Regioselective hydrogenation of alkenes over Pt-loaded zeolite BEA

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The hydrogenation of dec-1-ene and of (E)-dec-5-ene has been studied over platinum/Na-BEA and non-zeolitic platinum catalysts. Provided that the solvent does not compete with the substrates for sorption in the zeolite, and that the external surface platinum is deactivated with a bulky phosphine, dec-1-ene is hydrogenated 18 times faster than (E)-dec-5-ene, whereas the ratio is only *ca.* 2 for platinum on non-microporous supports. This regioselectivity is explained by steric constraints imposed by the microporous structure of the zeolite. The hydrogenation rate over platinum/Na-BEA is much lower than that observed over the amorphous supported platinum catalysts; further, for the zeolite-based catalyst, approximately first-order kinetics are found compared with zero-order for the amorphous catalysts. Both effects can be explained in terms of alkene coverage of the Pt sites in the two types of catalyst.

Platinum-loaded zeolites are important catalysts in reactions like aromatization, hydrocracking and hydroisomerization. Little attention, however, has been paid to the use of these catalysts in selective hydrogenation reactions. The encapsulation of noble-metal clusters in the micropores of a zeolite combines the possibility of shape selectivity with a hydrogenation function. This was first demonstrated by Huang and Schwartz who showed that rhodium complexes, encapsulated in Linde 13X zeolite, show improved selectivity towards the hydrogenation of smaller alkenes.¹ Similar results were obtained by Yamaguchi *et al.* with a rhodium/Na-Y catalyst.²

Corbin *et al.* found preferential hydrogenation of cyclopentene in competition with 4-methylcyclohexene over various (medium-pore) rhodium-containing zeolites.³ This was attributed to the different molecular dimensions of the substrates. The observed selectivities depended on the water content and could thus easily be tuned. Selective poisoning, using bulky phosphines, of the metal clusters located on the external surface was found to be essential to obtain high selectivities. Dessau prepared platinum clusters in the channels of ZSM-5.⁴ This catalyst showed preferential hydrogenation of the less branched alkene in competitive hydrogenation experiments. Again, improved selectivity was found upon poisoning of the outer-surface clusters with a bulky phosphine.

In addition to shape-selective alkene hydrogenation, zeoliteencapsulated noble-metal clusters have potential as catalysts in regioselective hydrogenation reactions. This type of reaction is important in the synthesis of various fine chemicals, especially in the fragrance and flavour industry. Regioselectivity is thought to occur as a result of geometric constraints imposed on the reactant by the zeolite structure. However, a single example appears to be known. Gallezot and co-workers showed that cinnamaldehyde can be reduced to cinnamyl alcohol with high selectivity over platinum clusters in zeolite Y (FAU) and Beta (BEA).^{5,6} These authors found the selectivity to be maximized with clusters larger than the supercage or channel intersections but still located in the zeolite matrix. The best results were obtained over clusters with a diameter of *ca.* 50 Å.

In this paper we will show that the monitoring of substrate selectivity in the hydrogenation of dec-1-ene and (E)-dec-5-ene is a suitable tool for understanding the factors that determine whether the platinum-loaded zeolite BEA can be used as a regioselective hydrogenation catalyst. It is expected that in platinum/Na-BEA, the adsorption of (E)-dec-5-ene on a platinum cluster will be sterically much more hindered than the

adsorption of dec-1-ene. The difference in hydrogenation rate will be used as a measure of regioselectivity. Also the observed reaction kinetics will be discussed.

Experimental

Synthesis of platinum/Na-BEA and Na-BEA (Si : Al = 11)

Zeolite BEA with an Si: Al ratio of 11 was synthesized according to Wadlinger and Kerr.⁷ Calcination of the assynthesized material was performed in air at 500 °C for 24 h (heating rate 1 °C min⁻¹). Platinum/H-BEA(11) was made as described previously.⁸ The acid sites of this catalyst were neutralized by three successive ion exchanges with 1 mol l^{-1} aqueous sodium nitrate (50 ml g⁻¹) at room temperature. By adding a few drops of 0.1 mol l^{-1} aqueous sodium hydroxide the pH was set at *ca.* 7. The obtained platinum/Na-BEA(11) catalyst was filtered, washed extensively with demineralized water, and finally dried at 120 °C for 16 h.

