

Review

Shape-selective hydrogenation and hydrogen transfer reactions over zeolite catalysts¹

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Abstract

A review of the application of zeolite systems in shape-selective hydrogenation and hydrogen transfer reactions is presented. Two different types of catalytic systems are discussed. The first consists of metal clusters or coordination complexes encapsulated in the micropores of a zeolite employing hydrogen as the reductant. Recent developments, such as the application of zeolite-containing composite catalysts are included. In the second system, zeolites are applied as catalyst in hydrogen-transfer reactions using a secondary alcohol as hydrogen donor in the Meerwein–Ponndorf–Verley reduction. © 1998 Elsevier Science B.V. All rights reserved.

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1. Introduction

Employing a zeolite as carrier for a noble metal enables the shape-selective properties of the microporous structure to be conferred on the hydrogenation function. In this way, highly selective hydrogenation catalysts can be prepared, many examples of which have been described. As far as we know, however, none of these systems are operated on an industrial scale.

The use of metal-loaded zeolites in shape-selective hydrogenations is of course limited to

molecules which are small enough to enter the zeolite pores. Because of their adsorption properties, zeolites with a hydrogenation function will not be the catalysts of choice when selectivity to an intermediate product is required. However, for other types of selective hydrogenation, the combination noble metal/zeolite is expected to be beneficial.

In competitive hydrogenation reactions, noble metal containing zeolites are recognised as useful catalysts. As a result of reactant shape selectivity, only those molecules which are small enough to reach the catalytic site are expected to be converted. Furthermore, when the sizes of the competing molecules are in the same range as the pore-size of the zeolite, mass-transport selectivity can occur which is a result of differences in the diffusivities of the competing reac-

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¹ Dedicated to Professor Herman van Bekkum on the occasion of his 65th birthday.

tants. It should be kept in mind, however, that the competing molecules can influence each other's transport.

In parallel hydrogenation reactions, chemo-, regio- and stereoselectivity may all be achieved with zeolite-based catalysts. Reactants having molecular dimensions close to those of the zeolite pores are expected to approach the metal cluster 'end-on'. Thus, in the case of α,β -unsaturated aldehydes, this is expected to result in chemoselective hydrogenation to the unsaturated alcohol. Similarly, terminal olefins are expected to be converted more easily than internal double bonds (regioselectivity).

Stereoselectivity may occur as a result of the confined space in which the reactions are constrained to proceed. In the hydrogenation of substituted cyclohexanones, for example, the side from which hydrogen is being transferred (axial or equatorial attack) determines whether the *cis*- or *trans*-alcohol is formed [1]. When the space around the reactant is limited, adsorption of the carbonyl on the metal cluster will occur from the most favourable side, thereby minimizing steric repulsion. Thus, because of steric constraints, stereoselectivity is expected. In fact, this example is closely related to restricted transition-state selectivity.

Some zeolites, such as ETS-10 [2] and beta (BEA) [3–6], can theoretically be synthesised in homochiral forms; however, this has not yet been achieved [7]. Encapsulation of metal clusters in the homochiral forms could yield a catalyst which is potentially capable of asymmetric hydrogenation. An alternative technique, the modification of the interior of a zeolite with a chiral reagent can induce a chiral environment with potential for enantioselective hydrogenations, as recently reported [8,9].

This article presents an overview of shape-selective hydrogenations using metal-loaded zeolites. The examples illustrate both the potential and limitations of these catalytic systems. The review includes the recent application of zeolites as new recyclable solid catalysts for the Meerwein–Ponndorf–Verley (MPV) reduction

of carbonyl compounds. The activity of these catalysts is related to their Lewis acid and/or basic properties. Some remarkable examples of shape-selective conversions resulting in high stereoselectivities have recently been reported.

2. Shape-selective hydrogenation of olefins and arenes over zeolite-encapsulated metal clusters

2.1. Gas phase 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 in 1960 by Weisz and Frilette [10] and Frilette et al. [11] of the Mobil Oil. A shape-selective catalyst was made by the incorporation of platinum in zeolite LTA. In a mixture of equal volumes of 1-butene, isobutene and hydrogen, at 25°C with a contact time of ca. 0.1 s, only the 1-butene was converted to butane, while approximately equal quantities of both olefins were converted over a platinum on alumina reference catalyst. Full experimental details on both the catalyst preparation and the catalytic reaction were published in 1962 [12]. As none of the available cationic or anionic platinum species can enter the 4.5 Å cage windows, an aqueous solution of platinum(II) tetra-amine chloride was added directly to the zeolite synthesis mixture and co-crystallised. Removal of extra crystalline platinum complex by repeated ion-exchange with aqueous calcium chloride was essential for the absence of isobutene hydrogenation activity.

Diffusion of molecules through the pores of a zeolite takes place in a regime which is called configurational diffusion [13]. It deviates from classical molecular and Knudsen diffusion because the sizes of the molecules are in the same range as the pore diameter of the zeolite channels. Moreover, very small changes in the relationship between pore diameter and molecular dimensions can induce large differences in the

diffusion coefficients of the reactants involved. These large differences belong to the fundamental effects that give rise to shape selectivity, as shown by Chen and Weisz [14]. The diffusion coefficient of *trans*-2-butene in A-type zeolite is about 200 times greater than that of *cis*-2-butene, even though these two molecules vary in their critical size by only 0.2 Å. Hydrogenation of a mixture of *cis*- and *trans*-2-butene, over the same Pt/LTA catalyst as discussed above, resulted in a much higher hydrogenation rate for the *trans*-isomer, indicating that the selectivity is controlled by configurational diffusion. Based on first-order kinetics, the relative rate constant of the *trans*-isomer was calculated to be 3.3 to 7 times higher as compared to that of the *cis*-isomer. Moreover, on non-microporous platinum catalysts, the reverse is observed, *cis*-2-butene reacting faster than the *trans*-isomer.

