ELSEVIER

Chemical Engineering Journal 103 (2004) 35–43

Chemical Engineering Journal

www.elsevier.com/locate/cej

Deactivation in liquid-phase hydrogenation of cinnamaldehyde over alumosilicate-supported ruthenium and platinum catalysts

J. Hájek[a,*], N. Kumar[a], V. Nieminen[a], P. Mäki-Arvela[a], T. Salmi[a],
D.Yu. Murzin[a,**], L. Červený[b]

[a] Laboratory of Industrial Chemistry, Process Chemistry Centre, Åbo Akademi University, Biskopsgatan 8, 20500 Turku/Åbo, Finland
[b] Department of Organic Technology, Institute of Chemical Technology, Prague, Czech Republic

Received 27 January 2004; received in revised form 23 June 2004; accepted 13 July 2004

Abstract

Liquid-phase hydrogenation of cinnamaldehyde over Pt and Ru supported (Y-zeolite, MCM-41) catalysts demonstrated deactivation accompanied by profound decrease of catalysts surface area and by the increase of carbon content. Three consecutive runs with the same catalyst batch typically indicated selectivity increase towards cinnamylalcohol. Changes of activity and selectivity were dependent on the active metal as well as on the support.

Keywords: Deactivation; Cinnamaldehyde; Cinnamylalcohol; Zeolite catalyst

1. Introduction

Production of bulk and fine chemicals as well as pharmaceuticals is based on extensive application of homogeneous and heterogeneous catalysts. Heterogeneous catalysis, however, dominates in commercial practice, particularly in petrochemical large-scale productions [1]. To meet environmental and technology demands sustainable approach within heterogeneous catalysis becomes more important also for the synthesis of fine chemicals [2].

Unsaturated alcohols are industrially valuable intermediates for the synthesis of flavours, perfumes, and pharmaceutical products [3–5]. Conventional synthesis involves selective chemical reduction of carbonyl group in unsaturated carbonyl compounds. Although the efficiency of heterogeneous catalysis is lower compared to stoichiometric reducing agents [6], high yields of unsaturated products are attainable particularly over osmium catalysts [7]. Other metals are less feasible but certain promotional factors were found to improve considerably their catalytic performance [8–11].

The yields of unsaturated alcohols were successfully increased in case of bimetallic catalysts [12]. Promotional effect of metal salts [13], pH as well as the influence of particle size and support character [14] on selectivity were also observed.

Despite the fact that the problem has been thoroughly investigated during the years few references are devoted to hydrogenation of cinnamaldehyde over metal modified zeolites, and there is no information in the open literature dealing with deactivation effects in liquid-phase hydrogenation over such catalysts.

Microporous molecular sieves (zeolites) are the primary catalysts for large-scale petroleum processes [15–17]. The diversity of structural types with well-defined pore systems, tunable porosity, hydrophobicity and variable acid–basic properties make them attractive also for the synthesis of fine chemicals [18–20].

One of the major problems related to heterogeneous catalysis is the activity and selectivity loss with time on stream.

---

* Corresponding author. Tel.: +358 2 215 4985; fax: +358 2 215 4479.
** Co-corresponding author.
E-mail addresses: jan.hajek@abo.fi (J. Hájek), dmitry.murzin@abo.fi, dmurzin@abo.fi (D.Yu. Murzin).

1385-8947/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cej.2004.07.005

The practical experience and evaluation of deactivation processes is associated mainly with gas-phase processes (catalytic cracking, hydrotreating, reforming, methanol synthesis etc.) [21–23]. Limited investigations within the batch liquid-phase reactions are accountable to apparent experimental and theoretical difficulties [24–26].

Deactivation of catalysts is generally of utmost importance affecting long-term performance of catalysts—their activity as well as the selectivity. Depending on the particular reaction and on the catalyst used the deactivation process may vary significantly. Some fundamental issues on deactivation are briefly described below.

Chemical and physical processes leading to deactivation are commonly divided into three main classes [27,28]: active phase transformation (sintering, leaching, etc.), fouling (coking) and poisoning.

Sintering, e.g. thermal degradation of the catalyst might be neglected as hydrogenations were carried out at moderately low temperature (373 K). Because neither leaching nor other type of phase transformation were observed they can be also ignored.