Zeolite Na-BEA(11) was made by three successive ion exchanges of the calcined zeolite with 1 mol 1^{-1} aqueous sodium nitrate (50 ml g⁻¹) at room temperature. The pH was set at *ca*. 7 as described above. The isolation of the sodium-exchanged zeolite was also carried out in a similar manner.

Characterization of the zeolite-based catalysts

The metal content and the exchange stoichiometry of the zeolite-based catalysts were determined by inductive-coupled-plasma atomic emission spectroscopy (ICP-AES) and atomic absorption spectrometry (AAS). The platinum content in platinum/Na-BEA(11) was 1.6 ± 0.1 wt.%. The Na : Al ratio of Na-BEA(11) and platinum/Na-BEA(11) was 1.0 ± 0.05 for both samples.

X-Ray powder diffraction (XRD) was performed on the zeolite-based catalysts to check the crystallinity after all preparation procedures. The powder patterns were recorded on a Philips PW 1877 diffractometer using Cu-K α radiation. No platinum lines were observed in the platinum-loaded zeolite indicating that either the clusters are too small for detection (<25 Å)⁹ or that the number of clusters which are above the detection limit is too low.

Scanning electron microscopy (SEM) analyses, obtained with a JEOL JSM-35 scanning electron microscope, of the assynthesized BEA(11) showed that the material consists of aggregates of spherical primary crystallites with a diameter of $ca. 0.5 \mu m$. Platinum/H-BEA(11) was extensively characterized by transmission electron microscopy (TEM) in combination with energy dispersive X-ray (EDX) analyses.⁸ It was found that the platinum clusters are uniformly distributed throughout the zeolite matrix and that all clusters have approximately the same diameter, 12 Å. With the aid of a test reaction, using a bulky alkene substrate, it was determined that *ca.* 5.6% of the platinum is exposed on the external and mesoporous surface.⁸

Origin of the other platinum catalysts

Europt-1, a well characterized platinum-on-silica catalyst made by Johnson Matthey,^{10,11} was kindly donated by Professor J. H. C. van Hooff of the Eindhoven University of Technology. The catalyst has a platinum loading of 6.3 wt.% and a mean dispersion of 0.6.

Platinum (5 wt.%) on γ -alumina (powder) was obtained from Janssen Chimica, Belgium. The platinum dispersion was 0.3, as determined independently by CO adsorption¹² and TEM.¹³

Adsorption experiments

Competitive adsorption experiments were performed at room temperature in a glass apparatus similar to that described by Choudary et al.14 Approximately 1 g of Na-BEA was activated in a sample tube, connected with the sorption chamber, at 350 °C for 2 h in vacuo (heating rate 1 °C min⁻¹). After cooling to room temperature the zeolite was introduced into the sorption chamber, and the vacuum line was closed. At t = 0, 1.5mmol (210 mg) alkene [dec-1-ene or (E)-dec-5-ene] together with 1.5 mmol (213 mg) decane and a known amount of bulky internal standard [ca. 60 mg, 1,3,5-tri(tert-butyl)benzene], dissolved in 10 g dry 1,3,5-tri(isopropyl)benzene (bulky solvent, incapable of entering the zeolite pores, at the temperature applied) were introduced rapidly into the sorption chamber. At the same time the vacuum was released and stirring was started. At regular time intervals, samples were withdrawn from the reaction mixture and analysed by gas chromatography (GC) on a Chrompack CP Sil 5 CB wide-bore column.

Counter diffusion experiments were performed in a similar manner. In this case, however, at t = 0 only decane (1.5 mmol, 213 mg) together with internal standard dissolved in 9 g bulky solvent was introduced. After the adsorption equilibrium was reached, at t = 15 min, 1.5 mmol (210 mg) alkene [dec-1-ene or (*E*)-dec-5-ene], dissolved in 1 g bulky solvent, was added to the mixture.