In the same paper, a method for the selective removal of ethene in propene streams is presented [14]. It is based on the sieving properties of Na-mordenite which can distinguish ethane from propane. The catalyst was made by exchanging platinum(II) tetra-amine into the H-form of mordenite, and then narrowing the pore opening by sodium-ion back exchange. The catalyst was activated in dry air at 450°C and then treated with triphenylphosphine in hydrogen at 260°C in order to poison selectively the platinum sites located on the external surface (external surface Pt). Catalytic testing indicated the selective conversion of ethene in a stream containing predominantly propene. The observed selectivity might be explained by product selectivity [15]. Both propene and ethene can reach the hydrogenation/dehydrogenation site; however, ethane is the only hydrogenation product that can leave the catalyst while propane remains entrapped. Normally, this would result in deactivation of the catalyst as a result of the accumulation of propane. This was not observed, however, which made the authors propose that equilibrium conditions might be established in the interior of the zeolite between all

reactants and products involved. As soon as these equilibrium conditions are reached, even though the interior of the zeolite is not saturated with propane, additional propene entering the catalyst will exit unconverted.

Steinbach and Minchev [16] examined the shape-selective properties of Ni/Ca-LTA by the single component hydrogenation of 1-hexene and of 2,3-dimethyl-2-butene at 35°C. No shape selectivity was observed for catalysts reduced in flowing hydrogen. This was caused by metal migration from the interior of the zeolite to the external surface during the reduction process, even at moderate reduction temperatures. Migration of nickel could be avoided, however, by using sodium in liquid ammonia as the reducing agent of the Ni-precursor. Subsequent removal of the excess ammonia in flowing hydrogen at 180°C gave a shape-selective catalyst over which 1-hexene was hydrogenated while 2,3-dimethyl-2-butene remained unconverted. Similar selectivity was obtained using a Ni/Ca-LTA catalyst, reduced in hydrogen at 450°C, from which the external surface located nickel was removed selectively by carbon monoxide at 80°C. In this way, nickel on the external surface is removed as Ni(CO)₄, a method which also proved to be suitable for the (partial) regeneration of catalysts which had lost their shape selective properties as a result of severe temperature treatments.

Dessau [17–19] developed the competitive hydrogenation of an equimolar mixture of di-branched 4,4-dimethyl-1-hexene and linear 1-hexene as a method to assess the location of platinum in Pt/Cs-ZSM-5 (Si/Al = 70). Direct reduction of platinum(II) tetra-amine exchanged Cs-ZSM-5 in flowing hydrogen at 300°C gave a catalyst which did not show shape-selective properties. Clearly, the platinum had migrated to the external surface. Reduction of the catalyst in the presence of olefins, however, yielded a catalyst which showed a strong preference for the reduction of the linear olefin. It was assumed that the olefins reacted with the platinum hydride species formed, which are responsible for platinum migration and agglomeration. Oc-

clusion of platinum clusters in the zeolite pores was also accomplished when the platinum-complex loaded zeolite was first activated in an oxygen stream at 300°C, prior to reduction in flowing hydrogen at the same temperature. The competitive hydrogenation of various other olefins was also investigated (Table 1). Even small Pt/Cs-ZSM-5 crystals, which have a relatively large external surface, behaved in a shape-selective manner. Addition of a bulky phosphine, tri-*p*-tolylphosphine, further improved the selectivity by poisoning the Pt located on the external surface. Repeated thermal treatment of the catalyst in hydrogen further improved its shape-selective properties, which indicates that the occluded metal clusters are stable, whereas external-surface platinum tends to agglomerate.

In addition to the test reaction discussed above, Weitkamp et al. [20] used a similar test reaction in order to discriminate between inter-crystalline platinum clusters in medium-pore zeolites and platinum located on the external surface. The branched probe molecule 4,4-dimethyl-1-hexene was replaced by the even more branched molecule 2,4,4-trimethyl-1-pentene and used in competition with 1-hexene. It was successfully applied to illustrate the shape-selective hydrogenation properties of the medium pore Pt/ZSM-5 and of the small pore, Pt/ZSM-58. In the latter, platinum was introduced by co-crystallisation of platinum(II) tetra-amine which was added to the zeolite synthesis mixture, as first reported by Weisz et al. [12]. The test reaction was also applied to

demonstrate the successful introduction of platinum, palladium and rhodium in the small pore molecular sieves ZSM-58, Rho, ZK-5 and SAPO-42 by solid-state ion exchange with the corresponding metal chlorides at elevated temperatures [21].

A shape-selective catalyst for the selective hydrogenation of acetylene in the presence of butadiene and ethylene was developed by Corbin et al. [22,23]. A rather fundamental study of the selective hydrogenation of acetylene impurities in ethene streams over palladium loaded zeolites had already shown the potential of catalysts of this type in such reactions [24]. In the production of ethene from steam cracking of natural gas liquids (NGL), small amounts of butadiene and acetylene are formed as by-products. Acetylene can cause explosions in downstream cryogenic separation units and should therefore be removed from the gas stream. The recovery of butadiene, however, is attractive from an economic point of view. On a conventional nickel catalyst, both acetylene and butadiene adsorb more strongly than ethylene so that minimal hydrogenation of ethylene is achieved while 60% of the butadiene and all the acetylene is converted.

Zeolite LTA was chosen as support for a more selective hydrogenation catalyst because its pore opening of about 4.3 Å is in the range of the molecular dimensions of the reactants: acetylene ~ 3.3 Å, ethylene ~ 3.9 Å and butadiene ~ 4.2 Å. Furthermore, the pore opening of zeolite LTA can be fine-tuned by ion exchange with alkali or alkaline earth metal

Table 1

Shape-selective competitive hydrogenations over Pt/Cs-ZSM-5^a. Data from Ref. [18]

Linear olefin	Branched olefin	Temperature (°C)	% Hydrogenation	
			Linear	Branched
Hexene-1	4,4-Dimethyl-1-hexene	275	90	1
Pentene-1	4,4-Dimethyl-1-pentene	300	97	2
Heptene-1	4,4-Dimethyl-1-pentene	300	91	1
Hexene-1	6-Methyl-1-heptene	300	25	2
Styrene	2-Methylstyrene	425	50	2

^aConditions: down-flow fixed-bed glass reactor; equimolar mixture of olefins.

cations. Nickel ions were introduced by ion exchange with aqueous nickel nitrate. Reduction of the metal ions was performed in hydrogen at 400°C. The accessibility of the ion-exchange zeolites was investigated by sorption studies performed with the probe molecules MeOH (~ 3.7 Å), EtOH (~ 4.0 Å) and *n*-PrOH (~ 4.3 Å), whose molecular dimensions are just slightly larger than those of the actual reactant molecules. No *n*-PrOH was adsorbed by K⁺, Rb⁺ and Cs⁺-exchanged zeolite LTA, which indicates that these catalysts should show reduced hydrogenation of butadiene. In addition, for Cs-LTA strongly reduced adsorption of EtOH was found, which means that ethylene, formed by hydrogenation of acetylene, might be unable to leave the Cs⁺-exchanged catalyst.

