrated with atmospheric moisture (about 1.3 kPa of water partial pressure). Figure 1g shows the changes: the stretching region bands are wrapped by the broad water band, and in the bending region, the 1630- cm^{-1} band reappears and a new, very intense 1413- cm^{-1} water-bending band is observed. This band has been reported by Mortland et al. (1963) at 1429 cm^{-1} in montmorillonite.

The spectrum of γ -alumina dried at 120 °C can be seen in Figure 2a. As for clays, the principal feature is a broad, noisy band centered about 3450 cm^{-1} . The protruding band at 3730 cm^{-1} was reported by Peri and Hannan (1960) as an isolated, surface hydroxyl band. It is worthwhile noting the very low intensity of the water-bending band, and its high frequency of 1690 cm^{-1} .



Figure 2. Infrared spectra of adsorbents dried at 120 °C: a) γ -alumina; b) silica-gel; and c) Cabosil.

Silica-gel dried at 120 °C also presented low transmittance in the hydroxyl stretching region but, unlike clays and alumina, the noise in this part of the spectrum was low. The bands identified (Figure 2b) were the silanols 3740 cm^{-1} band; 2 bands associated with hydrogen-bonded water at about 3650 and 3540 cm^{-1} ; and, finally, the 1630 cm^{-1} band.

Less intense are the Cabosil bands, Figure 2c; but, like porous silica-gel, the only remarkable difference is the shifting of the hydrogen-bonded water band from 3540 to 3510 cm^{-1} , possibly because of the pores' absence.

It is interesting to observe the behavior of the sharp silanol band at 3740 cm^{-1} . A clay dried at 120 °C still retains a considerable amount of molecular water. However, this band is already present in the spectra, as explained above for Figure 1a. One might think that water must be linked to the solvatable cations. While the other structural bands appear noisy, as imbedded in the broad water band, this one remains sharp and distinguishable at a side. Although silica has no metallic ions, the picture is still the same. On a sample of Cabosil, McDonald (1958) reduced by evacuation the broad band at about 3400 cm^{-1} to an absorbance

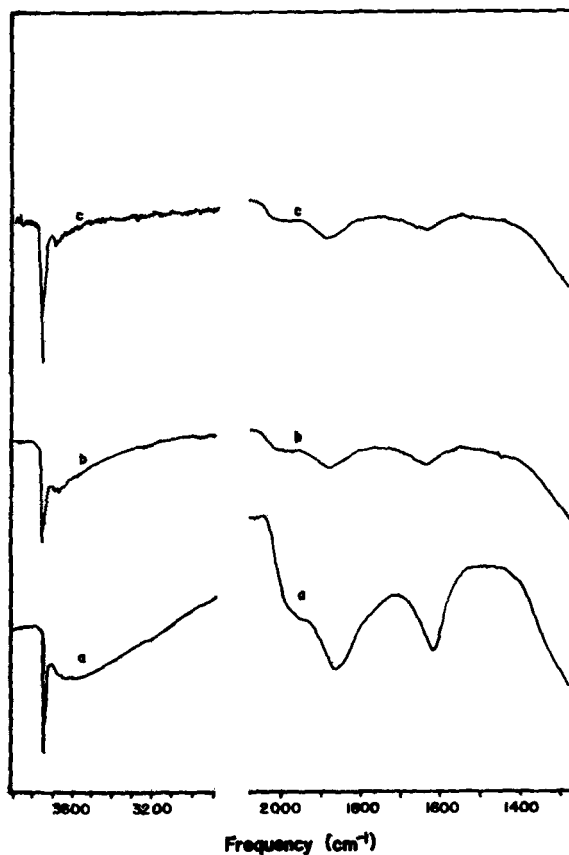


Figure 3. Infrared spectra of: a) F24 clay dried at 800 °C; b) Cabosil dried at 300 °C; and c) Cabosil dried at 400 °C.

of approximately 0.2. On reabsorbing water vapor, the broad band increased again to approximately 1.0. However, the 3747- cm^{-1} band remained almost unchanged throughout the process. As shown below, this band is affected by the adsorption of olefins. These facts suggest some hydrophobic character of the SiOH groups that generate this band.