In large number of catalytic processes carbonaceous deposits are formed from the reaction mixture. Such adsorbed species form through polymerisation and condensation complex polynuclear aromatic structures. The process is referred in industry as fouling or coking, where coke denotes the material originated by decomposition or condensation of hydrocarbons. Apparently there is a great variation in the morphology of the coke depending on the catalyst history, and on the nature of reactants. Particularly for supported catalysts a weight body of literature indicates the complex relation between the coke content its morphology and catalyst performance.

Poisoning is associated to changes in catalytic performance due to strong chemisorption processes (reversible or non-reversible). Compared to fouling certain vagueness involved in the process of coke formation allows classify poisoning as much better defined event [28].

In catalytic reactions involving hydrocarbons, formation of carbonaceous deposits (above referred as coke) might occur. Coke deposits may amount to 15 or even 20% (w/w) of the catalyst and they may deactivate the catalyst selectively or non-selectively—covering the active sites, respectively, causing the pore and surface blockage [29].

The coke deposition inside catalyst pores is related to existence of intraparticle diffusion, as the coke accumulates in the catalyst pores, the effective diameter of pores decreases. Coke concentrated near pore mouths is an effective barrier causing eventually complete pore blockage.

In low-temperature hydrocarbon reactions ($\leq$400 K), hydrocarbon transformation (formation of complex polynuclear aromatic structures via polymerisation and condensation) typically does not occur and the carbonaceous deposits are generally the non-desorbed reaction products and reactants [30].

Distribution of deposits may not be uniform. Depending on the size of molecules involved in reaction, deposition may start within the inner or outer surface of the catalyst [30]. Direct relationship between the aromatic character and the amount of deposited coke has been also revealed.

According to previous text the deactivation during hydrogenation of cinnamaldehyde at 373 K might be assumably attributed to combination of poisoning and catalyst fouling. Predominant adsorption and deposition of starting substrate and reaction products at the catalyst inner and outer surface, rather than some kind of hydrocarbon transformation, could be probably expected.

The main aim of the presented study was to report and evaluate the observed deactivation of alumosilicate-supported (Y-zeolite, MCM-41) ruthenium and platinum catalysts in liquid-phase hydrogenation of cinnamaldehyde.

2. Experimental

2.1. Catalyst synthesis

The Y-zeolite support was provided by Zeolyst International (CBV712), MCM-41 support has been synthesised according to published procedures [31,32]. The structure of mesoporous MCM-41 has been verified by XRD. Measured patterns exhibited characteristics typical for the MCM-41 material.

The 2.5% Ru/Y, 2.5% Pt/Y and 2.5% Ru/MCM-41 catalysts were prepared by wet impregnation of supports by aqueous solutions of $RuCl_3{\cdot}xH_2O$ ($x \leq 1$, Sigma–Aldrich) and H_2PtCl_6 (40% Pt, Degussa), respectively. The impregnation was carried out in rotary evaporator (Buchi Rotavapor R114) for a period of 24 hours. Impregnated catalysts were dried in oven at 383 K for 12 hours.

Surface areas of catalysts were obtained from full nitrogen adsorption–desorption isotherms at 77 K (Sorptomatic 1900, Carlo Erba Instruments). Areas of microporous catalysts (Y-zeolite support) were calculated according to Dubinin method, whereas areas of MCM-41 supported catalyst were evaluated by the BET method.

The content of organic residues in catalysts was determined by automatic CHN analyser (Perkin-Elmer 2400, USA). The average carbon content was calculated from three independent measurements.

The chlorine content was determined by the Wickbold method [33]. The applied technique is suitable for the determination of low chlorine loading.

The deactivation is widely studied in the gas-phase reactions, therefore, properties of spent catalysts deactivated in the liquid and gas-phase reactions were compared. One of the main problems in gas-phase isomerisation of 1-butene to isobutene over the 12-membered ring zeolites is well known: fast catalysts deactivation. Therefore, gas-phase deactivation of fresh 2.5% Ru/Y was realised at atmospheric pressure at 623 K by passing 1-butene stream (30 ml/min) over the catalyst for 10 minutes or 2 hours. Such deactivated catalysts were treated as described above (washing and activation) and tested in liquid-phase hydrogenation of cinnamaldehyde.

2.2. *Catalyst testing*

Prior to hydrogenation each catalyst sample (mean particle size 23 μm) was activated in hydrogen flow (2 hours, 573 K). Liquid-phase hydrogenations of cinnamaldehyde (98%, Aldrich) were carried out under total pressure of 5.0 MPa at 373 K in a 500 ml stirred batch reactor (Autoclave Engineers, USA). Reactions were performed within the kinetic region in cyclohexane (p.a., Merck).