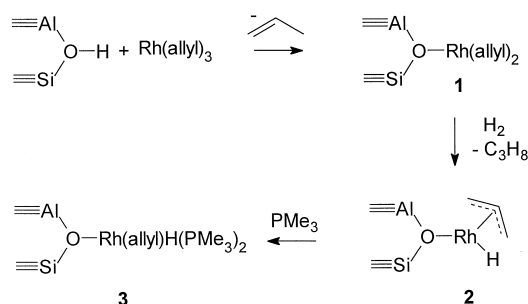
Initially, no shape selectivity was observed for any of the zeolite-based catalysts, indicating that the reaction occurred over nickel sites located on the external surface. The presence of external-surface nickel was confirmed by ESCA measurements. Poisoning of these sites by phosphines or thiophene, or modification with tetraethyl orthosilicate (TEOS) or lead(II) 2-ethylhexanoate proved successful in conferring shape selectivity. Only 20% butadiene loss was found at full acetylene conversion over Ni/K-LTA (thiophene/H₂S added) while using conditions close to those commonly applied in industry. A gradual decrease in activity made regeneration necessary after 30 days. Calcination in air at 450°C restored the activity; however, selectivity was decreased by about 5% per cycle. This was attributed to a resiting of the nickel.

Recently, Dessau [25] reported a shape-selective hydrogenation process which is capable of selectively removing certain aromatic compounds from a mixture with others. Such a process is needed, from an environmental point of view, for the reduction of the aromatic content (especially benzene) in gasoline. Furthermore, a decrease in the amount of aromatics in a refinery distillate employed in the production of kerosine results in a decrease in soot production during combustion. The catalyst consists of

non-acidic tin-, lead-, or indium-modified Pt/ZSM-5; typical reactants which can enter this zeolites comprise benzene, toluene and xylenes, as well as other monoalkylbenzenes and β -alkylnaphthalenes. Bulkier aromatics are excluded and thus remain unconverted. The modified Pt/ZSM-5 catalysts showed shape-selective hydrogenation of *para*-xylene, yielding 1,4-dimethylcyclohexane, when applied in the competitive hydrogenation of an equimolar mixture of *ortho*- and *para*-xylene at 325°C; selectivities up to 47 *para*/*ortho* were reported. Furthermore, in the competitive hydrogenation of an equimolar mixture of benzene, toluene and *para*-xylene at 250°C the order of reactivity was found to be benzene > toluene > *para*-xylene which is in contrast with the order found for a sulfided Ni/W on alumina catalyst.

2.2. Liquid phase reactions

Huang and Schwartz [26] have prepared rhodium complexes within the zeolite cavities of partially proton-exchanged Linde 13 × type molecular sieve (Na-X, FAU structure). Reaction of triallylrhodium with Brønsted acid sites, located in the supercages, gave the supported diallylrhodium complex **1** (Scheme 1). Subsequent treatment of **1** with hydrogen led to the formation of the zeolite-bound rhodium hydride **2** and the evolution of one equivalent of propane. No bridging hydride ligands were detected by IR analysis, which indicated that the complexes were monomerically distributed over the zeolite.



Scheme 1. Formation of zeolite-encapsulated rhodium-hydride **2**, according to Ref. [26].

The zeolite-encapsulated hydride **2** showed a linear uptake of hydrogen in the catalytic hydrogenation of all olefins studied, comparable to the behaviour of its silica-supported analogue. Negligible hydrogenation rates, however, were found for substrates larger than cyclohexene (e.g., cyclooctene), which clearly demonstrates the sieving properties of the catalyst. Furthermore, it proves that the active hydrogenation centres are located within the micropores of the zeolite-based catalyst. Whereas the hydrogenation rates for 1-butene, 1-hexene and 1-octene over silica-supported rhodium hydride complexes are rather similar, and greater than that of the branched olefin 2,3-dimethyl-2-butene, this is not true for the zeolite-bound complex. Over catalyst **2** the rates were found to decrease in the order 1-butene > 1-hexene > 2,3-dimethyl-2-butene > 1-octene, which was ascribed by the authors to transport limitations within the zeolite cavities. Selective poisoning experiments further confirmed that the active hydrogenation sites were located within the zeolite matrix. Coordination of two equivalents of PMe_3 to the zeolite-bound rhodium complex **2** yields **3**, while $n\text{-Bu}_3\text{P}$ because of its larger cone angle is not able to coordinate with the noble metal site within the zeolite structure. Addition of excess of $n\text{-Bu}_3\text{P}$ to the reaction

mixture did not change the hydrogenation rate of 1-butene over **2**. Addition of excess PMe_3 , however, caused the hydrogenation rate to decrease to ca. zero.

Yamaguchi et al. [27] and Joh et al. [28] reported the shape-selective hydrogenation of olefins by a rhodium zeolite-Y catalyst. The starting material was a rhodium(III) exchanged Na-Y zeolite (FAU structure), $[\text{Rh}(\text{NH}_3)_6]^{3+}/\text{Na-Y}$. Calcination of the dry material (400°C), followed by treatment with wet carbon monoxide (130°C) gave pink rhodium carbonyl clusters $\text{Rh}_m(\text{CO})_n/\text{Na-Y}$. The formation of rhodium carbonyl clusters was confirmed by IR spectroscopy. Subsequent decarbonylation with hydrogen (120°C) gave the active $\text{Rh}_x/\text{Na-Y}$ catalyst. Shape-selective hydrogenations of various olefins were performed without poisoning of rhodium clusters possibly present on the external surface. Relative hydrogenation rates were found to decrease in the order 1-hexene \approx 1-octene \approx cyclohexene > cyclooctene \gg cyclododecene. Competitive hydrogenation experiments using a mixture of cyclohexene and cyclododecene showed that only cyclohexene was hydrogenated over the zeolite-based catalyst while both substrates were converted over a Rh/C reference catalyst (Fig. 1). These results indicate the presence of the hydrogenation sites

