

INFRARED STUDIES OF 1-HEXENE ADSORBED ONTO Cr³⁺-EXCHANGED MONTMORILLONITE

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Abstract—When 1-hexene was adsorbed by Cr³⁺-montmorillonite at room temperature, all evidence of C=C(str) vibrations was lost. Protonation of the alkene occurred, and the secondary carbocation formed was bound at a site on the primary coordination sphere of the interlayer cation. Some of the hydrogen atoms of these primary-sphere water molecules were involved in strong hydrogen bonds to the silicate sheets, whereas others did not form such bonds, but were free and directed into the interlayer space. These latter hydrogen atoms were labile and protonated the alkene molecules.

Key Words—Adsorption, Alkene, Catalysis, Chromium, Hexene, Infrared spectroscopy, Water.

INTRODUCTION

The reactions of alkenes and dialkenes over montmorillonite clays have received considerable attention in recent years (Adams *et al.*, 1978, 1979, 1981a, 1982a, 1982b, 1983a, 1983b; Bylina *et al.*, 1980; Pinnavaia *et al.*, 1979; Pinnavaia and Raythatha, 1983). In many of the clay-catalyzed reactions studied, the proposed mechanisms have involved stages where proton addition to form carbonium ions is considered to be the principal step (Adams *et al.*, 1981b, 1982b, 1982c, 1983a, 1983b; Ballantine *et al.*, 1981a, 1981b). There are, however, some reactions where this mechanistic approach is not satisfactory (Adams *et al.*, 1978, 1979, 1981a, 1982a; Pinnavaia, 1977) and others where the site of reaction is an adsorbed (intercalated) active species such as a rhodium phosphine complex (Pinnavaia *et al.*, 1979; Pinnavaia and Raythatha, 1983). It is therefore of interest to study the interaction of alkenes with certain cation-exchanged clays in an attempt to clarify the reaction mechanisms involved.

The chosen adsorbate was 1-hexene, whose reactions over montmorillonites have been studied extensively (see, e.g., Adams *et al.*, 1982a; Pinnavaia and Raythatha, 1983). Over M²⁺- or M³⁺-exchanged montmorillonites the principal product below 100°C is di-2,2'-hexyl ether, which cannot be synthesized in significant yields by any other route (Adams *et al.*, 1979). This reaction is unusual in that all other acid-catalyzed reactions which occur over these catalysts at low temperatures proceed via tertiary or allylic carbocation intermediates (Adams *et al.*, 1983b), whereas a reaction mechanism written assuming that the clay acts merely as a solid source of protons would involve secondary carbocation production on protonation of the alkene (Figure 1). A further problem exists in that the later steps in such a mechanism imply the production of a secondary alcohol intermediate, yet doping the reaction with this alcohol slows the reaction (Adams

et al., 1982a). This effect, however, could be purely a result of miscibility or phase-transfer problems. To avoid these difficulties Adams *et al.* (1981a) proposed a reaction mechanism that involves direct coordination of the double bonds of the alkene molecules to the interlayer cation. Although this second proposal has many attractive features, including an explanation of the shape selectivity of the reaction, it has some faults, the main one being that many ion-exchanged clays catalyze the reaction, even those with interlayer cations which normally do not bond to alkenes.

Inasmuch as hydrocarbons have strong infrared (IR) absorption bands in the regions around 3000 and 1500 cm⁻¹, the water of the clay investigated here was exchanged for deuterium oxide. In this way the $\nu(\text{O-H str.})$ at 3500–2900 cm⁻¹ was exchanged for $\nu(\text{O-D str.})$ at 2600–2300 cm⁻¹. Thus, a 'window' was opened in which the adsorbate $\nu(\text{C-H str.})$ bands could be observed. In addition the $\delta(\text{H-O-H})$ band was lost at 1620 cm⁻¹ thus avoiding interference with the alkenes $\nu(\text{C=C})$ band. Comparisons of the spectra of the adsorbed and free species were then made to establish the nature of the adsorbed state.

EXPERIMENTAL

A cell was designed whereby a clay film, deposited on one of two IR-transparent windows, could be examined whilst in a controlled environment. The chosen arrangement (Figure 2) was compatible with the Pye Unicam SP3-200 instrument used to take the spectra. An atmosphere of chosen composition could be introduced into the cell via inlet 1. Having thus exposed the film to the desired adsorbate the cell could then either be evacuated via valve A or flushed with wet nitrogen of known water content (relative humidity). Spectra were recorded between 4000 and 600 cm⁻¹ at the temperature of the beam.