The reaction products were identified with GC–MS and analysed by GC (HP-6890, Hewlett-Packard, USA). Content of individual components in the reaction mixture was determined by the Internal Standardisation Method (*n*-decane, Aldrich, USA).

After the reaction, spent catalysts were filtered and carefully washed with small doses (10–20 ml) of p.a. acetone (total amount of acetone ∼ 500 ml). Washed catalysts were dried for 1 hour in oven at 378 K.

Since in some cases strong catalyst deactivation was observed, making the one-point evaluation of selectivity and activity misleading, the complete reaction courses for each reaction are presented.

3. Results

In principle, hydrogenation of cinnamaldehyde over Ru and Pt catalysts might give various undesired by-products such as aromatic ring hydrogenation and hydrogenolytic products. Formation of such compounds was observed in the present study, however, only for the fresh catalysts and their amount was insignificant. Therefore, the main reaction network can be described as presented in Fig. 1. The desired product is cinnamylalcohol (B).

3.1. *Catalyst activity and selectivity*

Repeated experiments carried out over the Ru/Y catalyst indicated an increase of selectivity towards cinnamylalcohol, however, activity remained constant (Fig. 2).

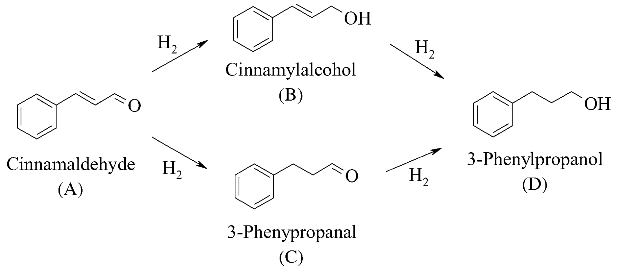

Fig. 1. Cinnamaldehyde hydrogenation network.

During the first hydrogenation run the obtained selectivity was ca. 25% (at 50% conversion), whereas the selectivity reached ca. 50% and 60% during the second and third experiment, respectively. Observed selectivity enhancement was accompanied with catalyst fouling and with surface area decrease.

The same Ru/Y catalyst but gas-phase deactivated under 1-butene flow (10 minutes, 2 hours) exhibited similar activity compared to liquid-phase deactivated catalyst. At the same time moderately improved selectivity compared to the fresh catalyst was noticed (Fig. 3), however, lower than the selectivity achieved over liquid-phase deactivated catalyst.

Deactivation of Ru/MCM-41 catalyst during the three experiments was more profound. The lowest activity was observed during the third run, along with (as in case of Ru/Y) the highest selectivity (Fig. 4). Selectivity increased from ca. 2% (first run) to 35% in second run and to 45% in the last third run (at 50% conversion).

Although impressive enhancement of cinnamylalcohol selectivity over the MCM-41 supported catalysts was achieved (from 2 to 45%), still the Y-zeolite supported catalyst exhibited higher selectivity (60%) after the third run.

The strongest catalyst deactivation was observed over the Pt/Y catalyst (Fig. 5A). Similar to previous cases, the selectivity towards cinnamylalcohol increased from one run to the following one (Fig. 5B).

3.2. *Characterisations*

The results presented in Table 1 confirm fast coke deposition in the microporous Y-zeolite catalysts, while slower coking has been observed over the mesoporous MCM-41 catalyst. Regarding the gas-phase pre-deactivation; the deposition was exceptionally fast, the indicated carbon content after 10 minutes of gas-phase reaction was equal to carbon content detected after 6 hours of liquid-phase hydrogenation.

In context with obtained results the maximum content of carbonaceous deposits in Y-zeolite can probably reach about 16–17%. These values correspond with the cited work of Forzatti and Lietti [29]. The deposition is assumed to occur mainly within the inner surface of the catalyst since higher content of coke was revealed in microporous catalysts.

Table 1
Carbon content (wt.%)

Catalyst	2.5 wt.% Ru/Y	2.5 wt.% Pt/Y	2.5 wt.% Ru/MCM-41
Fresh	0.0	0.0	0.0
After first run	14.1	7.0	5.3
After second run	15.8	12.8	7.5
After third run	16.1	16.3	8.1
Gas-phase pre-deactivated			
After 10 min TOS[a]	14.4		
After 2 h TOS	16.4		

[a] Time on stream.