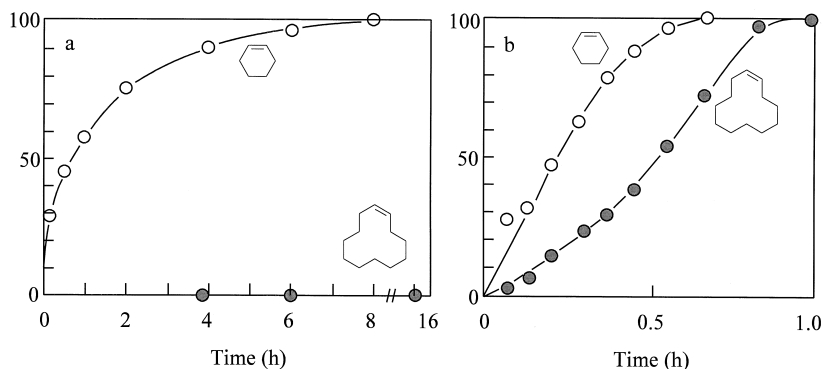


Fig. 1. Competitive hydrogenation of cyclohexene (○) and cyclododecene (●) (conversion): substrate 5 mmol each; hexane 20 ml; 101 kPa hydrogen; (a) $\text{Rh}_x/\text{Na-Y}$, 50 mg, 50°C ; (b) 5% Rh/C, 20 mg, 30°C . Redrawn using data from Ref. [27].

within the zeolite cavities. Furthermore, they indicate the potential of noble metal in zeolite systems as shape-selective hydrogenation catalysts.

Corbin et al. [29] prepared various rhodium-containing zeolites and tested them as catalysts in the competitive hydrogenation of cyclopentene and 4-methylcyclohexene in the liquid phase. Rhodium was either introduced by the method of Huang and Schwartz (introduction of tris(π -allyl)rhodium [26]) or by ion-exchanging the zeolites with aqueous rhodium(III) chloride. The zeolites used included the small-pore ZSM-34, the medium-pore ZSM-5 and ZSM-11, and the large-pore zeolites mordenite, X and Y. Sorption measurements were performed on the dehydrated zeolites with the probe molecules cyclopentane and cyclohexane, having dimensions comparable to those of the reactants (though methylcyclohexane would have been a better analogue for 4-methylcyclohexene). These indicated hardly any intrinsic size selectivity of the zeolite framework itself and in accordance with this, no correlation was observed between the pore size of the zeolites and the reaction selectivity in the hydrogenation experiments Table 2. Moreover, two additional factors, apart from pore-size differences, appeared to have a major impact on the reaction selectivity. The first was related to the location of the noble metal sites. Hydrogenation sites located on the external surface were expected to be essentially

non-selective. Furthermore, because of their accessibility, they might dominate the overall reaction selectivity. Selective poisoning of these surface-located rhodium clusters with n -Bu₃P, as reported by Huang and Schwartz [26], was found to increase the cyclopentene/4-methylcyclohexene selectivity by a factor 4 in case of Rh/ZSM-11. All catalysts were therefore treated with n -Bu₃P in order to maximize selectivity. The second factor involved the variable water content. For Rh/X the selectivity was found to increase from 1 to 30 with increasing water content (2 to 32 wt.%), while Rh/ZSM-11 exhibited a maximum of 47 at intermediate water content. This effect was explained as a tuning of the intracrystalline pore dimensions by means of a water coating, lining the zeolite pores and cages. Moreover, the hydrophilic character of the zeolite catalysts will increase. It should be noted, however, that the Rh/X zeolite with 32 wt.% water is completely saturated and can hardly accommodate additional organics. Probably the activity originates from some non-deactivated Rh on the external surface of the zeolite crystals.

A solid catalyst for the shape-selective hydrogenation of molecules with a diameter greater than about 9 Å was reported by Davis [30]. It consists of an aluminophosphate molecular sieve, VPI-5, which has been impregnated with a noble metal salt solution and subsequently reduced. The catalyst is claimed to show

Table 2
Selectivity in the competitive hydrogenation of cyclopentene/4-methylcyclohexene over Rh-containing zeolites^a. Data from Ref. [29]

Zeolite	Pore size (Å)	Sorption selectivity ^b	Reaction selectivity ^c	Water content (wt.%) ^d
ZSM-34	3.6 × 5.1	0.77	7.5	—
ZSM-5	5.3 × 5.6	1.54	15.0	1.2
ZSM-11	5.3 × 5.4	1.10	47.0	2.2
Mordenite	6.5 × 7.0	0.91	16.0	8.2
X	7.4	0.91	6.0	5.0
Y	7.4	0.96	1.0	3.6

^a Conditions: 30 mg Rh-zeolite, 65 ml n -octane, 0.3 ml cyclopentene, 0.3 ml 4-methylcyclohexene and 5 μ l PBu₃ at 60°C and 345 kPa hydrogen.

^b Sorption selectivity of the anhydrous zeolite for cyclopentane/cyclohexane.

^c Selectivity over the partially hydrated (see next column) Rh-zeolites in the competitive hydrogenation of cyclopentene/4-methylcyclohexene.

^d Water content that gave rise to the presented reaction selectivity.

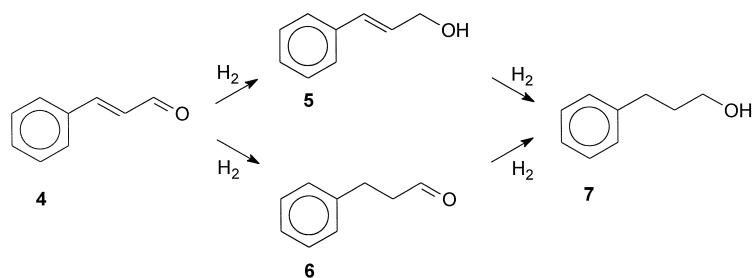
shape-selective properties in the hydrogenation of olefins, aldehydes and ketones, provided that external surface Pt is poisoned by bulky phosphines or mercaptans. The activity of a Rh/VPI-5 catalyst in the hydrogenation of molecules larger than about 9 Å was illustrated by the liquid-phase hydrogenation of a 1:1 (w/w) mixture of 1-octene and *cis*-cyclooctene, performed in decane at 30°C and 101 kPa hydrogen. Both reactants were converted over Rh/VPI-5 while only the linear olefin was converted over the large-pore molecular sieve Rh/AlPO₄-5.

