Crotonaldehyde hydrogenation over clay-supported platinum catalysts

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Abstract

Two clay-supported platinum catalysts were prepared by impregnation and tested in the liquid phase hydrogenation of crotonaldehyde. Over both catalysts, the unsaturated alcohol selectivity was increased (to 49%) compared to that obtained over platinum on conventional supports (maximum 20%). The effect of the solvent, the subtrate initial concentration, the hydrogen pressure and the reaction time was studied. The benefic effect of the support was observed only if an alcohol was used as solvent. A deuterium tracer study revealed the coaction of the Lewis acid sites of the clay supports in adsorption of the substrate leading to an increase in the crotyl alcohol selectivity. The self poisoning of the metal over the clay-supported catalysts was supposed to inhibit the C=C group hydrogenation. © 2001 Elsevier Science B.V. All rights reserved.

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1. Introduction

The hydrogenations of unsaturated carbonyl compounds belong to the most important reactions in the synthesis of fine chemicals used in the production of pharmaceuticals, flavorings and perfumes [1]. This is confirmed by the increasing efforts devoted to find new systems able to produce one of the products in high yields [2,3]. As shown in Scheme 1, the hydrogenation of these substrates (**A**) gives two semi-hydrogenated products: the saturated carbonyl compound (**B**) and the unsaturated alcohol (**C**) which can be further hydrogenated to the saturated alcohol (**D**). Depending on the reaction conditions side products may form by dehydration of the alcohol, condensation of the carbonyl compounds or reaction with an alcoholic solvent lead-

ing to acetals. From these products the most difficult to obtain, especially in the case of α,β-unsaturated carbonyl compounds, is the unsaturated alcohol.

Over supported noble metal catalysts, the C=C bond is hydrogenated more easily than the C=O bond. Several attempts have been made to develop suitable heterogeneous catalytic systems able to hydrogenate selectively the carbonyl group. The studies on selective hydrogenation of α,β-unsaturated aldehydes have been recently reviewed by Gallezot and Richard [4].

As these studies revealed, forcing the substrate molecule to a preferential adsorption through the C=O group or hindering the adsorption through the C=C group will increase the selectivity of the unsaturated alcohol. Accordingly, high α,β-unsaturated alcohol selectivities were obtained by using: (i) catalysts with low metal dispersion, (ii) bimetallic catalysts or alloys, (iii) metal salts or organometallic compounds as Lewis acid additives, (iv) alkali metal ion promoters,

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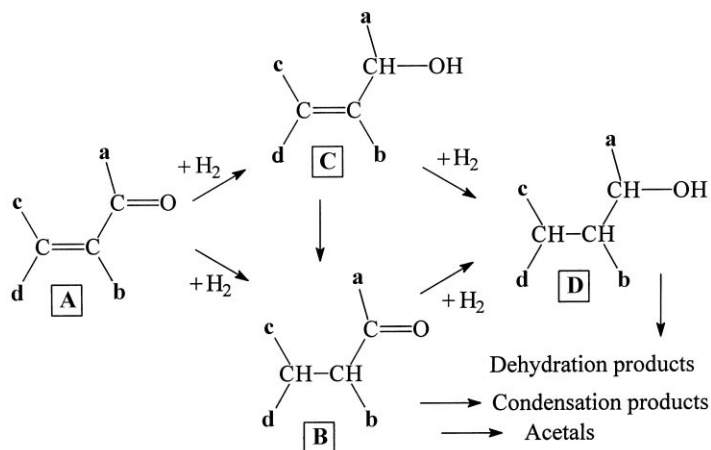
Scheme 1. Network of the hydrogenation of α,β-unsaturated carbonyl compounds.

(v) poisons of the C=C bond absorption sites, (vi) catalysts in the SMSI state and (vii) catalysts with noble metal crystallites immobilized in the pores of zeolites [4]. The use of sonochemical activation of the catalyst could also lead to increased unsaturated alcohol selectivity [5,6]. These methods of increasing the unsaturated alcohol selectivity were found not to be general, in several cases their effects being dependent of the reaction conditions, the structure of the catalyst and the substrate [7]. It is generally accepted that the enhanced adsorption through the carbonyl group in most cases is due to electron deficient centers created on the metal particles or at the metal-support interface. High unsaturated alcohol selectivities could be obtained mostly in the case of substrates bearing bulky groups on the C=C bond. However, recently several research groups have also reported high unsaturated alcohol selectivities in the case of molecules without a significant steric effect of these groups [8,9].

Amazingly, clays which could provide the same effects as the zeolites have been rarely applied as supports for noble metals. This is even more surprising if we consider the applicability of these materials as acid catalysts and the large number of clay supported catalysts prepared for other purposes [10–13].

Recently, we reported the use of a K-10 montmorillonite-supported platinum catalyst in the hydrogenation of cinnamaldehyde [14]. Although the metal particles were not immobilized in the interlamellar space of the clay, almost exclusive formation the cinnamyl alcohol was obtained. We have studied the influence of the nature of the clays in the case of substrates having different structure [15].

In the present paper, we disclose the results of a detailed study on the hydrogenation of crotonaldehyde over two clay-supported platinum catalysts. As support we chose two clays: K-10 montmorillonite (K-10) and Bentolite H (BenH) bentonite. We have optimized the reaction conditions particularly the hydrogen pressure, the substrate initial concentration and the conversion. In order to elucidate the causes of the increase of the unsaturated alcohol selectivity and to find a mechanistic explanation of this effect, we have carried out experiments in which deuterium was used as tracer. Several previous studies [16–19] have shown that the distribution of deuterium in the products can be a sensitive probe of the nature and the changes of the reaction sites on supported metal surfaces.