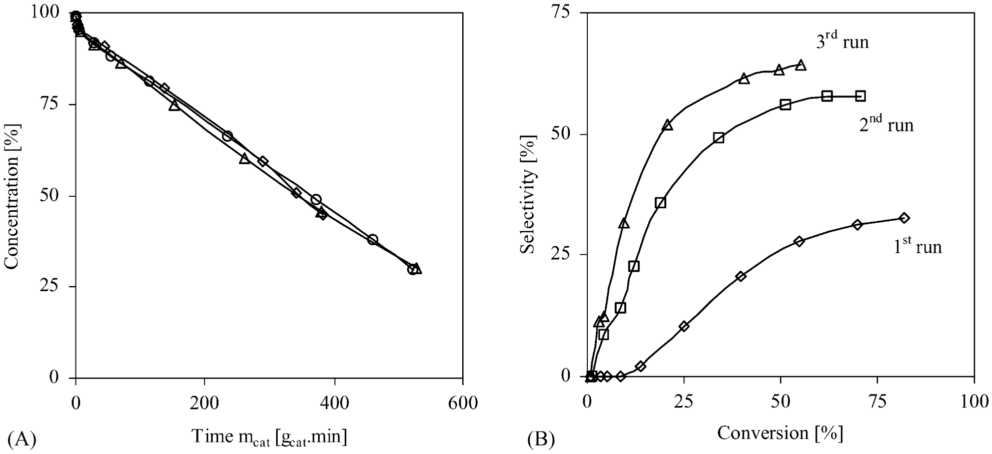

Fig. 2. Repeated runs with the 2.5% Ru/Y catalysts: (A) activity; (B) selectivity towards cinnamylalcohol.

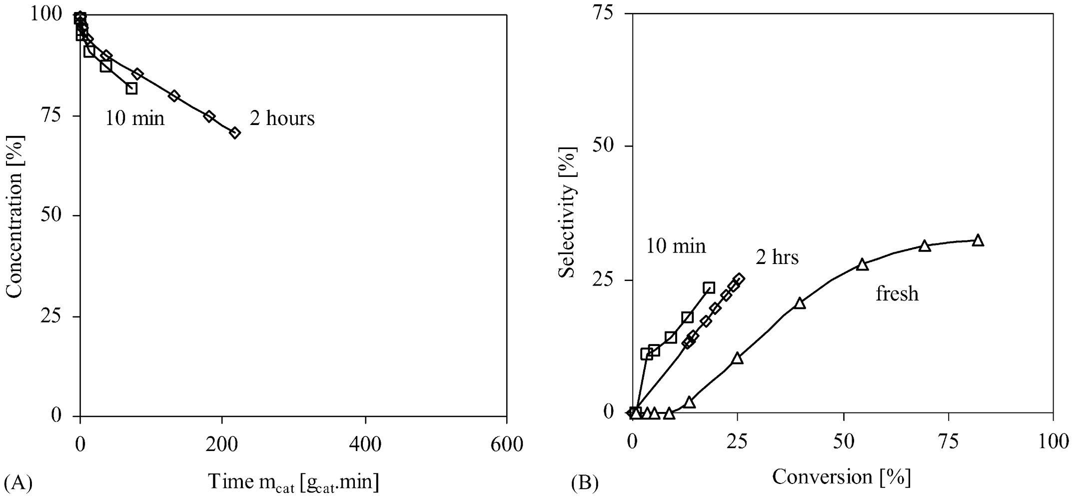

Fig. 3. Gas-phase (1-butene) deactivated 2.5% Ru/Y catalysts: (A) activity; (B) selectivity towards cinnamylalcohol.