Recently, Creighton et al. [31] reported on the liquid-phase regioselective hydrogenation of alkenes over Pt-loaded zeolite BEA. It was found that 1-decene was hydrogenated 18 times faster than *trans*-5-decene over Pt/Na-BEA, whereas the ratio was only about 2 for platinum on non-microporous supports. This regioselectivity was explained by steric constraints imposed by the microporous structure of the zeolite. Careful study of the possible adsorption sites on a zeolite-occluded platinum cluster indicated more possibilities for the adsorption of a terminal double bond, as compared to an internal double bond. However, regioselectivity was only obtained when the non-selective, external-surface located platinum clusters were selectively poisoned with triphenylphosphine. Furthermore, sorption experiments showed that strong competition between the solvent and the reactant for adsorption in the zeolite might exist, which prevents the reactants from attaining a significant concentration in the pores. As a result,

catalytic activity and regioselectivity were only obtained when non-polar or bulky solvents were applied. The hydrogenation rate over Pt/Na-BEA was found to be much lower than that observed over the amorphous supported platinum catalysts. Furthermore, for the zeolite-based catalyst, first-order kinetics were found and compared with zero-order for the amorphous catalysts. Both effects were explained in terms of alkene coverage of the Pt-sites in the two types of catalysts.

3. Chemoselective hydrogenation of α,β -unsaturated aldehydes over zeolite-encapsulated metal clusters

The chemoselective hydrogenation of cinnamaldehyde **4** to cinnamyl alcohol **5** over platinum and rhodium clusters encapsulated in Y-type zeolite was studied by Gallezot et al. (Scheme 2) [32]. From a thermodynamic point of view, both the hydrogenation of the C=C and the C=O bond are possible but the reaction enthalpy ($-\Delta H$) for the hydrogenation of the C=C bond is about 42 kJ/mol higher. Moreover, the selective hydrogenation of the C=C bond, to give 3-phenylpropanal **6**, is rather trivial, while it is much more difficult to selectively convert the carbonyl in order to obtain the unsaturated alcohol **5**. Three different catalysts were prepared by Gallezot et al. [32]; Pt/Y(1), Pt/Y(2) and Rh/Y. The platinum clusters in Pt/Y(1) were homogeneously distributed over the zeolite matrix and their sizes were in the



Scheme 2. Hydrogenation of cinnamaldehyde **4** to: cinnamyl alcohol **5**, 3-phenylpropanal **6** and 3-phenyl-1-propanol **7**.

range 1–2 nm. In contrast, Pt/Y(2) contained platinum clusters of about 50 nm, located in the vicinity of the external surface but still within the matrix. Rh/Y contained small clusters in the range of 1 ± 0.3 nm, homogeneously distributed throughout the zeolite crystal. The hydrogenation reactions were performed in a stirred autoclave at 60°C and 40 bar hydrogen. At a conversion of 50%, the selectivities to **5** were found to be 82 and 97% for Pt/Y(1) and Pt/Y(2), respectively, while the selectivity for a Pt/C reference catalyst was only 55%. Similarly, 30% selectivity was found for Rh/Y, which is relatively high for a rhodium catalyst as this metal is known to be very unselective. Moreover, only 5% selectivity was observed for a Rh/C reference catalyst. These unusually high selectivities were explained by geometric constraints imposed by the zeolite structure. Because of its rigidity, **4** can only adsorb end-on across the 12-membered oxygen ring that gives access to the supercage-encapsulated metal clusters. This argument also holds for clusters larger than the supercage which is still claimed to be located within the matrix. Small metal clusters, however, which contain only a few atoms, would leave enough space in the supercages for **4** to adsorb laterally via the C=C bond. This could well be the case for Pt/Y(1) and Rh/Y. For the latter, external-surface located rhodium particles, which have a high activity for C=C hydrogenation, were also considered.

This research was extended to Ru/Na-Y and Ru/K-Y which also gave improved selectivities to **5** as compared with Ru/C [33]. In order to investigate the importance of steric considerations, an aliphatic molecule, 3-methylcrotonaldehyde, was also included. This less bulky molecule has more space to adsorb in many orientations in the confined interior of the zeolite; steric effects were therefore suggested to be less important. The selectivity to the unsaturated alcohol could be increased, however, by replacement of the Na-ions by K-ions. This was explained by Blackmond et al. [33] to be the result of an electronic effect, related to the

higher basicity of the K-exchanged zeolite. The suggested enhancement of electron density thus induced on the metal clusters was assumed to result in a decreased C=C hydrogenation activity, as well as in an increase in C=O hydrogenation caused by the interaction of the carbonyl with the zeolitic cation.

Gallezot et al. [34] continued their investigation of the regioselective hydrogenation of **4** to **5** over zeolite Pt/BEA. Two catalysts were prepared, differing in metal cluster size and location. Pt/Na-BEA(1) was prepared by direct reduction of the platinum(II) tetra-amine exchanged zeolite, by heating in flowing hydrogen from 25 to 200°C at 2°C/min, while Pt/Na-BEA(2) was obtained by calcination from 25 to 300°C at 1°C/min in flowing oxygen, cooling under argon to 100°C and heating under flowing hydrogen from 100 to 300°C. The Pt/Na-BEA(1) contained zeolite-encapsulated grape-like agglomerates of 50–200 nm, which consisted of metal crystallites of 2–5 nm, comparable to Pt/Y(2) [14]. The Pt/Na-BEA(2) contained small platinum clusters with size comparable to the pore opening (< 1 nm), homogeneously distributed over the zeolite matrix. A high selectivity to **5** was obtained (86–88%) over Pt/Na-BEA(1), independent of the conversion. As in the case of Pt/Y(2) [32], this was explained by a hindered approach of the C=C bond; end-on adsorption of the C=O is favoured when the molecule diffuses parallel to the linear channel wall, until it reaches the encapsulated platinum cluster (Fig. 2).