2. Experimental

2.1. Materials

Crotonaldehyde purchased from Fluka was of analytical grade and distilled before use. The organic solvents: 2-propanol, *tert*-butyl alcohol, cyclohexanol, butyl ether, tetrahydrofuran, dichloromethane, chloroform and hexane with a minimum purity of 99.5% were Reanal products, d_4-methanol of 99.8 at.% D was an Aldrich product. High purity, oxygen-free hydrogen (99.995%) and deuterium (99.8%) was purchased

from Linde. As a platinum precursor $H_2[PtCl_6]\cdot H_2O$ having 37.5% Pt content (Aldrich) was used. The clays, K-10 montmorillonite from Aldrich and Bentolite H from Laporte Inc. were used as received. The MgO was purchased from Fluka, SiO_2 (Cab-O-Sil M5) from BDH. The 3% Pt/SiO_2, 2.5% Pt/MgO, catalysts were prepared by impregnation [20]. Commercial Pt/Al_2O_3 and Pt/C catalysts both of 5% metal loading were obtained from Engelhard.

2.2. Preparation and characterization of the clay-supported catalysts

The clay-supported catalysts were prepared by impregnation. The clay (4 g) was suspended in $80\,cm^3$ distilled water and swelled for 5 h. Then an appropriate amount of 1% aqueous solution of the platinum precursor was added dropwise and stirred for another 2 h. The water was removed under reduced pressure and the solid was suspended in $40\,cm^3$ of 95% aqueous ethanol. The resulting suspension was stirred for 10 h and heated under reflux for 6 h. After filtration, the solid was washed thoroughly with deionized water and dried at 383 K under reduced pressure.

The catalysts were characterized by transmission electron microscopy (TEM) and X-ray diffraction (XRD). The TEM measurements were performed with a Philips CM10 electron microscope at 90 kV at a magnification of 300,000. Samples were dispersed in hexane, mounted and air-dried on a plastic film supported by a Formvar grid. The mean metal particle diameters were calculated as the average of individual diameters ($\sum n_i d_i / \sum n_i$, $n = 200$) determined from the magnified TEM images. The results obtained in this way were checked in several cases by H_2 chemisorption [20]. The XRD measurements were carried out using a Philips PW 1820 diffractometer (Cu Kα, $\lambda = 0.15\,nm$, PW 1830 Philips generator). The basal distances were calculated according to the Bragg equation, using the PW 1877 automated powder diffraction program with an accuracy of $\pm 0.01\,nm$.

2.3. Hydrogenation of crotonaldehyde

Hydrogenation reactions were performed in a thermostated, well stirred (1000 rpm) stainless steel autoclave of $100\,cm^3$ volume. Before the reaction, the catalyst was activated in $20\,cm^3$ of solvent at 298 K under an adequate hydrogen pressure. After the activation period, crotonaldehyde was introduced and the reaction was started by turning on the stirrer. The reaction temperature was 298 K. Several experiments using different amounts of each catalyst were carried out in order to determine the diffusion control region in order to eliminate mass transfer limitations during our studies.

The products were indentified on the basis of their mass spectra using a HP 5890 GC-HP 5970 MSD system equipped with a 50 m long HP-1 capillary column and on the basis of their retention times, which were compared to those of authentic samples. Quantitative analysis was performed with an SRI 8610A gas chromatograph equipped with a 30 m long, 0.53 mm ID DB-WAX capillary column and FID. The reproducibility of the reactions was found to be $\pm 2\%$.

2.4. Deuterium tracer study

The deuterations were performed in the same autoclave. The pretreatments and reactions were carried out as in the case of the hydrogenations, but using deuterium instead of hydrogen. The deuterium distributions of the products were determined using a HP 5890 GC-HP 5970 MSD system equipped with a 50 m long HP-1 capillary column. The usual corrections were made for natural isotopes, for the O–H, O–D fragmentation in case of alcohols and for the first C–H, C–D fragmentation which corresponds to fragmentation at the aldehydic hydrogen [21]. The other corrections were small enough to be neglected.

3. Results and discussions

3.1. Characterization of the catalysts

As the metal particle size may play an important role in determining the product selectivity in the hydrogenation of α,β-unsaturated aldehydes [5], the mean platinum particle diameters were determined by TEM. These data were used for calculating the metal dispersions. The results were checked in several cases by chemisorption measurements (Table 1). The mean platinum particle size of the clay-supported catalysts were close to those of SiO_2- and MgO-supported ones.

Table 1
Characteristics of the platinum catalysts

Catalyst	Metal loading (%)	Mean platinum diameter (nm)[a]	Dispersion (%)[b]
Pt/Al$_2$O$_3$	5	3.5	32
Pt/SiO$_2$	3	6.7	15
Pt/C	5	3.3	34
Pt/MgO	2.5	6.1	18
Pt/K-10	2.5	8.8	13
Pt/BenH	3.2	9.5	12

[a] Determined by TEM ($\sum n_i d_i / \sum n_i$, $n = 200$).

[b] Fraction of platinum atoms exposed to the liquid phase, calculated from TEM data and checked by H$_2$ chemisorption measurements.

As a result of impregnation and subsequent reduction to metallic platinum changes in the clay structure may occur. The XRD patterns of the Pt/BenH catalyst in comparison with that of the parent clay is illustrated in Fig. 1. A similar study has already been published for K-10 supported platinum catalyst [14]. In the XRD patterns of both catalysts, the appearence of a small and broad peak characteristic of platinum crystallites could be noticed at 40° 2Θ.