A batch of Cr³⁺-montmorillonite catalyst was pre-

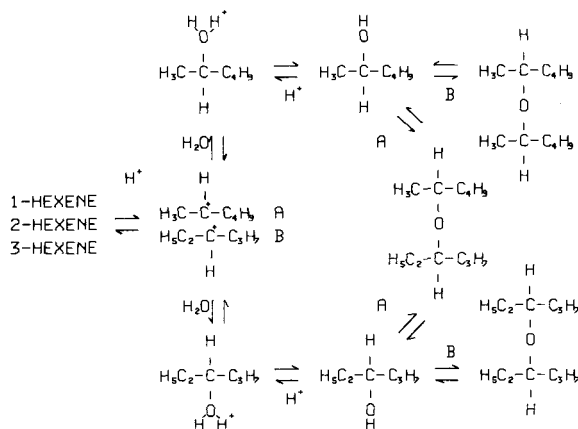


Figure 1. Possible mechanism for production of di-2,2'-hexyl ether from 1-hexene. This mechanism assumes the clay to act solely as a source of protons.

pared from Wyoming bentonite (Volclay foundry grade) after the method of Adams *et al.* (1982a). The cation and charge capacity of this clay is ~ 70 meq/100 g (Adams *et al.*, 1983b). Films were prepared by suspending ~ 10 mg of the clay in 0.1 cm^3 of distilled water, dropping the resultant suspension onto a clean zinc selenide disc (window), and allowing it to evaporate to dryness. The cell was then assembled, and the 'as prepared' clay-film spectra were recorded to optimize the instrument settings for the clay matrix. Deuterium oxide was then introduced into the cell and the clay film allowed to equilibrate (24 hr). After evacuation ($\ll 5$ mm Hg) to remove gaseous D_2O from the IR beam, the spectrum was recorded for ' D_2O '-exchanged clay ($\text{CrWM} \cdot \text{D}_2\text{O}$). The D_2O -equilibration and evacuation steps were repeated until the 1620-cm^{-1} 'scissoring' mode of H_2O was absent (see Figure 3). The film was exposed to the alkene (1-hexene) by ad-

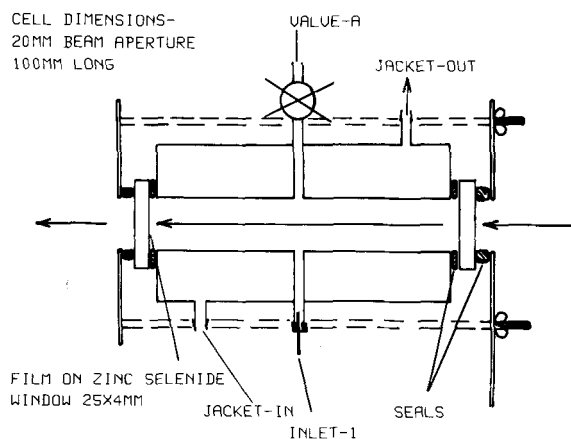


Figure 2. Sample cell for infrared studies.

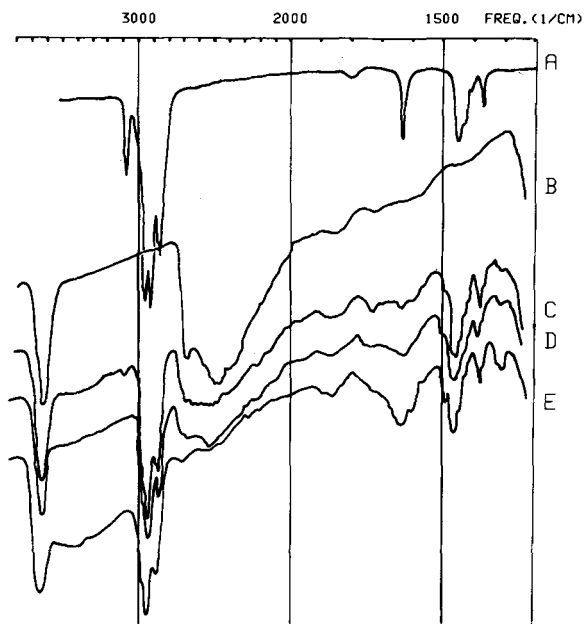


Figure 3. Infrared spectra of 1-hexene (A), D_2O -exchanged Wyoming montmorillonite (B), 1-hexene on clay 15 min (C), after 24 hr (D), after 96 hr (E).

mitting a sample through inlet 1 and allowing the film to equilibrate (15 min was found to be sufficient) before evacuating and recording a spectrum for the clay film plus adsorbed 1-hexene. Spectra were recorded at intervals over a period of some days during which time the cell was continuously evacuated. A typical series of spectra are traces C through to E in Figure 3.