In contrast, over Pt/Na-BEA(2) a low initial selectivity (0–5%) for the unsaturated alcohol was obtained, while 3-phenyl-1-propanol **7** was the main product. After 1 h, however, the formation of **5** became predominant (50–55%) which was accompanied by a decrease in hydrogenation rate. It was proposed that the reaction initially occurred over metal clusters of low nuclearity, which leave enough space between the cluster and the zeolite wall to allow the lateral adsorption of **4**, resulting in the hydrogenation of both double bonds. During reaction,

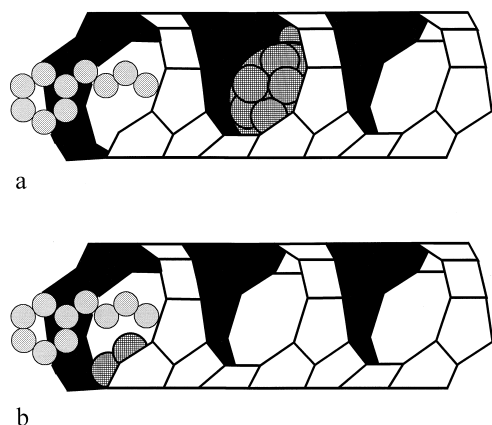


Fig. 2. Cinnamaldehyde approaching a metal cluster; (a) pore filling cluster; (b) low-nuclearity cluster, allowing lateral adsorption. Illustration adapted from Ref. [34].

the number of these clusters decreases by sintering and the reaction continues over a smaller number of pore-filling platinum clusters where steric constraints predominate. Recycle experiments showed that the initial selectivity of the second run was identical with the selectivity during the second part of the first run, which supports this hypothesis.

Li et al. [35] studied the chemoselective hydrogenation of **4** over Pt/L (M = alkali or alkaline earth metal cation). High selectivities to **5** (> 90%) were obtained over rubidium- and strontium-exchanged catalysts at conversions up to 95%. By X-ray powder diffraction some characteristic peaks for platinum were identified on the Pt/M-LTL catalysts, which indicates that the clusters are rather large (> 2.5 nm). Presumably, these large clusters are located on the external surface, in contrast to the situation with the catalysts described by Gallezot et al. [32,34] and Blackmond et al. [33], while some small clusters might be located inside the micropores; further characterisation (e.g., TEM) might confirm this hypothesis. The high selectivity to the unsaturated alcohol is controlled by several factors including the nature of the noble metal (Pt 'favours' C=O hydrogenation), the metal morphology, and electronic effects induced by the basicity of the zeolite. Steric considerations,

related to the zeolite structure, play a minor role as evidenced by the predominant formation of the saturated aldehyde over Pd/K-LTL. Moreover, liquid-phase reactions in the one-dimensional channel system of zeolite LTL are expected to be slow as a result of diffusional limitations.

4. Shape-selective hydrogenations of olefins over zeolite-occluded coordination compounds; ship-in-a-bottle systems

The encapsulation of metal/ligand complexes in zeolites combines the catalytic properties of the coordination complex with the shape-selective properties of the molecular sieve. Moreover, the heterogenised catalysts offer the benefit of easy catalyst separation. Furthermore, possible deactivation by complex oligomerisation is prevented. So far, most papers on ship-in-a-bottle systems focus on selective oxidation catalysis, while the number of papers dealing with the application of ship-in-a-bottle complexes in selective catalytic hydrogenation is still very limited.

Kowalak et al. [36] reported on the catalytic properties of Pd(II)(salen) (Fig. 3) encapsulated in the supercages of zeolites Y and X. Upon hydrogenation of 1-hexene at room temperature and 54.3 kPa hydrogen (liquid phase), significant isomerisation to *trans*-2-hexene was observed, which complicated the evaluation of shape selectivity based on single-component hydrogenation rate measurements for the reactants 1-hexene and *trans*-2-hexene. Furthermore, cyclohexene was converted solely to cyclohexane over both homogeneous and encapsulated Pd(salen) while for palladium-exchanged zeolites dehydrogenation to benzene was also ob-

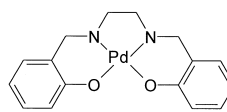


Fig. 3. Pd(II)(salen).

served. The latter result was attributed to the formation of Pd(0) in the zeolite. In a competitive hydrogenation experiment, applying a 1:1 (v/v) mixture of 1-hexene and cyclohexene, the zeolite-encapsulated Pd(salen) produced only hexane and *trans*-2-hexene while cyclohexene was not converted. No preference was observed for the homogeneous Pd(salen) complex. The preferential conversion of the terminal double bond was also observed in a 20/1 (v/v) cyclohexene/1-hexene mixture. Apparently, the presence of a terminal double bond which is sterically less demanding largely denies the cyclic alkene access to the supercage. Alternatively, the coordination of cyclohexene to supercage located Pd(II)(salen) might be strongly hindered because of steric considerations.

The hydrogenation of cyclohexene, cyclooctene, 1-hexene and benzene by Ni(salen) encapsulated in zeolite Y, performed in the liquid phase at 40°C and 60 atm (1 atm = 101.325 kPa) hydrogen, was studied by Chatterjee et al. [37]. All the olefins and the benzene were successfully converted to their hydrogenated products. The mechanism was proposed to involve the formation of a high-valent hydrido nickel complex which transfers hydrogen atoms to the substrates. In the competitive hydrogenation of a 1/1 (v/v) mixture of 1-hexene/cyclohexene, *n*-hexane was observed as the only product. The terminal double bond, which is sterically more accessible, was believed to prevent the cyclic alkene from coordinating to the catalytic centre.

5. Noble metal containing zeolites as enantioselective hydrogenation catalysts

Enantioselective hydrogenation reactions are of increasing importance in the pharmaceuticals and agrochemicals industry. Recently, Corma et al. [38] synthesised Rh-complexes with chiral N-containing ligands, derived from L-proline. These complexes were successfully anchored on silica and zeolite USY (Fig. 4). The USY-zeolite

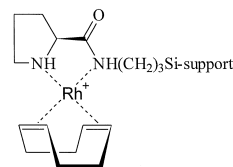


Fig. 4. The immobilised chiral rhodium complex applied by Corma et al. for the asymmetric hydrogenation of prochiral alkenes. Illustration adapted from Ref. [38].

was made by steam calcination of 80% ammonium-exchanged Na-Y and contained a well developed micro-/mesoporous channel system with pore diameters between 12 and 30 Å. Both the homogeneous and the immobilised chiral complexes were tested as catalysts in the liquid-phase hydrogenation of prochiral alkenes (α -acylaminocinnamate derivatives). Whereas induction periods were observed for both the homogeneous and silica-anchored catalysts, this was not the case for the USY-supported complex. This result was explained by a concentration effect, occurring in the pores of the zeolite, and/or the specific electrostatic interaction between the substrate and the zeolitic support. Furthermore, the USY-anchored catalyst gave the highest activity in combination with increased enantiomeric excess (ee). The improved ee was most pronounced for the less bulky substrates, suggesting an (important) role for steric constraints imposed by the zeolite structure. Later, similar results were reported for comparable USY-supported rhodium and nickel complexes [39].