Due to the high temperature treatment with mineral acids included in the preparation method of K-10 montmorillonite [22], besides kaolinite and montmorillonite transformed in H-form, this clay contained a quartz-like material due to dealumination. The pres-
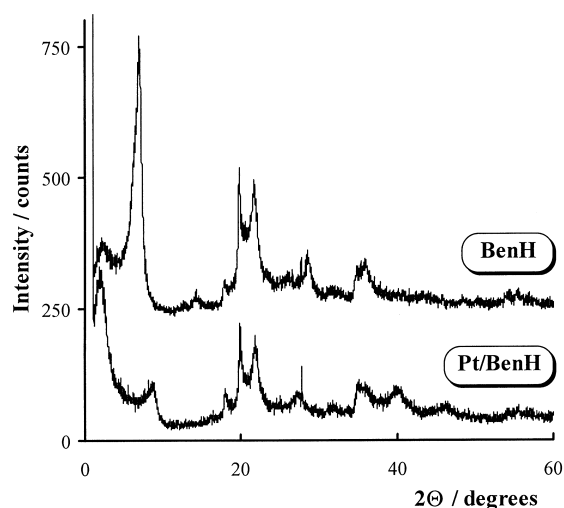
ence of these phases was proved by ^{29}Si NMR studies [14,23]. However, the H-form is unstable which results in leaching of the Al^{3+} ions from the clay lattice and their relocation in cation exchange positions [24,25]. Impregnation of this support had little effect on the structure of the parent clay [14].

The other clay used as support was a bentonite in its Na$^+$ form in which besides the isomorphous substitutions in the octahedral sheets (Fe^{3+}, Mg^{2+} $\Rightarrow$ Al^{3+}) part of the Si^{4+} ions from the tetrahedral sheets was also replaced by Al^{3+} ions, as the general formulae shows: Si$_{7.84}$Al$_{0.16}$O$_{20}$(OH)$_4$Al$_{2.96}$Fe$^{3+}_{0.36}$Mg$_{0.67}$ M$^+_{0.83}$. In this case, the very intense peak observed at 7.1° 2Θ in the diffractogram of the parent clay was drastically reduced and shifted to 9.0° 2Θ (Fig. 1). This shift showed a decrease in the basal distance from 1.25 to 1.00 nm as a result of impregnation. Furthermore, the small peak from 2.7° 2Θ was shifted downwards to 2.3° 2Θ revealing that certain pores have suffered a small enlargement from 2.3 to 2.4 nm. As a consequence, one can assume that only a small part of the metal crystallites are located in the interlamellar space, the major part being deposited on the clay sheets and in the pores of the clay.

3.2. Hydrogenation of crotonaldehyde

The hydrogenation of crotonaldehyde (Scheme 1; **A**; **a,b,c** = H; **d** = CH$_3$) resulted in the formation of butyraldehyde (**B**), crotyl alcohol (**C**), 1-butanol (**D**) and side-products formed by aldol condensation and acetals when an alcohol (2-propanol) was used as solvent. In our experiments, the major product of hydrogenation over platinum on conventional supports was butyraldehyde. These catalysts afforded small crotyl alcohol/butyraldehyde ratios (**C/B**) and low reaction rates (Table 2). Using the clay-supported catalysts the crotyl alcohol selectivity, the **C/B** ratio and the reaction rate were significantly increased.

It was demonstrated in the hydrogenation of cinnamaldehyde over K-10 supported platinum that the Lewis acid centers situated at the metal-support interface were acting as anchoring sites of the C=O group [14]. It must be stressed that when the substrates used were bearing groups with no or only small hindering of the adsorption of the C=C group, the increase in the unsaturated alcohol selectivity was only moderate [15]. Thus, in the interpretation of the

Fig. 1. X-ray diffraction patterns of bentolite H and the Pt/BenH catalyst.

Table 2
Hydrogenation of crotonaldehyde over supported platinum catalysts[a]

Catalyst	Conversion (mol%)	Reaction rate[c]	Selectivity (mol%)[b]				C/B
			B	C	D	E	
Pt/Al$_2$O$_3$	86	4.68	25	16	17	42	0.6
Pt/SiO$_2$	73	14.17	25	18	8	49	0.7
Pt/C	60	3.07	53	7	15	25	0.1
Pt/MgO	70	13.60	47	20	20	13	0.4
Pt/K-10	82	22.02	8	31	14	47	3.9
Pt/BenH	84	19.08	6	43	17	34	7.2

[a] Catalyst (50 mg) in 20 cm^3 2-propanol, crotonaldehyde initial concentration: 0.57 M, hydrogen pressure: 2 MPa, reaction time: 9 h.
[b] **B**: butyraldehyde, **C**: crotyl alcohol, **D**: 1-butanol, **E**: by-products.
[c] Rate of transformation of crotonaldehyde (mol crotonaldehyde reacted on mol surface platinum in one minute).

results obtained in the hydrogenation of crotonaldehyde, we may disregard the steric effect of the methyl group. The metal particle size may play a role only by determining the ratio between the metal atoms situated at the interface region and of those far from the support.

Using more bulky alcohols than 2-propanol, the selectivity of by-product formation could be lowered, especially in the case of *tert*-butyl alcohol (Table 3). Surprisingly, the solvent also had an important effect on the selectivities of the primary hydrogenation products, the **C/B** and **C/D** ratios, respectively. The bulkiness of the *tert*-butyl group also hindered the hydrogenation, leading to a lower overall reaction rate. It is noteworthy that enhanced crotyl alcohol selectivities could be observed only in alcohols. Although in ethers the conversions were comparable with those obtained in alcohols, the formation of butyraldehyde was predominant. The transfer hydrogenation of crotonaldehyde may be excluded as experiments carried out in He did not lead to significant amounts of hydrogenated products.

It seems that beside the anchoring role of the Lewis acid sites of the support another effect will also influence the reaction pathway. This effect, dependent on the nature and bulkiness of the solvent was revealed by evaluating the consequences of the variations of the reaction time and the crotonaldehyde initial concentration. Some representative results are illustrated in Figs. 2a,b and 3.