To check the stoichiometry of Cr:water, clay samples were held at vacua similar to those used for the IR work and, after equilibration, the temperature was raised until all of the interlayer water was desorbed. Weight losses of 2.5–3% indicated ~ 6 –7 water molecules per Cr^{3+} ion.

RESULTS

The IR absorption spectra of free 1-hexene and the same species adsorbed on $\text{CrWM} \cdot \text{D}_2\text{O}$ are listed in Table 1; the IR absorption bands for the clay matrix, before and after sorption of the alkene, are listed in Table 2. The principal features of the normal 1-hexene spectrum (Figure 3) are readily visible in the spectrum of the adsorbed material, with the notable exception of the $\text{C}=\text{C}(\text{str})$ which is scarcely detectable, suggesting that the alkene molecules were modified or bound at the position of the double bond. In addition, the $\text{C}-\text{H}(\text{str, vinyl})$ absorption band at 3070 cm^{-1} was greatly reduced in intensity initially and with time disappeared entirely. The intensity of the 2950-cm^{-1} band ($\text{C}-\text{H, str}$) was also significantly reduced. Unfortunately, the

Table 1. Observed 1-hexene infrared absorptions.

Adsorbed (CrWM) ¹ ν (cm ⁻¹)	Free (liquid film) ν (cm ⁻¹)	Assignment
3070 (vw)	3070 (m)	C-H str (vinyl)
2950 (sh)	2950 (s)	C-H str (CH ₃)
2920 (s)	2920 (s)	C-H str (alkane CH ₂ , CH ₃)
2850 (s)	2850 (s)	C-H str (alkane CH ₂ , CH ₃)
	1635 (m)	C=C str
1480 (sh)		
1450 (m)	1455 (m)	-CH ₂ -bend
1375 (m)	1375 (m)	-CH ₃ bend
1300 (w, b)		
	990 (m)	C-H bend
	905 (s)	(vinyl)

Abbreviations: vw = very weak; w = weak; m = medium; sh = shoulder; s = strong; v = variable; b = broad; str = stretching mode; bend = bending mode; lib = librational mode.

¹ Cr-exchanged Wyoming montmorillonite.

adsorptions due to the clay in the region below 1200 cm⁻¹ did not allow changes in the bending modes associated with these features to be observed.

Between 1000 and 850 cm⁻¹, changes in the envelope suggest adsorbate features or may possibly arise from changes in hydration status (Russell and Farmer, 1964); however, the resolution was too poor to allow any conclusions to be drawn.

A further interesting feature of the clay (plus adsorbate) spectra is due to isotope exchange. A *selective* loss of intensity of the 2680-cm⁻¹ band of the O-D (str) envelope occurred. This proceeded, with time, with the parallel evolution of O-H (str) and HOH (bend) intensity in the regions of 3500–3200 cm⁻¹ and 1620 cm⁻¹, respectively. Thus, both the structure and intensity of the D₂O feature at ~2500 cm⁻¹ changed with time. The background in the region of C-D (str) absorptions increased during this time period but without any noticeable development of intense spectral features. The general loss of D₂O features was not entirely made up for by development of H₂O features. Thus, some loss of D₂O/H₂O to the vacuum must have occurred. Moreover, during the period of study (96 hr) the development of absorption bands at ~1590, 1480, and 1300 cm⁻¹ are consistent with the formation of a small amount of di-2,2'-hexyl ether (Reid, 1978). It is therefore possible that some 'water' was lost to this reaction (2 hexene + H₂O → di-2,2'-hexyl ether, Adams *et al.*, 1978, 1979).

To obtain information about the orientation of hydroxyl groups at interlayer water molecules, IR spectra were collected with clay samples held at various angles to the IR beam. The intensity of the high-frequency hydroxyl stretch (2680 cm⁻¹ for OD) followed the intensity of the stretch of the OH groups of the layers themselves, which are known to be almost parallel to the basal plane (Brindley, 1972).