The enantioselective hydrogenation of ethyl pyruvate over (–)-cinchonidine-modified platinum, introduced in zeolite Y, ZSM-5, ZSM-35 and BEA, was studied by Reschetilowski et al. [40]. The highest activity and enantioselectivity was obtained for the ZSM-35 based catalyst. However, enantiomeric excess was also observed to be strongly influenced by the type of solvent. Unfortunately, the specific benefit and/or influence of the zeolite support on the enantioselectivity was not discussed. Additional work can be found in Refs. [41,42].

6. Shape-selective hydrogenation of olefins over zeolite-containing composite catalysts

A novel type of hydrogenation catalyst consisting of a $\text{TiO}_2/\text{Pt}/\text{silicalite-1}$ composite was recently reported by van der Puil et al. [43,44]. The TiO_2 support offers high stability for the catalytic phase (platinum) while a thin continuous layer of oriented silicalite crystals, which covers the active sites, creates separation selectivity and steric constraints at the zeolite/platinum interface (Fig. 5). The composite was made by sputtering of platinum onto one side of a TiO_2 single crystal platelet, followed by the hydrothermal synthesis of a silicalite-1 layer. This resulted in a monofunctional catalyst which contained platinum clusters with a diameter of 5–20 nm, distributed homogeneously over the support, and covered with a silicalite-1 layer with a thickness of about 1 μm . Careful removal of the organic template by calcination (350°C) and subsequent treatment in ozone (120°C) cleared the access to the platinum sites through the micropores while minimizing the formation of mesopores/cracks. In the competitive gas-phase hydrogenation of 1-heptene and 3,3-dimethyl-1-butene, performed at 100°C, a maximum hydrogenation selectivity of 70 in favour of the conversion of the linear olefin was found. This was attributed to diffusional limitation, resulting in mass-transport selectivity. Upon raising the reaction temperature to 200°C, the influence of diffusion limitations decreased. As a result, the conversion rates of both olefins increased while the selectivity decreased to a

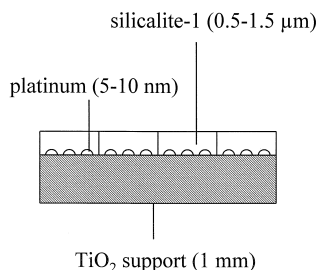


Fig. 5. Schematic representation of the $\text{TiO}_2/\text{Pt}/\text{silicalite-1}$ composite catalyst. Illustration adapted from Ref. [44].

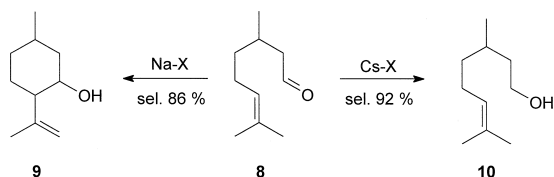
value of 9. Although these experiments could not exclude the presence of mesopores in the zeolite layer, they did show the specific influence of the zeolite micropores. An interesting observation was the more pronounced double-bond migration in the case of the composite catalyst, as compared to uncovered Pt/TiO_2 . Because of the absence of acid sites on the monofunctional catalyst system, it was proposed that the hydrogen-to-olefin ratio at the catalytic site of the composite was relatively low as a result of a retarded hydrogen supply through the zeolite layer. In the competitive hydrogenation of 1-decene and *trans*-5-decene, preferential hydrogenation of the terminal olefin was observed. This regioselectivity was explained by steric constraints present at the catalytic site [31]. Moreover, this indicates a close contact between the zeolite and the catalytic phase at the zeolite/platinum/ TiO_2 interface.

7. Zeolite-catalysed Meerwein–Ponndorf–Verley (MPV) reductions

Shabtai et al. [45] studied the potential of alkali or alkaline earth exchanged X-type zeolites in the gas-phase (100–180°C) MPV reduction of various saturated and unsaturated aldehydes and ketones, using isopropanol as reducing agent [45]. In the reduction of linear aldehydes over Na-X, a gradual decrease in the reduction rate was observed upon increasing chain length, which was attributed to increasing diffusional limitations in the micropores. Selectivities to the corresponding 1-alcohols were generally high (> 95%). Application of Lewis-acidic Ca-X gave acetalisation of the aldehydes as an important side-reaction. This could be prevented, however, by applying higher reaction temperatures. Unfortunately, the X-type zeolite/isopropanol system was not capable of reducing α,β -unsaturated aldehydes. Shape selectivity was found in the selective conversion of citronellal **8** under MPV conditions. In Na-X there was enough space for the substrate to

perform an intramolecular ring closure to isopulegol **9** whereas, over Cs-X, reduction to the linear citronellol **10** was observed (Scheme 3). In the reduction of methylcyclohexanone isomers (100°C), it was observed that the 4-isomer reacted relatively fast and gave a thermodynamically determined product distribution (cis:trans = 24:76). The 2- and 3-methylcyclohexanone reacted more slowly and gave a kinetically determined product distribution (cis:trans = 62.5:37.5 and 23.5:76.5 for the 2- and 3-isomer, respectively). The mechanism was proposed to involve the formation of a surface isopropoxide group attached to a cationic site (basic mechanism). It could not be excluded, however, that incompletely coordinated Si- or Al-sites contributed to the catalytic activity (Lewis-acid mechanism).