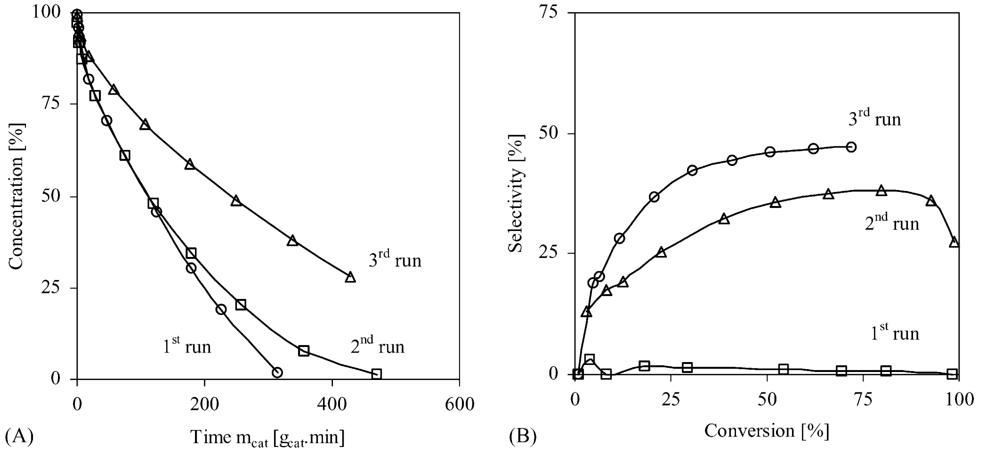

Fig. 4. Repeated runs with the 2.5% Ru/MCM-41 catalysts: (A) activity; (B) selectivity towards cinnamylalcohol.

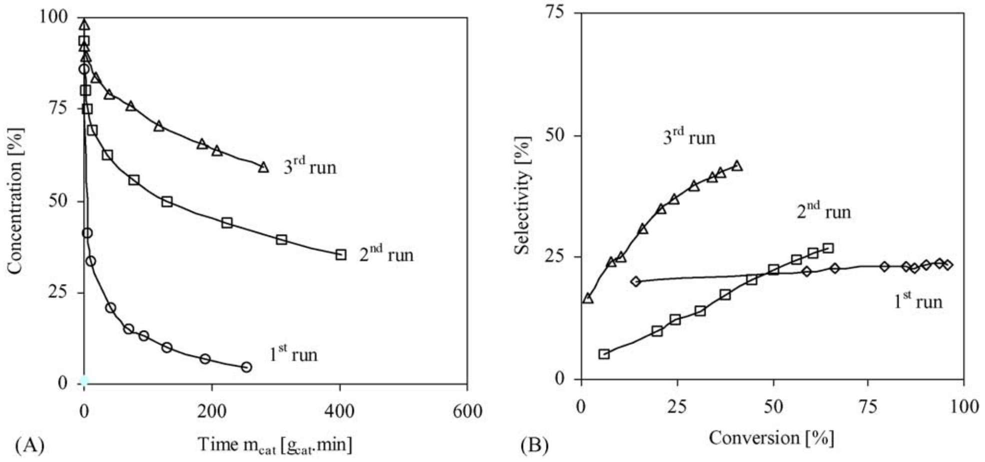

Fig. 5. Deactivation of 2.5% Pt/Y catalysts: (A) activity; (B) selectivity towards cinnamylalcohol.

Various analytical methods can be employed in the characterisation of coke deposits [30]. The identity can be well established by spectroscopic methods (IR, UV–vis) and other common analytical techniques (GC–MS, NMR). To determine coke composition the coke must be first separated from the catalyst. Simple separation for alumosilicate catalysts is based on the dissolution of catalyst in 40% HF [30]. Liberated deposits are extracted by CH_2Cl_2 and identified. Characterisation of insoluble fraction (complex and often very polyaromatic compounds) is usually reduced to elemental composition analysis.

Although it was verified that this procedure does not cause any transformation of the coke [34], some reaction products of cinnamaldehyde hydrogenation (including cinnamaldehyde itself) are relatively unstable. Furthermore, all compounds are poorly soluble in highly apolar solvents. Therefore an alternative way—soxhlet treatment—to extract the coke was employed. Spent and washed catalyst samples were boiled for 12 h under total reflux in methanol (p.a., Merck), and extracted material was analysed by GC–MS. Analysis proved the only presence of the main reactants (A, B, C, D).

Surface measurements of fresh and spent catalysts confirmed results presented in Table 1. The surface decrease of the microporous catalysts (Y-zeolite) was profound. After the first reaction the surface decreased by about 70% while three consecutive reactions caused 90% surface area loss (Table 2).

The identified deposits were well soluble in polar solvents, i.e. in acetone (washing). According to results reported in Tables 1 and 2 washing procedure applied between runs (see Section 2.2) did not remove them. Most probably molecules adsorbed on the outer surface of the catalyst particles were removed, whereas capillary forces in micropores restricted the removal from the inner surface of Y-zeolite catalyst support. The mesoporous catalyst (Ru/MCM-41) did not exhibit such high carbon content and deep area decrease, the plausible explanation for it should be related to support structure with larger mesopores.