Hydrogenation reactions

Hydrogenation reactions were carried out either at 0°C [in ethyl acetate as the solvent (EtOAc)] or at room temperature [1,3,5-tri(isopropyl)benzene and heptane] under atmospheric pressure in a 50 ml reaction vessel equipped with a magnetic stirrer, a sample tube and a gas burette. A known amount of catalyst, between 5 and 50 mg, and 19 g freshly distilled solvent, dried over zeolite KA, were introduced into the reactor. The zeolite-based catalyst was dried in the sample tube connected with the reaction vessel and subsequently heated in vacuo to 350 °C for 2 h (heating rate 1 °C min⁻¹). After cooling to room temperature the catalyst was introduced into the reactor, the vacuum was released and dry solvent was added. The entire unit was first flushed several times with nitrogen and then with hydrogen. Finally, the gas burette was filled with hydrogen and the catalyst was prereduced for 0.5-1 h. The reaction was started by the introduction of 1 mmol (140 mg) alkene dissolved in 1 g solvent, which was injected through a septum. At regular time intervals the hydrogen consumption was monitored and samples

were withdrawn from the reaction mixture and analysed by GC. A Chrompack CP Sil 5 CB column was used.

Experiments were also performed employing catalysts, surface poisoned by triphenylphosphine. This was introduced into the reactor together with the catalyst and solvent. An amount of phosphine equal to the amount of catalyst (w/w) was used.

Results and Discussion

Adsorption experiments

The results of the competitive adsorption experiments with decane-dec-1-ene and decane-(*E*)-dec-5-ene, from 1,3,5-tri-(isopropyl)benzene as non-adsorbing solvent, are shown in Fig. 1 and 2, respectively. Equilibrium is reached at 25 °C within 5 min in both cases. For the adsorption of alkanes the dispersive and repulsive interactions are the major contributors to the sorption enthalpy,¹⁵ while the observed preference for the adsorption of the alkenes is due to their electrostatic and charge-transfer interaction, mainly with the sodium ions contained in the zeolite.¹⁶ It is known from infrared studies, that cations can act as adsorption centres for alkenes.¹⁷ Furthermore, the alkene concentration in the zeolite is about 25% higher in the case of dec-1-ene, which has a dipole, than with (*E*)-dec-5-ene, for which the most stable conformation is highly symmetrical.

A competitive adsorption experiment with dec-1-ene-EtOAc showed a strong preferential adsorption of EtOAc in Na-BEA. Here again the polarity of the molecule seems to play a decisive role. It should be noted that the dipole



Fig. 1 Competitive adsorption of dec-1-ene (\bigcirc) and decane (\bigcirc) in zeolite Na-BEA at 25 °C (mg g⁻¹). Initially: 210 mg dec-1-ene, 213 mg decane, 10 g 1,3,5-tri(isopropyl)benzene and 1 g Na-BEA.



Fig. 2 Competitive adsorption of (E)-dec-5-ene (\bigcirc) and decane (\bigcirc) in zeolite Na-BEA at 25 °C (mg g⁻¹). Initially: 210 mg (E)-dec-5-ene, 213 mg decane, 10 g 1,3,5-tri(isopropyl)benzene and 1 g Na-BEA.

moment of EtOAc is 1.78 D^{\dagger} (ref. 18) while that of dec-1-ene in its most stable conformation (all-*trans*) is only 0.59 D (molecular-mechanics calculation). Similarly, the presence of water, with a dipole moment of 1.854 D,¹⁸ reduced the maximum adsorption of dec-1-ene significantly.

The results of counter diffusion experiments are shown in Fig. 3 and 4. It can be seen from these figures that both alkenes are able to displace decane rapidly, the system returning to its equilibrium situation within a few minutes (cf. Fig. 1 and 2).