Table 3
Hydrogenation of crotonaldehyde over clay-supported platinum catalysts in different solvents[a]

Catalyst	Solvent	Conversion (mol%)	Selectivity (mol%)[b]			C/B	C/D
			B	C	D		
Pt/K-10	2-Propanol	82	8	31	14	3.9	2.2
	tert-Butyl alcohol	30	19	49	27	2.6	1.8
	Cyclohexanol	69	4	44	14	11.0	3.1
	Butyl ether	55	59	13	26	0.2	0.5
	Tetrahydrofuran	63	50	1	4	0.02	0.3
	Dichloromethane	13	33	–	3	–	–
	Chloroform	16	80	8	2	0.1	4
	Hexane	25	32	8	5	0.3	1.6
Pt/BenH	2-Propanol	84	6	43	17	7.2	2.5
	tert-Butyl alcohol	51	27	33	34	1.2	1.0
	Cyclohexanol	68	8	26	15	3.3	1.7

[a] Catalyst (50 mg) in 20 cm^3 solvent, crotonaldehyde initial concentration: 0.57 M, hydrogen pressure: 2 MPa, reaction time: 9 h.
[b] **B**: butyraldehyde, **C**: crotyl alcohol, **D**: 1-butanol.
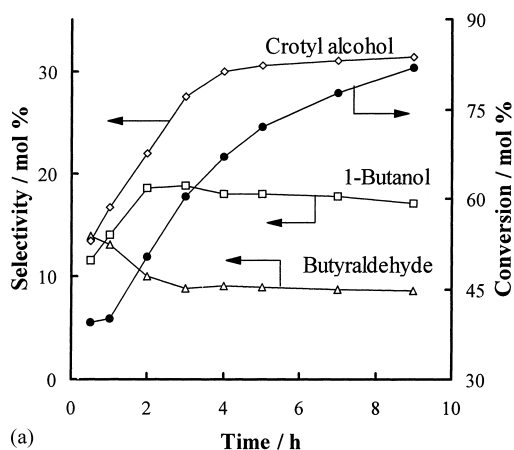
(a)
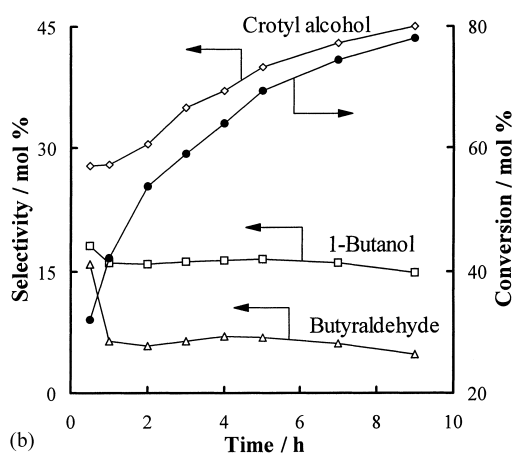
(b)

Fig. 2. Time dependence of the conversion and product selectivity in crotonaldehyde hydrogenation over clay-supported catalysts (reaction conditions: 50 mg catalyst in 20 cm^3 2-propanol, substrate initial concentration 0.57 M) Pt/K-10, H$_2$ pressure 2 MPa (a); Pt/BenH, H$_2$ pressure 1 MPa (b).

Fig. 3. Product selectivity vs. initial concentration of crotonaldehyde over Pt/K-10 catalyst (hydrogenation conditions: 50 mg Pt/K-10 in 20 cm^3 2-propanol, hydrogen pressure 2 MPa, reaction time: 9 h).

In every case after an initial modification, both the butyraldehyde and the 1-butanol selectivity remained constant over a prolonged reaction time. The selectivity of butyraldehyde decreased in the initial period over both catalysts (see Fig. 2a,b). This phenomenon cannot be explained by a faster transformation of the resulted aldehyde, as the 1-butanol selectivity was essentially constant and that of the by-products decreased in time. A plausible explanation may be the self-poisoning of the bare metal surface at the begining of the reaction. A similar observation has already been published by Chambers et al. in the case of hydrogena-
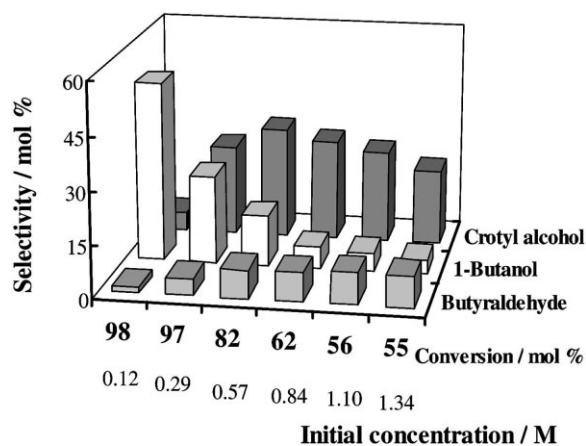
tion of cinnamaldehyde [19]. They suggested that the catalyst surface was initially modified by hydrocinnamaldehyde, before further reaction to give cinnamyl alcohol could occur. In our case, the modification of the metal surface probably led to a partial coverage of the sites on which the C=C group is hydrogenated. It is likely that the more active metal sites such as kinks or edges are covered first. Thus, the hydrogenation of the C=C group is forced to take place on the partially uncovered plain surface of the Pt.

The selectivity of crotyl alcohol increased during almost the whole reaction, although the selectivities of the other hydrogenated products quickly became constant. This means that the two semi-hydrogenated product were formed on different surface sites and the modifying effect proposed above had different influences on these sites. Accordingly, we may consider that crotyl alcohol is formed through adsorption on sites located at the metal-support interface where the Lewis acid sites will anchor the substrate. On the other hand, butyraldehyde will form on the bare metal sites.