The 1630- cm^{-1} band must be considered carefully. This band has been associated generally with the scissor bending of molecular water. However, when samples of F24 and F124 clays were heated in a vacuum at 800 °C, a treatment that eliminates all possible molecular water, the spectra retained an important band at 1626 cm^{-1} (Figure 3a). Little and Mathieu (1960) failed to eliminate this band by heating silica glass and assigned it—as the companion at 1870 cm^{-1} —to a combination of fundamental frequencies of the silicious skeleton. Figures 3b and 3c correspond to spectra of Cabosil heated in a vacuum at 300 and 450 °C, respectively. They show that while molecular water has virtually disappeared (bands at 3670 to 3675 cm^{-1}), the bands at 1980, 1870 and 1630 cm^{-1} remained constant.

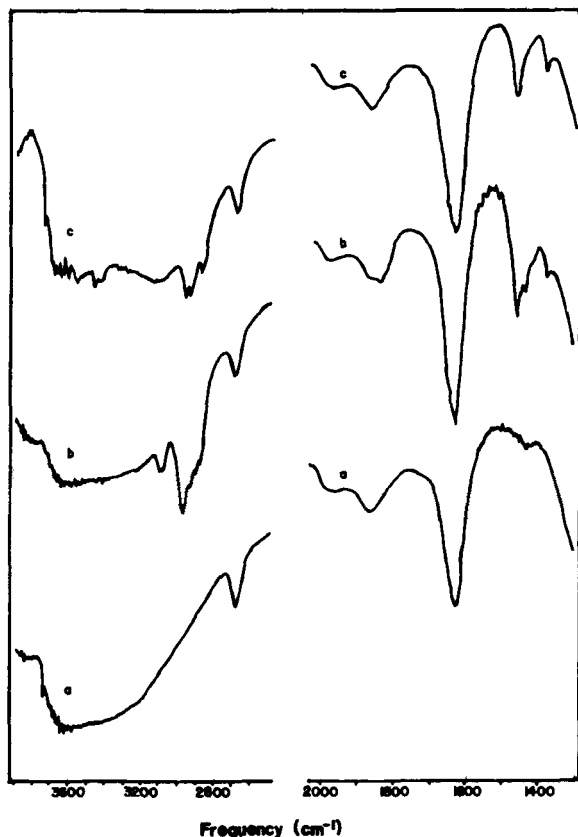


Figure 4. Infrared spectra of 1-butene-F24 clay: a) F24 clay deuterated, dried at 120 °C, previous adsorption; b) initial adsorption of butene; and c) irreversible adsorption of butene.

Infrared Spectra of Adsorbed 1-butene

The spectra of adsorbed 1-butene provide information about the olefin-solid interaction. The F24 and F124 clays give similar results.

As the stretching bands of structural hydroxyls are very noisy, samples of the clays were exchanged with heavy water as described in the experimental section. Figure 4a shows only 1 deuteroyl band at 2680 cm^{-1} , which, together with the isotopic conversion, corresponds to the hydroxyl band at 3640 cm^{-1} . Figure 4b shows the initial adsorption spectrum of butene, in which the characteristic bands of the olefin are, in reality, the sum of the adsorbed hydrocarbon and the gas-phase. The important aspects are the disappearance of the 3740- cm^{-1} band and the invariability of the deuteroyl band. Serratos and Bradley (1958) assigned the band at 3630 cm^{-1} to structural hydroxyls that are oriented towards the vacant octahedral positions. Perhaps these positions can exchange protons or deuterons with water molecules but are inaccessible to the olefin. Whatever the reason, the fact is that olefins interact only with some of the structural hydroxyls (or deuteroyls) of clays. Another interesting feature of

this spectrum is the sharper and longer 1630- cm^{-1} band due to the superposition of the stretching C=C bond upon the bending water band. Figure 4c shows the spectrum of the butene irreversible adsorption after sweeping the cell with Ar. The clay has suffered a visible loss of water. This water was not eliminated during drying at 120 °C and is now dragged off by Ar at room temperature. As Breen et al. (1987) suspected, it appears that the olefin displaces water from the adsorption sites. The band at 3740 reappears and the 3700–3000 cm^{-1} region looks very noisy. The hydrocarbon part of the spectrum is in complete agreement with the results of Lucchesi et al. (1962) for the adsorption of ethylene onto deuterated alumina, that is, disappearance of the olefinic character of the residue and no exchange with deuteroyl.

Similar results were obtained for 1-butene adsorption onto T1 clay, with the obvious difference of weaker hydrocarbon bands attributable to lesser adsorbed amounts.

The initial adsorption spectra of alumina and silicas presented similar characteristics to those obtained with clays. The final spectra resemble those of the clean adsorbents, with disappearance of hydrocarbon bands; i.e., the hydrocarbon does not leave residues on them. In alumina, the participant hydroxyls were the ones corresponding to the 3735- cm^{-1} band.