Hydrogenation reactions in EtOAc

The hydrogenation of dec-1-ene and (*E*)-dec-5-ene over various platinum catalysts, performed in EtOAc, showed zeroorder kinetics in reactant concentration up to conversions exceeding 80%. This type of kinetics is often observed in hydrogenation reactions,¹⁹ and facilitates the determination of initial rates of hydrogenation. The results are presented in Table 1. Very little difference is observed in the ratio of initial hydrogenation rates of dec-1-ene and (*E*)-dec-5-ene ($R_{1/5}$) for the different platinum catalysts, including platinum/Na-BEA. This observation suggests that the reaction occurs on platinum clusters located on the external surface only. This is supported by a poisoning experiment: addition of triphenylphosphine, which is far too bulky to enter the micropores of BEA, resulted in a complete deactivation of the catalyst. Small polar molecules, like acetone and allyl alcohol,



Fig. 3 Counter diffusion of decane (----) after addition of dec-1ene (---) from zeolite Na-BEA at 25 °C (mg g⁻¹). Initially: 213 mg decane, 9 g 1,3,5-tri(isopropyl)benzene and 1.0 g Na-BEA; at t = 15min, 210 mg dec-1-ene in 1 g 1,3,5-tri(isopropyl)benzene was added.



Fig. 4 Counter diffusion of decane (------) after addition of (*E*)-dec-5-ene (- - - -) from zeolite Na-BEA at 25 °C (mg g⁻¹). Initially: 213 mg decane, 9 g 1,3,5-tri(isopropyl)benzene and 1.0 g Na-BEA; at t = 15 min 210 mg (E)-dec-5-ene in 1 g 1,3,5-tri(isopropyl)benzene was added.

 $+ 1 D \approx 3.335 64 \times 10^{-30} C m.$

Table 1 Hydrogenation of dec-1-ene and (*E*)-dec-5-ene over various platinum-containing catalysts, performed in EtOAc at $0 \,^{\circ}\text{C}$

catalyst	Pt (wt.%)	r _{dec-1-ene} a	r _{(E)-dec-5-ene} a	R _{1/5} ^b
EuroPt-1	6.3	5.56	1.71	3.3
Pt/Al ₂ O ₃	5.0	1.51	0.29	5.2
Pt/Na-BEA	1.6	1.06	0.19	5.6
$Pt/Na-BEA + PPh_3$	1.6	0	0	

^a $r = \text{Initial rate (mol h⁻¹ g_{Pt}⁻¹). ^b <math>r_{\text{dec-1-ene}}/r_{(E)-\text{dec-5-ene}}$.

however, could still be hydrogenated over the clusters inside the zeolite matrix with a high rate. A competitive adsorption experiment with dec-1-ene–EtOAc (see above) confirmed that the solvent (EtOAc), which is present in excess and which is preferentially adsorbed, prevents the alkenes from attaining a detectable concentration inside. This is no longer the case when either a non-polar solvent or a solvent which is too bulky to enter the zeolite is employed, as described below.

Hydrogenation reactions in heptane and 1,3,5-tri(isopropyl)benzene

When the hydrogenations of dec-1-ene and of (E)-dec-5-ene are performed in heptane, zero-order kinetics in reactant concentration are again observed up to conversions exceeding 80% for all platinum-containing catalysts, including platinum/Na-BEA. Only very small differences in $R_{1/5}$ are observed between the amorphous supported platinum catalysts and platinum/Na-BEA (Table 2). It is therefore suspected that again the selectivity is dominated by platinum clusters located on the external surface of the zeolite. Poisoning of these clusters resulted in a catalyst which showed a completely different behaviour. A transition in dec-1-ene concentration from zero-order kinetics to approximately first-order kinetics is observed, and the activity of the catalyst was found to be much lower (Fig. 5). Comparable results were obtained by Yamaguchi *et al.* for the hydrogenation of cyclohexene over

Table 2 Hydrogenation of dec-1-ene and (*E*)-dec-5-ene over various platinum-containing catalysts, performed in heptane at $25 \,^{\circ}\text{C}$

catalyst	Pt (wt.%)	r _{dec-1-ene} a	r _{(E)-dec-5-ene} a	$R_{1/5}^{b}$
EuroPt-1	6.3	18.3	11.9	1.5
Pt/Al ₂ O ₃	5.0	11.2	9.5	1.2
Pt/Na-BEA	1.6	4.02	1.64	2.5
$Pt/Na-BEA + PPh_3$	1.6	0.34 ^c	0.02^{c}	17

^{*a*} Initial rate (mol h^{-1} g_{Pt}^{-1}). ^{*b*} $r_{dec-1-ene}/r_{(E)-dec-5-ene}$. ^{*c*} Assuming first-order kinetics in reactant concentration.