Increasing the initial concentration up to a certain value (0.57 M), the selectivities of the primary hydrogenation products, especially that of crotyl alcohol, increased markedly (Fig. 3). A further increase in the initial concentration led to a slow decrease in the crotyl alcohol selectivity, but more importantly, to a drastic increase in the by-product formation. It is
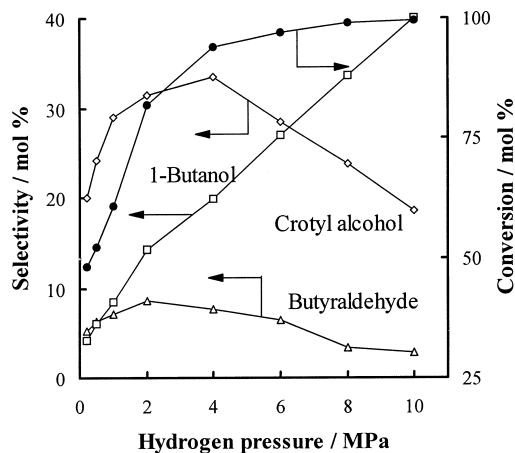
Fig. 4. Hydrogen pressure dependence in the hydrogenation of crotonaldehyde over Pt/K-10 (reaction conditions: 50 mg Pt/K-10, 20 cm^3 2-propanol, substrate initial concentration 0.57 M, reaction time: 9 h).
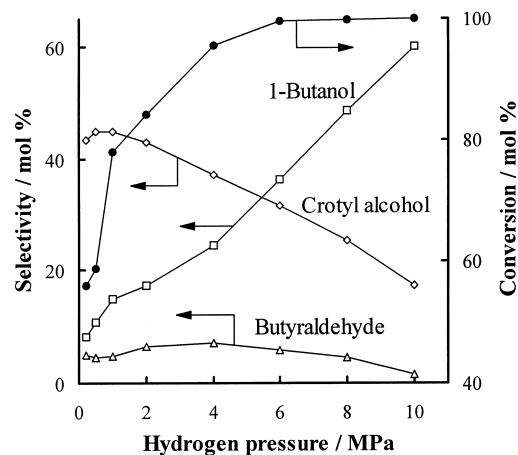

Fig. 5. Hydrogen pressure dependence in the hydrogenation of crotonaldehyde over Pt/BenH (reaction conditions: 50 mg catalyst, 20 cm^3 2-propanol, substrate initial concentration 0.57 M, reaction time: 9 h).

likely that on the acid sites of these clays formation of dimers from the aldehyde, their dehydration and a subsequent strong adsorption on the metal takes place. This might be responsible for the appearence of this poisoning-modifying effect. If the value of 0.57 was exceeded the sites on which the unsaturated alcohol is formed could also be slowly poisoned.

The hydrogen pressure dependence study over the clay-supported catalysts revealed that in all instances the selectivity of crotyl alcohol had a maxima at low hydrogen pressures (Figs. 4 and 5). A significant difference was found in the amount of by-products formed. Over the Pt/BenH catalyst these products were produced in smaller amounts. The main side reaction was found to be the formation of the aldol from butyraldehyde and its subsequent dehydration and hydrogenation, but acetal formation could also be observed. This was confirmed also by mass spectrometric measurements.

As the shapes of these curves in the case of butyraldehyde were dependent on the solvent and not on the clay used one may conclude that the solvent had a significant effect in determining the degree of the above mentioned poisoning of the metal surface. A more bulky solvent will exert a stronger hindering effect on the adsorption of these substances. In the case of crotyl alcohol, in the shapes of the hydrogen de-

pendence curves differences were obtained for the use of different supports, and the solvent had little effect. These hydrogen dependence curves demonstrated that on the clay-supported catalysts these products were formed on totally different active sites. The butyraldehyde was formed on the metal atoms far from the support while crotyl alcohol on centers situated near the Pt-support interface.

3.3. Deuterium tracer study

Seeking for evidence which could help clarifying the pathways over the clay-supported catalysts we have carried out experiments using deuterium (D) as a tracer. Unfortunately, it was not possible to determine the position of the D atoms in the products having incorporated more than one D atoms, due to superimposition of the fragments.

We have to note that under our experimental conditions very little H–D exchange occurred in the substrate even after long reaction times. The exchange after 9 h was found to be 1.5% on Pt/C, 1.9% on Pt/BenH and 2.2% on Pt/K-10 in 2-propanol, 1.8% in *tert*-butyl alcohol and 2.5% in hexane. No exchange in the terminal –CH$_3$ group was observed. On Pt/C after 9 h, the aldehydic and the β hydrogens (Scheme 1; **A**; **a** and **c**) were exchanged in equal amounts (∼45%).

Table 4
Deuterium distribution in the formed butyraldehyde[a]

Catalyst	Solvent	Reaction time(h)	Deuterium distribution (%)					$\sum id_i$ [b]
			d_0	d_1	d_2	d_3	d_4	
Pt/C	2-Propanol	9	10	38	44	8	–	1.50
Pt/K-10	2-Propanol	1	3	25	63	9	–	1.79
		9	4	26	56	13	1	1.81
		16[c]	90	10[d]	–	–	–	0.10
	tert-Butyl alcohol	9	6	31	53	10	–	1.67
	Hexane	9	2	29	63	6	1	1.77
	d_4-Methanol[e]	1	73	24[f]	3	–	–	0.30
Pt/BenH	2-Propanol	1	35	42	23	–	–	0.88
		9	9	31	51	9	–	1.60

[a] Catalyst (50 mg) in 20 cm^3 solvent, crotonaldehyde initial concentration: 0.57 M, D$_2$ pressure 2 MPa.
[b] Average number of deuterium atoms per molecule.
[c] Butyraldehyde was used as starting material.
[d] Distribution of D: **a** 53%, **b** + **c** 47% (see Scheme 1).
[e] In this reaction, hydrogen was used.
[f] Distribution of D: **a** 25%, **b** + **c** 75% (see Scheme 1).

On Pt/K-10 the **a/c** exchange ratio was found to be 70%/30% and on Pt/BenH 75%/25%. No or very little exchange of the α-H (**b**) occured. A comparison of the inital (1 h) and final (9 h) **a/c** exchange ratio revealed that an inversion took place over Pt/K-10 from 30%/65% (∼0.5) to 70%/30% (∼2.3). This inversion may be caused by the modification in time of the exchange sites or/and by the relocation of these on different metal atoms.