In the adsorption spectra, the time persistence of the 3090- cm^{-1} band, corresponding to the $=\text{CH}_2$ stretching of terminal olefins, indicates that isomerization does not occur under the experimental conditions on all the adsorbents.

Adsorption spectra of butane and cyclohexane on all the adsorbents showed the participation of the same hydroxyls already identified with olefins, confirming the physical, unspecific character of reversible adsorption of olefins and paraffins.

The following experiment was carried out with F124 and *cis*-2-butene: after the adsorption was initiated, butene pressure was reduced to a few Pa. After several hours, the simultaneous increase of the 3740- cm^{-1} band and decrease of the 3020- cm^{-1} band suggested that at least part of the feeding to the condensation sites is provided by the reversibly adsorbed monomer.

The preliminary remarks formulated in Choren et al. (1997) are now complemented with infrared evidence.

CONCLUSIONS

1) Adsorption-condensations of olefins onto clays are fast processes, diffusion-controlled. The rapid initial adsorption gives way, through a transition, to a very slow increase of adsorbed mass. This transition might result from the obstruction of access to the active sites by the reaction products that remain on the

surface, possibly due to lack of a leaching solvent, as Tennakoon et al. (1983) proposed.

2) The low participation of the interlamellar sites may be due to blocking of their edges by product molecules.

3) Paraffins are reversibly adsorbed by the same structural surface hydroxyls that adsorb olefins, confirming the physical, unspecific character of this adsorption.

4) These hydroxyls are not active for condensation. When the gas-phase is evacuated or swept with an inert gas, the reaction terminates.

5) Oligomeric residues are paraffinic.

6) The reappearance of the structural hydroxyl bands suggests that condensed molecules are not adsorbed onto the surface, but remain on it because of its low vapor pressure.

7) The reversible adsorption sites participate in feeding the olefins to the condensation sites.

8) On clays, alumina and silicas dried at 120 °C, double-bond isomerization of olefins was not observed at room temperature.

ACKNOWLEDGMENTS

The authors gratefully acknowledge G. Arteaga's invaluable help with the IR spectra, and A. Palmer's English assistance. This work was partially supported by CONDES-LUZ institutional sponsorship.

REFERENCES

- Breen C, Deane AT, Flynn JJ. 1987. Vapor-phase sorption kinetics for methanol, propan-2-ol, and 2-methyl propan-2-ol on Al³⁺-, Cr³⁺-, and Fe³⁺-exchanged montmorillonite. *Clays Clay Miner* 35:336–342.
- Choren E, Moronta A, Varela G, Arteaga A, Sánchez J. 1997. Condensation of olefins on clays. Gas-solid systems Part I: Gravimetric methods. *Clays Clay Miner* 45:213–220.
- Fripiat JJ, Toussaint F. 1963. Dehydroxylation of kaolinite II. Conductometric measurements and infrared spectroscopy. *J Phys Chem* 67:30–36.
- Little LH, Mathieu MV. 1960. Étude de la déshydratation d'un verre poreux. *Actes du Deuxième Congrès International de Catalyse*. Paris: Editions Technip. p 771–785.
- Lucchesi PJ, Carter JL, Yates DJC. 1962. An infrared study of the chemisorption of ethylene on aluminum oxide. *J Phys Chem* 66:1451–1456.
- McDonald R. 1958. Surface functionality of amorphous silicas by infrared spectroscopy. *J Phys Chem* 62:1168–1178.
- Mortland MM, Fripiat JJ, Chaussidon J, Uytterhoeven J. 1963. Interaction between ammonia and the expanding lattices of montmorillonite and vermiculite. *J Phys Chem* 67: 248–258.
- Peri JB, Hannan RB. 1960. Surface hydroxyl group on γ -alumina. *J Phys Chem* 64:1526–1530.
- Serratos J, Bradley WF. 1958. Determination of the orientation of OH bond axes in layer silicates by infrared adsorption. *J Phys Chem* 62:1164–1167.
- Tennakoon DTB, Schlögl R, Rayment T, Klinowski J, Jones W, Thomas JM. 1983. The characterization of clay-organic systems. *Clay Miner* 18:357–371.
- van der Marel HV, Beutelspacher H. 1976. Atlas of infrared spectroscopy of clay minerals and their admixtures. Amsterdam: Elsevier Science. p 130–149.
- (Received 20 November 1995; accepted 10 May 1996; Ms. 2716)