Fig. 5 Hydrogenation of dec-1-ene (\Box, \bigcirc) and (E)-dec-5-ene (\blacksquare, \bullet) over outer-surface-poisoned platinum/Na-BEA performed in 1,3,5-tri-(isopropyl)benzene (square symbols) and heptane (round symbols) at 25 °C and 1 atm hydrogen

Rh/NaY under similar reaction conditions.² Furthermore, (*E*)-dec-5-ene was hydrogenated even more slowly, which resulted in an increase of $R_{1/5}$ to 17.

As it had been determined that ca. 6% of the exposed platinum is located on the external surface, comparison of the initial rates of hydrogenation of dec-1-ene over platinum/Na-BEA with and without outer-surface poisoning gives the difference in the apparent hydrogenation rate. It was calculated that the hydrogenation activity of the clusters located on the surface is ca. 180 times higher than the activity of the zeoliteencapsulated platinum clusters, which emphasizes the need for outer-surface poisoning if selectivity is to be achieved in these reactions.

The results of the hydrogenation experiments in the bulky solvent 1,3,5-tri(isopropyl)benzene, which is unable to enter the micropores of the zeolite, are presented in Table 3. Again, zero-order behaviour in alkene concentration was observed for the amorphous platinum-containing catalysts, and only small differences in $R_{1/5}$ were found. Hydrogenation of dec-1ene and (E)-dec-5-ene over surface-poisoned platinum/Na-BEA gave an $R_{1/5}$ of 18, which is comparable with the result obtained in heptane. Here a transition from zero- to approximately first-order behaviour in alkene concentration was observed (Fig. 5). The absolute initial rates, however, are almost twice as high. This is explained by a higher alkene concentration in the zeolite which, in contrast to the experiments performed in heptane, does not have to compete for adsorption with the solvent.

As all experiments were performed under mild conditions we exclude in our discussion the possibility of the formation of carbonaceous residues on the noble-metal surface, as recently discussed by Webb.²⁰

In heterogeneously catalysed liquid-phase hydrogenation reactions of alkenes the reaction rate may be appropriately treated, using Langmuir-Hinshelwood kinetics.²⁰ At constant hydrogen pressure, eqn. (1) is used, in which r'_{alkene} and k'_{alkene} are the reaction rate and the pseudo-reaction-rate constant per weight amount of catalyst, respectively:

$$r'_{alkene} = -\frac{\partial [alkene]}{\partial t} = k'_{alkene} \Theta_{alkene}$$
(1)

The fraction of catalyst covered with alkene, Θ_{alkene} , can be described by the Langmuir adsorption isotherm. If there is no competition for adsorption on the metal surface between the reactant, the product and the solvent, eqn. (2) is used in which K_{alkene} is the adsorption constant.

$$\Theta_{alkene} = \frac{K_{alkene}[alkene]}{1 + K_{alkene}[alkene]}$$
(2)

Upon combination of eqn. (1) and (2), the Langmuir rate eqn. (3) is obtained.

$$r'_{\text{alkene}} = k'_{\text{alkene}} \frac{K_{\text{alkene}}[\text{alkene}]}{1 + K_{\text{alkene}}[\text{alkene}]}$$
(3)

As long as almost all active sites are covered with alkene $(\Theta \approx 1)$ a constant reaction rate is expected. This was indeed found for all amorphous supported platinum catalysts, and for