Table 2. Observed infrared absorptions of Cr-exchanged Wyoming montmorillonite (showing only 'clay' features).

Clay film with adsorbate (1-hexene) (cm ⁻¹)	Clay film alone (D ₂ O equilibrated) (cm ⁻¹)	Assignment
3610 (s)	3610 (s)	Struct. OH str
3500–3200 (v)		O-H str H ₂ O
2680 (v)	2680 (s)	O-D _a str ¹
~2470 (v)	~2470 (s, b)	O-D _b str ¹
~2380 (v)	~2380 (sh)	
1615 (v)		H-O-H bend
~1050 (s, b)	~1050 (s, b)	
915 (s)	915 (s)	AlAlOH lib
885 (sh)	885 (sh)	AlFe ³⁺ OH lib
845 (sh)	845 (sh)	AlMgOH (lib)
795 (m)	795 (m)	
775 (sh)	775 (sh)	
690 (w)	690 (w)	

¹ O-D_a represents a weakly 'hydrogen' bonded deuterium whilst features at lower frequency relate to progressively stronger 'hydrogen'-bonded deuterons.

DISCUSSION

The stoichiometry found for the interlayer species suggests that initially the chromium cations were likely coordinated octahedrally to six molecules of D₂O. Clementz *et al.* (1973) suggested a similar arrangement of water molecules around Cu²⁺ in the interlayer space of montmorillonites at certain relative humidities. The structure of the IR absorption band in the O-D (str) region is indicative of strong and weak/non-existent hydrogen bonding (Farmer and Russell, 1971). Inasmuch as the octahedral [Cr(D₂O)₆]³⁺ moiety lies obliquely to the silicate ditrigonal sheet (Clementz *et al.*, 1973; Figure 4), the observed hydrogen bond associations indicate an ordered coordination structure (Farmer and Russell, 1971) with the coordination complex interacting with the oxygen sheet of the silicate layers. Farmer and Russell (1971) considered that the 'strong' hydrogen bonding must result from a linking of the O-D groups of the coordinated D₂O molecules with the oxygen atoms of the oxygen sheet or with any D₂O molecules in the interlayer which are not involved in the primary cationic sphere. Under the experimental conditions used here, very few interlayer water molecules were present which were not part of the first coordination sphere of the chromium cations. Consequently, the lower frequency OD-stretching vibrations (which correspond to stronger H bonding) were likely to have arisen when hydrogen bonds were formed from D₂O molecules to framework oxygen atoms. The higher frequency O-D band (2680 cm⁻¹) was associated with OD groups not involved in hydrogen bonding. Such groups are likely to have projected into the "free space" of the interlayer region and therefore were oriented approximately parallel to (001) in agreement with the pleochroic studies discussed above. The deuterium atoms of such groups, labelled D_a in Figure 4, appear

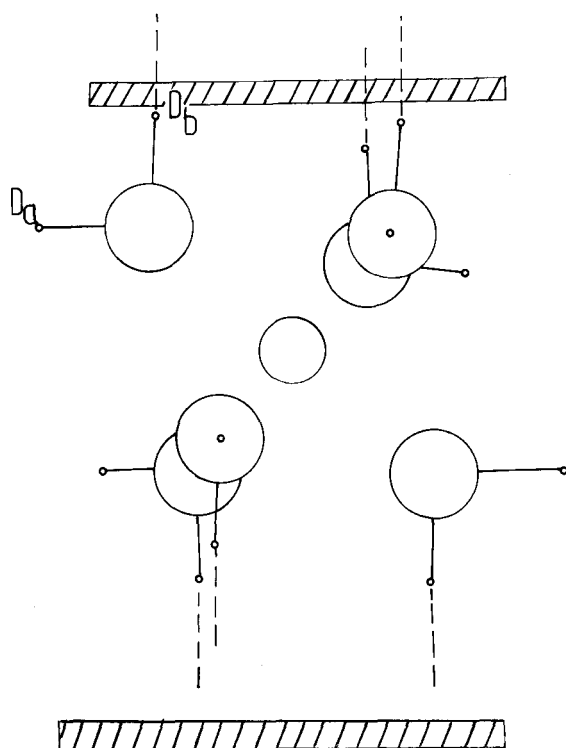


Figure 4. Expected configuration for $[\text{Cr}(\text{D}_2\text{O})_6]^{3+}$ in the interlayer region of montmorillonite at a pressure of ~ 0.5 mm Hg.

to have been most intimately involved with the adsorbed 1-hexene. It is known that montmorillonite clays act as Bronsted acids because the water coordinated to the interlayer cation is polarized (Mortland and Ramon, 1968), i.e.,



The present data suggest that the absorptions associated with the O– D_a group selectively lost intensity with time. It appears that the O– D_a bond was capable of being broken, with the D_a atoms being the ‘protons’ made available for interaction with the carbon–carbon double bond of the alkene.