Chlorine content in fresh catalysts (prior activation) indicated the exact content of active metals, since both Ru and Pt precursors ($RuCl_3$, H_2PtCl_6) contain chlorine. The measured values (Table 3) correspond well with anticipated ones. The level of residual chlorine content in spent catalysts after activation shows that complete metal reduction has been achieved. Temperature 573 K is reported, however, dependent also on support, as sufficient one to achieve total reduction of chlorine precursors of both metals [35–37]. Complete $RuCl_3$ reduction at 473 K on the Y-zeolite support was previously confirmed by ESCA [38].

The mean metal particle sizes were measured by X-ray diffractometer (Philips PW 1800) using the Scherrer equation. The measured XRD patterns of metal modified supports were compared to pattern of the pure support in order

Table 2
Surface area of catalysts

Catalyst (m^2/g)	2.5 wt.% Ru/Y	2.5 wt.% Pt/Y	2.5 wt.% Ru/MCM-41
Fresh	903	1088	1105
After first run	333	290	869
After second run	140	171	1069
After third run	85	80	837
Gas-phase deactivated			
After 10 min TOS	185		
After 2 h TOS	128		

Table 3
Chlorine content (wt.%)

Catalyst	2.5 wt.% Ru/Y	2.5 wt.% Pt/Y	2.5 wt.% Ru/MCM-41
Fresh	2.5	3.1	2.3
After first run	0.2	0.4	0.4
After second run	0.2	0.2	0.4
After third run	0.3	0.2	0.4
Gas-phase deactivated			
After 10 min TOS[a]	0.9		
After 2 h TOS	0.9		

[a] Time on stream.

Table 4
Mean particle sizes according to XRD

Catalyst	Mean particle size (nm)
Ru/Y	3.1–3.3
Ru/MCM-41	20.9–21.9
Pt/Y	3.5–3.7

to eliminate the possibility the metal peaks coincide with the support patterns. According to our previous experience the obtained results could give overestimated values [39]. The XRD results are presented in Table 4.

From the results it is not apparent where the majority of particles is located. However, since the catalysts were prepared by wet impregnation and the mean particle size is higher than support openings it is probable that majority of metal particles is located outside pores.

Since the openings of Y-zeolite are smaller compared to mean metal particle sizes it is apparent that the particles on the outer surface are mostly the larger one. For the mesoporous MCM-41 catalyst the situation is analogous.

4. Discussion

Since catalytic performance during the repeated runs turns up to be related to the character and the amount of carbon deposits it can be presumably affected also by the location of deposits.

Guisnet [30] for the transformation of *n*-hexane over microporous HZSM-5 zeolite reported that the deposition started within the inner surface, whereas during the final period of the reaction the deposition took place at the outer surface. At the same time the coke formed from mesitylene (1,3,5-trimethylbenzene) was deposited only at the outer surface [30].

The results might be probably associated to molecular sizes of reacting molecules. To confirm this assumption and to asses the possible diffusion of cinnamaldehyde, hexane and mesitylene in zeolites—molecular modelling was applied. Geometries were optimised by the Hartree–Fock (HF) approximation with the 6–31+G* basis set [40–43] using the Gaussian 98 program [44].

The size of the molecules of HF optimised conformations along *x*-, *y*- and *z*-axis are given in Table 5. The diameters along the three axes are estimated calculating Connolly-surface [45] with a probe radius of 1.4 over an optimised molecule geometries. Estimations of the minimum diameters of the molecules are given in Table 5. The sizes of the molecules compared to the pore sizes of FAU (Y-zeolite) and MFI-structures (HZSM-5) are illustrated in Fig. 6. Visualisations and estimations were done by Cerius2 (version 4.6, Accelrys inc.) and Molekel (version 4.0, Swiss Center for Scientific Computing, 2000) software.

Table 5
Estimated distances of HF optimized geometries along *x*-, *y*- and *z*-axes

Molecule	*x*	*y*	*z*	Minimum diameter[a]
Hexane	1.03	0.47	0.41	<0.5
Mesitylene	0.82	0.88	0.41	>0.8
Cinnamaldehyde	1.10	0.34	0.67	<0.5

Distances are given in nm.