Table 3 Hydrogenation of dec-1-ene and (E)-dec-5-ene over variousplatinum-containingcatalysts,performedin1,3,5-tri(isopropyl)benzene at 25 °C

catalyst	Pt (wt.%)	r _{dec-1-ene} a	$r_{(E)-\text{dec-}5-\text{ene}}^a$	R _{1/5} ^b
EuroPt-1	6.3	9.07	4.10	2.2
Pt/Al ₂ O ₃	5.0	8.04	2.76	2.9
$Pt/Na-BEA + PPh_3$	1.6	0.72 ^c	0.04 ^c	18

^{*a*} Initial rate (mol $h^{-1} g_{Pl}^{-1}$). ^{*b*} $r_{dec-1-ene}/r_{(E)-dec-5-ene}$. ^{*c*} Assuming first-order kinetics in reactant concentration.

those hydrogenations that occurred over surface located platinum clusters. Transition from this type of kinetics implies that a complete coverage of all active sites is no longer maintained. The latter situation was found for the hydrogenation reactions that were performed with dec-1-ene and (E)-dec-5-ene over platinum clusters located in the zeolite matrix. For this concentration-dependant hydrogenation rate, three possible explanations have been considered.

The first is that the alkene concentration in the zeolite might be much lower than in the bulk solvent. For small alkene concentrations the Langmuir isotherm can be simplified to $\Theta \approx K_{alkene}$ [alkene], which results in first-order reaction kinetics. The observation that transition from zero-order behaviour starts at conversions exceeding 80% indicates that a concentration difference of a factor of *ca*. 5 is necessary for obtaining a transition from zero-order kinetics. For firstorder-like behaviour, even lower alkene concentrations are required. However, as adsorption experiments reveal that the alkenes are preferentially adsorbed, this situation is not very likely. Furthermore, when the reaction is performed in the bulky solvent 1,3,5-tri(isopropyl)benzene, the zeolite catalyst is expected to be essentially fully filled with alkene

Another explanation could be the existence of diffusion limitations. The outcome of the counter diffusion experiments, however, does not support this possibility. In case of diffusional limitations the observed reaction order changes from n to (n + 1)/2² Here it would mean that the reaction order would change from zero to 0.5. However, it did not prove possible to fit the data satisfactorily assuming a half-order dependence in alkene concentration. The Wheeler-Weisz modulus (Φ), a criterion for the existence of diffusion limitations, was estimated. For the observed reaction rate the initial hydrogenation rate of dec-1-ene, performed in 1,3,5-tri(isopropyl)benzene, was used. As no effective diffusivity (D_{eff}) of dec-1-ene in Na-BEA is reported in the literature, the self-diffusivity (D_s) of decane in excess liquid phase and 50 °C in NaX, divided by ten was used $(5 \times 10^{-13} \text{ m}^2 \text{ s}^{-1})^{23}$ The latter adjustment is a correction for the difference in D_s between decane and dec-1-ene; it is known from the literature¹⁶ that the D_s for alkanes in NaX is one order of magnitude larger than that for alkenes. As a Φ value of 10^{-3} , far below the threshold value of one, was obtained, diffusional limitations can be excluded.

In a third approach the coverage of Pt sites by reactant alkene molecules is considered. To understand the 'molar' ratio alkene : active site during the actual reaction some calculations were carried out concerning the amorphous supported platinum catalysts. As the metal loading and dispersion are reasonably well known, the number of potential adsorption sites can be calculated. The adsorption site (Pt site) was defined as two adjacent surface platinum atoms, the number required for a di- σ Pt-alkene complex. For both catalysts the ratio alkene : Pt site was approximately 2500. Transition from zero-order kinetics was only observed at conversions exceeding 80%, i.e. at alkene: Pt site ratios below 500. For the zeolite-based catalyst a similar calculation can be made. However, it should be noted that the alkene does not have adsorptive interaction with the platinum cluster and the zeolite wall only, but also with the sodium ions as illustrated by the preferential adsorption on Na-BEA. For platinum/Na-BEA with Si : AI = 11 and 1.6 wt.% platinum it can be calculated that the atomic ratio Na^+ : Pt is ca. 15. If we assume that a platinum cluster, located in the micropores of BEA, with a diameter of ca. 12 Å contains 55 atoms, while this cluster when located at a channel intersection has a maximum of four adsorption sites (Pt site), then the ratio Na⁺ : Pt site is over 200. Furthermore, the total number of Na⁺ and Pt sites was calculated to be 1200 and 6 μ mol g⁻¹ zeolite, respectively.