This interaction could have involved the association of the deuterium (D_a) and the carbon–carbon double bond which bound the alkene at this site. Alternatively, complete dissociation of the D_2O molecule could have occurred with subsequent carbocation formation. In the latter case, the carbocation should have undergone further reaction to form products after interaction with other species (water or alkene) in the interlayer space.

From earlier work (Adams *et al.*, 1978, 1979, 1981a, 1982a, 1983a, 1983b) it is known that reactions of 1-alkenes over metal-exchanged montmorillonites give different products at different temperatures. For reac-

tions carried out below 100°C , almost a 100% yield of the di-2,2'-alkyl ether (based upon the initial water content of the clay) can be obtained. Above 100°C the yield is much reduced in favor of products such as dimers and oligomers suggestive of secondary carbonium-ion intermediates. Because very few products of this nature have been observed at low temperatures, despite the apparent protonation of the alkene demonstrated here, we believe that it is only at 100°C that the secondary carbonium ions formed become sufficiently labile to react further. The presence of another free nucleophile such as excess water or methanol does not alter the reactivity (see, e.g., Adams *et al.*, 1983a) of secondary carbonium ions, indicating that these species, once formed, must be shielded from further reaction until their thermal motions or lability increase.

In the light of the present observations, the selectivity displayed in the reaction of 1-alkenes over clays below 100°C is significant. This reaction proceeded to the di-2,2'-alkyl ether; the di-2,3-alkyl ether and other analogues did *not* form. This result is anomalous when considered in the light of other findings. First, hydride shifts in free hydrocarbons should occur to give the most stable ion which would result in the charge being as far into the chain as possible. The carbocation which was initially formed with the charge on the 2-position should have rearranged to place the charge on the 3-position, and such scrambling should have given a mixture of ether products. Second, 2-alkenes are unreactive as starting materials for this reaction (Adams *et al.*, 1981a), even though on protonation they should have given at least some carbocations with charges on the 2-position as is found on protonation of a 1-alkene. Third, alteration of the reactant to one with a branched chain, even if the branching was some distance from the double bond (e.g., 4-methyl-pent-1-ene) also caused a cessation of activity (Adams *et al.*, 1981a), a shape selectivity which is unlikely with unbound carbocation intermediates. These aspects of the reaction lead to the conclusion that intermediates must have been bonded in some way such that they retained configuration but were shielded from further attack. A selective reaction then proceeded about the 2-position which incorporated interlayer water to give the di-2-alkyl ether.

It is proposed that the observed reactivity of clay catalysts above and below 100°C is greatly influenced by the arrangement of interlayer species. At temperatures much less than 100°C , the alkenes may be protonated to give the appropriate carbonium ions. For 1-alkenes, a secondary carbonium ion may be formed (or perhaps incipiently formed) by the binding of the double bond at a site on the primary coordination sphere of the cation. This site is a proton (deuteron) attached to the highly polarized water (deuterium oxide) coordinated about the cation—the proton (deuteron) not involved in hydrogen bonding to the clay layer. At this