The deuterium distribution in butyraldehyde is presented in Table 4. As one can see on Pt/C an average of 1.5 D atoms were incorporated in this molecule determined by the H/D ratio on the metal surface. Using the clay-supported catalysts the average number of D per molecule ($\sum id_i$) was higher. As described above during poisoning the more active metal sites (kinks and edges) are first covered. In such cases, the hydrogenation of the C=C group is forced to take place on the partially uncovered plain surface of the metal where the H/D ratio is lower than on the above mentioned centers, as this ratio is determined by the adsorption of the solvent. This may be the reason of the higher D content of butyraldehyde obtained over the clay supported catalyst compared with that obtained over Pt/C which is supported by the results obtained in d_4-methanol. The butyraldehyde formed in this solvent had 24% of d_1-product in its composition with 25% of the D situated on the carbonyl group.

Noteworthy is the increase in time of the D content of the aldehyde over the clay-supported catalysts especially in the case of Pt/BenH. The lower acidity of this support led to slower side-product formation and consequently to a lower D content in butyraldehyde. It seems that in the initial period the dissociatively chemisorbed solvent located on the support near the metal surface will have a significant effect. As a result, near these more active metal sites situated not far from the metal-support interface, a high surface H/D ratio will be developed. This will determine the initial low D content of this product. However, after longer reaction times, poisoning of these sites will occur even in the case of this support, and the above described modifying-poisoning effect will be predominant. Actually, on this catalyst a relocation of the active sites on which the formation of butyraldehyde proceeds can be observed during the reaction.

Butyraldehyde having the lowest D content was formed in *tert*-butyl alcohol. This is understandable as a more bulky solvent will exert a stronger hindering effect on the adsorption of the poisoning substances. Using butyraldehyde as a substrate high exchange ratio was obtained, 10% d_1-aldehyde being recovered. Compared to the very low exchange ratio of the crotonaldehyde one can suppose that this molecule is more strongly adsorbed on the surface, i.e. anchored on Lewis acid sites of the support.

Table 5
Deuterium distribution in the formed crotyl alcohol[a]

Catalyst	Solvent	Reaction time (h)	Deuterium distribution (%)			$\sum id_i$[b]
			d_0	d_1	d_2	
Pt/C	2-Propanol	9	1	58	41	1.40
Pt/K-10	2-Propanol	1	1	57	42	1.41
		9	–	68	32	1.32
		0.5[c]	50	50[d]	–	0.50
	tert-Butyl alcohol	9	4	59	37	1.33
	Hexane	9	15	59	26	1.11
	d_4-Methanol[e]	1	52	46[f]	2	0.50
Pt/BenH	2-Propanol	1	19	65	16	0.97
		9	9	68	23	1.14

[a] Catalyst (50 mg) in 20 cm^3 solvent, crotonaldehyde initial concentration: 0.57 M, D_2 pressure 2 MPa.
[b] Average number of deuterium atoms per molecule.
[c] Crotyl alcohol was used as starting material.
[d] Distribution of D: **a** + (O–D) 98% (see Scheme 1).
[e] In this reaction, hydrogen was used.
[f] Distribution of D: **a** + (O–D) 90%, **b** + **c** 10% (see Scheme 1).

The D content of the crotyl alcohol showed that on clay-supported catalysts this product was formed on totally different active sites from those of Pt/C and different from those on which butyraldehyde is formed (Table 5). The average D content of crotyl alcohol formed over the clay-supported catalysts after 9 h reaction was lower than that formed over Pt/C. This may be explained by considering that the Lewis acid sites on the metal-support interface will act as anchoring sites of the substrate [14,15]. At the interface the H/D ratio will be different from that of the bulk of the metal. The interface sites are modified in a way that the surface H/D ratio will increase during the reaction. Initially, this will be imposed by the equilibrium of the H–D exchange of the alcohol used as solvent. During the reaction it will be modified due to the above mentioned self-poisoning of the metal. As was assumed this modification will proceed rather on the coordinatively more unsaturated metal atoms situated in the interface region. The strong adsorption of the modifying substances in this region will lead to an increase of the H/D ratio by multiple exchange. This may explain the decrease of the D content of crotyl alcohol during the reaction.

The nature of the clay was found to have a fundamental effect on the evolution in time of the D content. Over Pt/BenH this value displayed an opposite tendency from that observed on Pt/K-10. As

a result of the lower activity of the BenH in aldol dimerization, a high H/D ratio will be developed near the interface region by the exchange reaction between the surface –O–H and the D atoms chemisorbed on the metal. The –O–D groups formed can be further exchanged by the hydroxyl groups of the solvent. An evidence of this is the D content of the two primary products in the case of the hydrogenation in d_4-methanol. The crotyl alcohol formed during this hydrogenation was composed of 46% d_1-product. However, the slow poisoning of the surface in this region and the dissociation of the D_2 molecules will develop a H/D ratio on Pt/BenH similar to that existing on Pt/K-10.

Over Pt/K-10 in *tert*-butyl alcohol although the average D content was similar to that obtained in 2-propanol, the D distribution differed. The higher amounts of d_2-products obtained demonstrated the effect of the bulkiness of the solvent by hindering the adsorption of the modifying species.

The similar evolution in time of the D content of 1-butanol (Table 6) to that observed in the case of butyraldehyde showed that this product was formed mainly on the bulk platinum. However, part of this product could also be formed in the interface region and mainly at the beginning of the reactions, as the high D content of 1-butanol formed in d_4-methanol showed.