The maximum adsorption of dec-1-ene in BEA can be calculated by assuming that the alkene molecules prefer an alltrans conformation and that these molecules are linearly positioned in the straight channels. An approximately linear orientation of dec-1-ene in the straight channels of BEA is expected to result in an optimum interaction with the zeolite wall and the cations. In a simple model, the total pore volume of BEA, 0.26 ml g⁻¹ as determined from cyclohexane adsorption,²⁴ can be represented by a cylinder with a diameter of 7 Å [(6.4 + 7.6)/2]. The length of this cylinder was calculated to be 7×10^{11} m g⁻¹. The length of a decane molecule in all-*trans* conformation is approximately 15 Å, which means that the maximum adsorption capacity is 0.8 mmol g⁻¹ or 110 mg g⁻¹. This value is in excellent agreement with the results of our adsorption experiments.

The calculations presented above show that when the platinum/Na-BEA catalyst is completely filled with alkene, which is actually very unlikely, the ratio alkene : Pt site is only 135 (0.8 mmol : 6 µmol). This value is already much lower than the ratio calculated for the amorphous catalysts at conversions over 80%, which resulted in a concentration-dependent reaction rate. Furthermore, if we take into account the competitive adsorption on non-active Na⁺ sites, for which concentration in the zeolite was calculated to be 200 times as high as the concentration of platinum sites, it can easily be understood that only a fraction of the active platinum sites will be covered with alkene during reaction ($\Theta_{alkene} \ll 1$).

Although the arguments given above explain sufficiently the much lower initial reaction rate observed for platinum/Na-BEA, they are not sufficient to explain the observed approximately-first-order rate dependence. As long as the alkene concentration in the zeolite is constant, a low but constant reaction rate is expected. For first-order kinetics to be observed it is necessary for the alkene concentration in the zeolite to change linearly with the alkene concentration in the liquid. As the adsorption of reactants in a zeolite can also be described by a Langmuir isotherm [eqn. (2)], this linear dependence will only occur at low values for $K_{\text{alkene}}[\text{alkene}]_{\text{liquid}}$ (where K is the adsorption constant zeolite/liquid). Obviously, at the reactant concentration employed (0.05 mol 1^{-1}) this is indeed the case and thus both the reduced initial rates and the transition from zero- to firstorder kinetics are satisfactorily explained in terms of the alkene coverage of the Pt sites in the internal BEA structure.

Origin of regioselectivity

The observed preferential hydrogenation of the terminal double bond can only for a small part be ascribed to differences in the alkene concentration in the zeolite. The competitive adsorption experiments show that the difference is only about 25% (see above). A more convenient explanation might be related to the number of platinum sites that are available for the adsorption of dec-1-ene and (E)-dec-5-ene, respectively.

The tetrahedral framework structure of BEA is disordered along [001].²⁵ Three polytypes can be recognized which are related to the disordered structure by displacements on [001]planes. All three polytypes possess two mutually perpendicular 12-ring channel systems which are both perpendicular to [001]. These channels are linear and have a diameter of 7.6 × 6.4 Å. The third non-linear channel system is parallel to [001] and has channels with a diameter of 5.5 × 5.5 Å.²⁶

Unlike zeolites such as A and FAU, zeolite BEA does not possess cages. It is well documented that in FAU small noblemetal clusters can be stabilised in the supercage.²⁷ This supercage provides a highly symmetric surround for the cluster, which can only be reached through four identical cage windows. As a consequence, four identical adsorption sites can be defined. For noble-metal clusters in zeolite BEA the situation is more complicated. The largest internal space in BEA is the intersection of two linear channels which has an approximately cylindrical shape with a diameter of approximately 12.5 Å along the [001] direction. This means that for the accommodation of a spherical platinum cluster with a diameter of 12 Å (or larger), the local crystal structure has to be partially destroyed. This effect has indeed been reported for many noble-metal-loaded zeolites.^{5,6,28} Although the location of the platinum clusters in the intersections of the straight channels is plausible, it cannot be excluded that, during the reduction of the platinum ions, platinum clusters are also formed at other positions in the channel system. These may grow to exceed the channel dimensions and also lead to local destruction of the zeolite structure. Clusters with different local environments may thus be formed, leading to many different adsorption sites on the clusters and differences in accessibility. Two possible positions will be discussed.