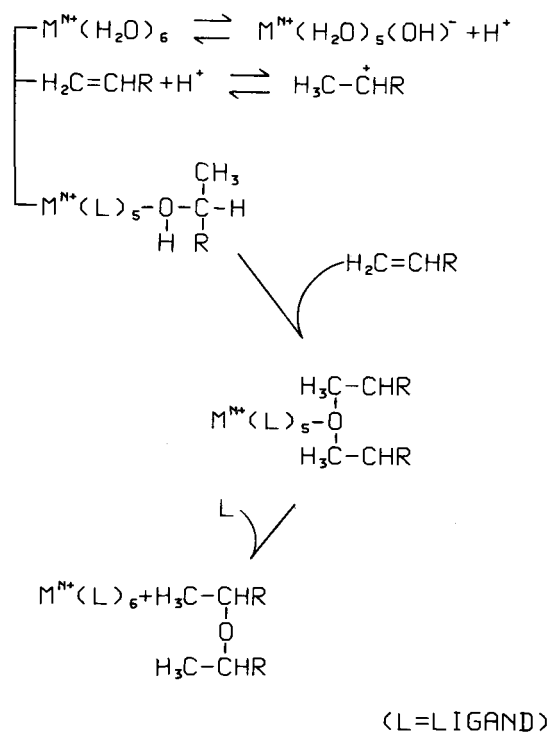


Figure 5. Suggested reaction mechanism for the production of di-2,2'-alkyl ether based upon the present infrared evidence and the known involvement of an alk-2-ol-like intermediate.

point further reaction of the activated alkene may take place provided it has a suitable structure, which, for straight chain 1-alkenes, leads to the formation of the di-2,2'-alkyl ethers (Figure 5). If the conformation is not suitable, increasing the lability of the carbonium ion (by raising the temperature or perhaps using certain solvents) promotes other reactions. Thus, the reaction may proceed via routes analogous to homogeneous acid-catalyzed reactions, and the interlayer ordering is either reduced or lost.

Mortland (1970) noted that a cautious approach is advisable when comparing the results of experiments performed in a reaction vessel with those under the controlled conditions of the spectrometer. Under the conditions used for many clay-catalyzed reactions, however, a mechanism of the sort indicated here is possible. In such reactions, clays pre-equilibrated to give low water contents are placed in dry solvent/reactant systems. In such circumstances other workers have proposed that the observed catalytic activity may have several causes. Mortland (1968) and Mortland and Raman (1968) showed that the field gradients around the cation are sufficient to cause hydrolysis. These same forces affect the delocalized π electron systems in organic molecules (see, e.g., Pinnavaia, 1977). The existence of water-bridged coordination complexes in the

interlayer region of clays has been well demonstrated (Farmer and Russell, 1971; Mortland, 1970). Thus, in the absence of a medium with a high dielectric constant the reactant/water bridge will feel the full polarizing power of the cation. All of these effects are synergic and increase with the electrostatic forces around the cation. Hence, in the present work we are reasonably sure that we are examining the limiting case for the inter-layer environment under the usual reaction conditions.

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Резюме—После адсорбции 1-гексена на Cr^{3+} -монтмориллоните при комнатной температуре, исчезло все доказательство колебаний $\text{C}=\text{C}$ (растягиваний). Появлялось протонирование алкенов, а вторичный образованный катион углерода был связан в основной координационной сфере межслойных катионов. Некоторые атомы водорода молекул воды этих основных сфер были связаны сильными водородными связями с силикатовыми слоями, в то время, как другие атомы не образовывали таких связей, а оставались свободными и направлялись в межслойное пространство. Эти свободные атомы водорода являлись неустойчивыми и протонировали молекулы алкенов. [E.G.]

Resümee—Wenn 1-Hexen bei Raumtemperatur an Cr^{3+} -Montmorillonit adsorbiert wird, so gibt es für $\text{C}=\text{C}$ (str)-Schwingungen keinen Hinweis mehr. Protonierung der Alkene trat ein, und die auftretende sekundäre Carbonierung war an eine Stelle der primären Koordinationshülle des Zwischenschichtkations gebunden. Einige der Wasserstoffatome dieser primären Wassermolekülhülle waren durch eine starke Wasserstoffbindung an die Silikatschicht gebunden, während andere keine derartige Bindung aufwiesen sondern ungebunden und in den Zwischenschichtraum ausgerichtet waren. Diese letzteren Wasserstoffatome waren labil und protonierten die Alkenmoleküle. [U.W.]

Résumé—Lorsque l'hexène-1 a été adsorbée par la montmorillonite- Cr^{3+} à température ambiante, toute évidence de vibrations $\text{C}=\text{C}$ (str) a été perdue. La protonation de l'alkalène s'est produite, et la carbocation secondaire formée a été liée à un site sur la sphère de coordination primaire de cation intercouche. Certains atomes d'hydrogène de ces molécules d'eau de sphère primaire ont été impliqués dans de très fortes liaisons d'hydrogène avec les feuillets silicates, tandis que d'autres n'ont pas formé de telles liaisons, mais étaient libres et se sont dirigés vers l'espace intercouche. Ces derniers atomes d'hydrogène étaient labiles et ont protonaté les molécules alkalènes. [D.J.]