Table 6
Deuterium distribution in the formed 1-butanol[a]

Catalyst	Solvent	Reaction time (h)	Deuterium distribution (%)								$\sum i d_i$ [b]
			d_0	d_1	d_2	d_3	d_4	d_5	d_6	d_7	
Pt/C	2-Propanol	9	–	4	14	26	44	11	1	–	3.47
Pt/K-10	2-Propanol	1	–	–	8	27	49	16	tr.	–	3.73
		9	–	1	8	26	45	15	4	1	3.81
		16[c]	2	48	46	4	tr.	–	–	–	1.52
		0.5[d]	1	34	49	14	2	–	–	–	1.82
	tert-Butyl alcohol	9	–	2	13	33	35	17	tr.	–	3.52
	Hexane	9	–	–	2	11	52	21	9	5	4.39
	d_4-Methanol[e]	1	1	60	31	8	tr.	–	–	–	1.46
Pt/BenH	2-Propanol	1	1	14	34	30	19	2	–	–	2.58
		9	–	3	15	28	43	11	tr.	–	3.44

[a] Catalyst (50 mg) in 20 cm^3 solvent, crotonaldehyde initial concentration: 0.57 M, D_2 pressure 2 MPa.

[b] Average number of deuterium atoms per molecule.

[c] Butyraldehyde was used as starting material.

[d] Crotyl alcohol was used as starting material.

[e] In this reaction, hydrogen was used.

In the deuterated products, we could detect large amounts of d_5- and products having even higher D content. The amounts of these products were highest on the Pt/K-10. The average D content of the saturated product was much higher than the sum of the average D content of the two semi-saturated primary products. These results showed that 1-butanol was formed by a stronger adsorption of the substrate and not by further hydrogenation of the primary products. As the formation of this product proceeded on the same sites as that of butyraldehyde the interpretation of these results can be made in a similar manner. In *tert*-butyl alcohol the d_3- and d_4-products overwhelmed while in hexane the amounts of the d_5- and d_6-products were increased in such a degree that the average value past over four D per molecule which was a result of the weaker adsorption of hexane on the metal.

Finally in the by-products formed, the d_2-products were overwhelming in addition to significant amounts of monodeuterated ones. Only low amounts of three or higher number of D atom containing products were formed.

3.4. Mechanistic interpretations

According to these results it seems reasonable that on Pt/C both butyraldehyde and crotyl alcohol are formed on the same sites as the close deuterium con-

tent of these products showed. These are probably bare metal sites as was proposed by Yoshitake and Iwasawa in the hydrogenation of acrolein on LTR Pt/Nb$_2$O$_5$ catalyst [17]. A classical Horiuti-Polanyi mechanism will be in good compliance with these experimental data. The possible reaction route for the formation of the butyraldehyde is sketched in Scheme 2 by the sequence A-A2-AB-B. 1-Butanol is formed directly from adsorbed crotonaldehyde and not by the consecutive hydrogenation of one of the primary products. The η^4(C–C–C–O) intermediate (Scheme 2; AD2) gives the most probable explanation to the high D content of this product.

The experimental results obtained on clay-supported catalysts excluded the existence of the same reaction pathways. The D content and its distribution in the primary products are so different on the clay-supported catalysts, that these products must be formed on different active sites of different surface H/D ratios. The results confirmed the role of the Lewis acid centers from the metal-clay interface region which act as anchoring sites of the substrate molecule in the formation of crotyl alcohol. The reaction route of crotyl alcohol formation is illustrated in Scheme 2 by the sequence A-AA-A1-AC-C. Furthermore, this effect in the case of crotonaldehyde was complemented with a self-modifying-poisoning effect of the by-products formed during the reaction. As a result,
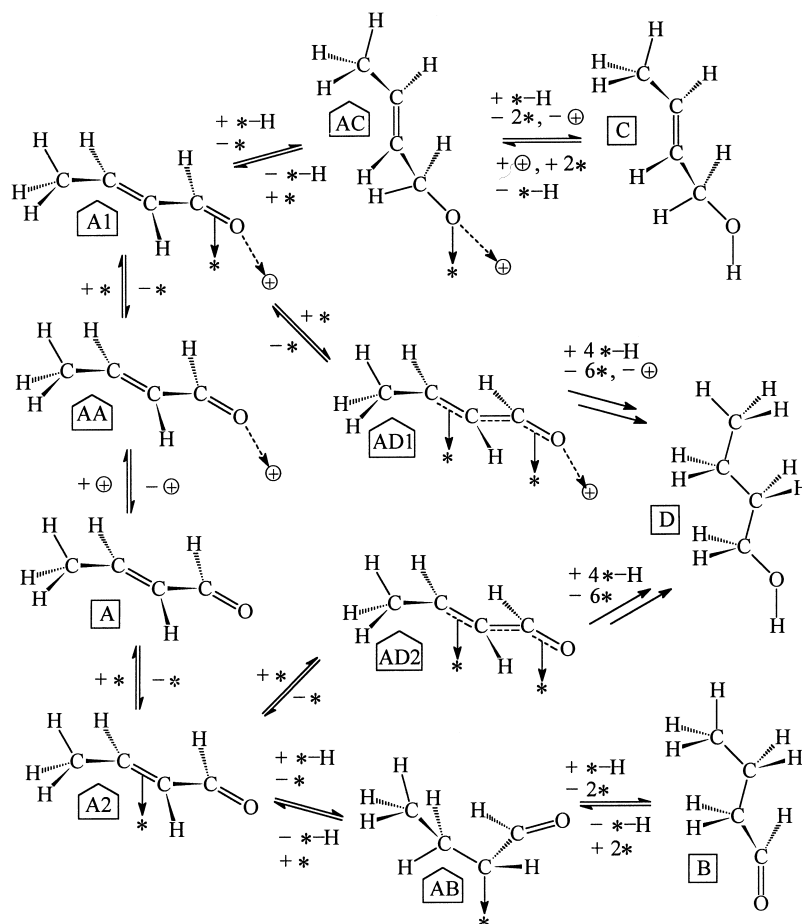
Scheme 2. Reaction pathways over clay-supported platinum catalysts.

the hydrogenation of the C=C group will be hindered on the more active coordinatively unsaturated metal atoms. The hydrogenation of this group will take place on the plain metal surface where the H/D ratio is different.