In Fig. 6 the [100] and [010] projections of the A polymorph of BEA with a platinum cluster of *ca.* 12 Å, located in the intersection of two straight channels, are presented. Several channels give access to possible adsorption sites, designated by 1, 2 and 3 in the [100] and 4, 5 and 6 in the [010] projection. As mentioned earlier, the critical diameter of an alkane is about 4.9 Å, which is 2/3 of the largest diameter of the elliptical straight channels. For both dec-1-ene and (*E*)dec-5-ene a similar critical diameter can be assumed. This



Fig. 6 Zeolite BEA with a platinum cluster of 12 Å located at the intersection of two straight channels. Left [100] projection, right [010] projection.



Fig. 7 Zeolite BEA with a platinum cluster of 12 Å located in the centre of a straight channel. Left [100] projection, right [010] projection.

means that it is impossible to accommodate two alkene molecules next to each other in a straight channel. A consequence of this is that it is impossible for (*E*)-dec-5-ene to adsorb on the platinum cluster at sites 1 or 4, because of the need to accommodate two butyl chains. The adsorption of dec-1-ene, however, can easily occur at these sites as this molecule is not subject to steric hindrance. No differences in sterical hindrance are expected for the adsorption of dec-1-ene and (*E*)dec-5-ene on the clusters at the essentially identical sites 2 and 5 or 3 and 6.

In Fig. 7 the [100] and [010] projections of the A polymorph of BEA with the same platinum cluster, positioned in the centre of a straight channel, are presented. In the direction perpendicular to the [100] projection only one channel gives entrance to an adsorption site at the cluster, designated as site 1. For the same reasons as discussed above, the corresponding adsorption site on the platinum cluster is not accessible for the internal double bond in (E)-dec-5-ene. It is, however, accessible for adsorption of the terminal double bond in dec-1-ene. A different situation occurs when the same cluster is viewed along the [010] projection, three different adsorption sites can be recognised, designated as 2, 3 and 4. It is clear that, for steric reasons, (E)-dec-5-ene is unable to adsorb on site 2. However, for adsorption on sites 3 and 4 the situation is more complicated. It can be seen from the figure that (E)-dec-5-ene should first pass the platinum cluster, which partially blocks the zeolite channel with one butyl chain, before it can adsorb with the double bond. This will only occur if the space between the channel wall and the cluster is large enough (ca. 4.9 Å). Site 3, however, is expected to be accessible for the adsorption of both alkenes. This discussion also illustrates how very small differences in cluster size can determine whether a platinum site is active or inactive in the hydrogenation of (E)-dec-5-ene.

It should be emphasized that these steric hindrance considerations are related to both the specific position and the size of the platinum cluster. We have discussed only two possible cluster positions but presumably many other, slightly different locations are possible. However, independent of the specific position of the clusters, more platinum sites will always be available for the adsorption of dec-1-ene than for (E)-dec-5-ene.

Conclusion

The platinum/Na-BEA system shows a high dec-1-ene : (E)dec-5-ene hydrogenation-rate ratio, provided that the outer

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surface platinum is properly poisoned, and that the solvent does not compete strongly with the reactant for adsorption in the zeolite. This regioselectivity is explained by an analysis of the possible approaches of the two alkenes to the Pt surface within the BEA channel system. Compared with platinum/Na-BEA, platinum on an amorphous meso/macroporous support exhibits a higher activity in the catalytic hydrogenation of dec-1-ene and (E)-dec-5-ene but a much lower regioselectivity. The hydrogenation over platinum/Na-BEA deviates from zero-order kinetics which can be understood in terms of less efficient alkene adsorption in the zeolite microdomains.

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