Recently, Creighton et al. [46,47] reported the application of zeolite beta (BEA) in the stereoselective (> 95%) reduction of 4-*tert*-butylcyclohexanone to *cis*-4-*tert*-butyl-cyclohexanol in the liquid phase. This zeolite-based catalyst proved to be fully regenerable without loss in activity or stereoselectivity. This is of industrial relevance, as the *cis*-isomer is a fragrance-chemical intermediate. Other active solid catalysts, including zeolites, invariably gave the thermodynamically more stable *trans*-isomer. The activity of the BEA catalyst was found to increase upon increasing activation temperature. Furthermore, deep-bed calcination conditions gave a higher catalytic activity than a shallow-bed procedure, indicating a relation between the catalytic activity and the extent of framework dealumination since the former method results in a greater degree of auto-steaming. However,



Scheme 3. Shape selective conversions of citronellal **8** to isopulegol **9** or citronellol **10** under MPV conditions, according to Ref. [45].

²⁷Al-NMR spectra did not show any increase in octahedral aluminium. FT-IR results indicated a relation between the catalytic activity and the amount of aluminium which is only partially bonded to the framework (Lewis-acid sites). The MPV mechanism was therefore proposed to involve a six-membered transition state, analogous to that of Al(OPr^{*i*})₃-catalysts, formed upon chemisorption of a secondary alcohol on a Lewis-acid aluminium site and coordination of the ketone to the same site. A base mechanism was ruled out because of the low aluminium content (Si/Al = 12), the absence of alkali or alkaline earth cations in the active H-BEA catalysts and the very similar activity of the Li-, Na-, K-, Rb- and Cs-exchanged catalysts. Furthermore, the catalyst could be poisoned by the base piperidine.

The transition states which lead to the *cis*- or *trans*-alcohol differ substantially in spatial requirements (Fig. 6). That for the *cis*-isomer is more or less linear in form and aligned with the BEA channel, while the formation of the *trans*-alcohol requires an axially oriented (bulkier) transition state (for spatial pictures, the reader is referred to Fig. 8 of Ref. [47]). Although the latter might still fit in the intersections of BEA it is questionable whether there is an active site available at the required position. More coordination possibilities are available for the *cis*-transition state, which can easily be accommodated within the straight channels of BEA. The observed kinetically determined product distribution is thus satisfactorily explained by true transition-state selectivity.

In an extension of this work, van der Waal et al. [48] reported the catalytic activity of aluminium-free titanium beta ([Ti]-BEA) zeolite in the same stereoselective MPV reaction. Again, a very high selectivity of 98% to the *cis*-isomer was found, explained by a restricted transition state, in this case around a Lewis-acid titanium site. The Lewis-acid properties of tetrahedrally incorporated titanium in zeolite [Ti]-BEA had already become clear during catalytic studies on the epoxidation of olefins with hydrogen perox-

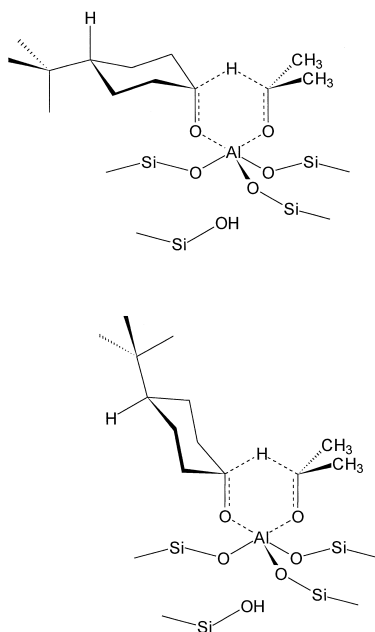


Fig. 6. Transition states for the formation of *cis*-4-*tert*-butylcyclohexanol (top) and *trans*-4-*tert*-butylcyclohexanol (bottom) in the proposed reaction mechanism over zeolite BEA. Illustration from Ref. [47].

ide in alcoholic solvents [49]. The oxophilic Lewis acidity of the titanium site was confirmed by UV–Vis spectroscopy, which showed an increased coordination number for the originally 4-coordinated titanium atom upon adsorption of alcohols and water. Kinetically determined product distributions were also obtained in the MPV reduction of 2-, 3- and 4-methylcyclohexanone; the *cis*-, *trans*- and *cis*-alcohols, respectively, being the major products. The catalytic activity of [Ti]-BEA was found to be much lower than that of its aluminium analogue, although its tolerance for water was observed to be much higher. The latter property, which is related to the hydrophobic character of the aluminium-free zeolite, illustrates its catalytic potential for this type of reaction.

8. Concluding remarks

Many examples of shape-selective hydrogenation reactions using zeolite-encapsulated

metal clusters or coordination complexes have been reported. Most of them exemplify the sieving properties of these catalysts, resulting in the selective hydrogenation of those substrates which can enter the micropores, while leaving the larger substrates unaffected. In order to observe and maximise this reactant shape selectivity, metal clusters located on the external surface should be deactivated by selective poisoning.

A new approach involves the construction of zeolite-containing composite catalysts, in which supported metal clusters are covered with a thin, oriented zeolite layer. The support offers high stability for the catalytic phase, while the zeolite creates selectivity by its separation capacity and steric constraints created at the catalytic sites, as first illustrated for a TiO₂/platinum/silicalite-1 composite.

For chemo-, regio- or stereoselectivity in a single molecule, only a few examples appear to be known. They clearly demonstrate the potential of metal-loaded zeolites as highly selective hydrogenation catalysts. However, the factors that govern selectivity and activity are not yet fully elucidated and may include, in addition to competitive adsorption of reactants, products and solvents, also steric and electronic effects. Moreover, further improvement in our understanding of these catalytic phenomena is required in order to make optimal use of the possibilities which metal-in-zeolite systems certainly offer.

The recognition of the utility of zeolites as catalysts in the MPV reduction of carbonyl compounds is very recent. Their potential is related to the possibility of shape-selectivity, as illustrated by an example showing almost absolute stereoselectivity as a result of restricted transition-state selectivity. In the case of alkali or alkaline earth exchanged zeolites with a high aluminium content (X-type), the catalytic activity is most likely related to basic properties. For zeolite BEA (Si/Al > 10), however, aluminium atoms which are only partially connected to the framework appear to play a role in the catalytic

activity. Similarly, the activity of aluminium-free [Ti]-BEA in the MPV-type hydrogen-transfer reaction is ascribed to the Lewis-acid character of the titanium atoms.

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