The two primary products will be formed on different sites: the butyraldehyde on sites of the bulk metal, while the crotyl alcohol on sites in the interface region. The poisoning effect can also hinder the simultaneous adsorption of the C=C group at the Pt-support interface. Consequently, no 1-butanol will be formed on these sites. Our data did not support a reaction pathway involving a 1,4-hydrogen transfer in an η^4-intermediate induced by the attack of surface H atoms on the β-C (see **a/c** exchange ratio)

described by Yoshitake and Iwasawa for the mechanism of crotyl alcohol formation on HTR Pt/Nb_2O_5 [17].

The Lewis acid sites at the interface can act in two different ways via a "through-metal" and a "through-space" effect. Neither of these effects can be excluded. Even if the metal particles of our catalysts are large enough and the direct interaction of the Lewis acid sites with the substrate may take place only at the interface region, the self-poisoning of the metal surface may lead to a catalyst on which the reaction at these interface sites will become predominant. However, the same result can be expected if we consider that these acid sites will increase the electron density of the platinum atoms close to the interface region.

4. Conclusions

Two clay-supported platinum catalysts were prepared and tested in the hydrogenation of crotonaldehyde. The metal particles were deposited on the outer surface of the clay sheets. These catalysts were proved to be efficient in increasing the crotyl alcohol selectivity in the hydrogenation of crotonaldehyde. A detailed study of this reaction showed that beside the nature of the clays the solvents used also had a significant effect. Increased selectivities were obtained only if alcohols were used as solvents. On the basis of the experimental results, a self poisoning-modifying effect of the metal surface was proposed. This effect combined with the anchoring role of the Lewis acid centers situated at the metal-support interface was presumed to be responsible for the increased selectivities obtained over these catalysts.

These interpretations were confirmed by measurements in which deuterium was used as tracer. It was demonstrated that the hydrogenation of the C=C group took place on metal atoms situated remote from the interface region. Using clays as support the more active coordinatively unsaturated sites of the metal particles were covered hindering the adsorption through the C=C group. We ascertained that the formation of crotyl alcohol took place on the sites close to the interface region with the coaction of the Lewis acid sites of the clays in the adsorption of the substrate.

Acknowledgements

References

[1] M. Bartók, Á. Molnár, in: S. Patai (Ed.), The Chemistry of Double-Bonded Functional Groups (Suppl. A3), Wiley, New York, 1997, Chapter 16, p. 843.

[2] B. Török, Á. Molnár, K. Borszéky, E. Tóth-Kádár, I. Bakonyi, Stud. Surf. Sci. Catal. 78 (1993) 179.

[3] G.V. Smith, F. Notheisz, Heterogeneous Catalysis in Organic Chemistry, Academic Press, New York, 1999.

[4] P. Gallezot, D. Richard, Catal. Rev.-Sci. Eng. 40 (1998) 81.

[5] Gy. Szöllösi, B. Török, G. Szakonyi, I. Kun, M. Bartók, Appl. Catal. A 172 (1998) 225.

[6] B. Török, Gy. Szöllösi, K. Balázsik, K. Felföldi, I. Kun, M. Bartók, Ultrasonics Sonochem. 6 (1999) 97.

[7] T.B.L.W. Marinelli, S. Nabuurs, V. Ponec, J. Catal. 151 (1995) 431.

[8] M. Englisch, A. Jentys, J.A. Lercher, J. Catal. 166 (1997) 25.

[9] C. Ando, H. Kurokawa, H. Miura, Appl. Catal. A 185 (1999) L181.

[10] A. Cornélis, P. Laszlo, Synthesis (1985) 909.

[11] M. Balogh, P. Laszlo, Organic Chemistry Using Clays, Springer, Berlin, Heidelberg, 1993.

[12] B. Török, Gy. Szöllösi, M. Rózsa-Tarjáni, M. Bartók, Mol. Cryst. Liq. Cryst. 311 (1998) 289.

[13] M. Bartók, Gy. Szöllösi, Á. Mastalir, I. Dékány, J. Mol. Catal. A 139 (1999) 227.

[14] Gy. Szöllösi, B. Török, L. Baranyi, M. Bartók, J. Catal. 179 (1998) 619.

[15] Gy. Szöllösi, I. Kun, B. Török, M. Bartók, Stud. Surf. Sci. Catal. 125 (1999) 539.

[16] H. Yoshitake, K. Asakura, Y. Iwasawa, J. Chem. Soc., Faraday Trans. 1 85 (1989) 2021.

[17] H. Yoshitake, Y. Iwasawa, J. Catal. 125 (1990) 227.

[18] R. Touroude, J. Catal. 65 (1980) 110.

[19] A. Chambers, S.D. Jackson, D. Stirling, G. Webb, J. Catal. 168 (1997) 301.

[20] F. Notheisz, M. Bartók, J. Catal. 71 (1981) 331.

[21] H. Budzikiewicz, C. Djerassi, A.E. Williams, Mass Spectrometry of Organic Compounds, Holden-Day, San Francisco, 1967.

[22] T. Cseri, S. Békássy, F. Figueras, E. Cseke, L.C. de Ménorval, R. Dutartre, Appl. Catal. A 132 (1995) 141.

[23] C. Cativiela, F. Figueras, J.M. Fraile, J.I. Garcia, J.A. Mayoral, L.C. de Ménorval, E. Pires, Appl. Catal. A 101 (1993) 253.

[24] C.N. Rhodes, D.R. Brown, Catal. Lett. 24 (1994) 285.

[25] A. Vaccari, Catal. Today 41 (1998) 53.