[a] Minimum pore diameter accesible for molecule.

The pore size of FAU structure is 0.74 nm × 0.74 nm, for MFI 0.55 nm × 0.51 nm and 0.53 nm × 0.56 nm, respectively [46]. While comparing these values with calculated distances in Table 5 and illustrations in Fig. 6, it can be inferred that hexane diffuses inside the pores of MFI as well as cinnamaldehyde in FAU, but mesitylene is too bulky having serious difficulties to penetrate pores of MFI.

Aforesaid calculations confirm results of Guisnet [30] proving that the deposition in *n*-hexane transformation might start within inner surface which is accessible for the reactant molecule. At the same time deposits formed from mesitylene can be placed only on the outer catalyst surface since the molecule cannot easily enter the micropores of HZSM-5.

Following Guisnet [30] in conclusions we can infer that in our case coke deposition in liquid-phase hydrogenation of cinnamaldehyde most probably started within inner structure of the Y-zeolite support and after the pores were more or less filled the deposition took place at the outer surface. This correlates well with characterisation data, e.g. amount of coke and surface area decrease. Similar mechanism will be probably applicable also for the mesoporous MCM-41 support.

Based on characterisation data and aforesaid results we present two concepts that might partially explain the observed reaction behaviour.

1. Particle size effect concept.
2. Concentration dependent mode of the adsorption concept.

4.1. Particle size effect

Due to adsorption on the inner surface of the catalysts that proceeds from the early beginning of hydrogenation, the small metal particles inside pores would become inaccessible and the only free active sites (relatively large particles) remain at the outer catalyst surface.

The fact that formation of cinnamylalcohol is favoured on larger particles was previously noticed in several studies [39,47–49]. The observed selectivity increase during the reaction thus might be associated to reaction progress as the small metal particles, found inside pores that lower selectivity, are stepwise blocked (since it can be assumed metal particles on the outer surface are bigger than these in pores). The minor deactivation in repeated runs will then correspond with the fact that majority of active sites is located on the outer catalyst surface that is accessible to washing procedure applied among runs thus removing deposits from it. Relatively high initial reaction rates, presented reaction pathways as well as the high content of coke support the assumption of fast pores blocking. Presented concept cannot explain, however, much more pronounced deactivation over Pt/Y catalyst as well as

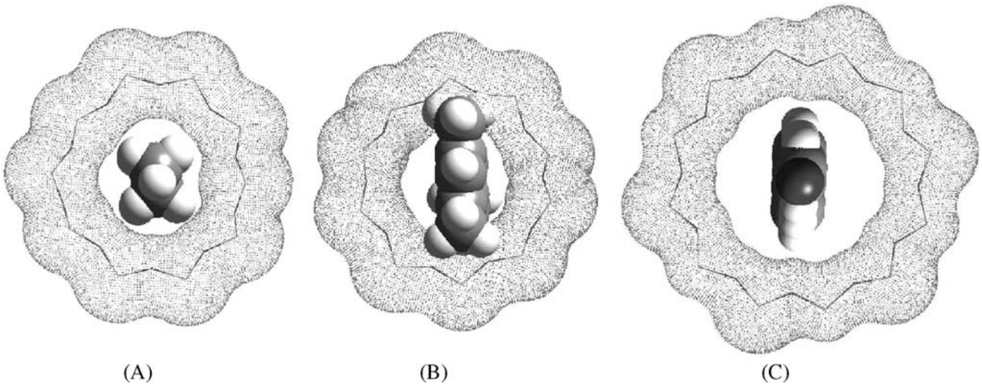

Fig. 6. Comparison of molecular and pore sizes: (A) hexane; (B) mesitylene and the MFI pore; (C) cinnamaldehyde and the FAU pore.

lower selectivity of gas-phase deactivated catalysts. In this case probably also other phenomena such as the metal effect or nature of coke should be taken into account.

4.2. Concentration dependent adsorption mode

As the analysed deposits were only the reaction products the observed activity and selectivity-conversion dependence is discussed below in terms of reactants adsorption.

Concentration dependent mode of cinnamaldehyde adsorption was recently demonstrated by Berger et al. [50]. It was supposed that the adsorption mode of cinnamaldehyde at high concentrations differs from that at lower concentrations. In particular, cinnamaldehyde was thought to adsorb perpendicular to the catalyst surface with the aromatic rings in parallel arrangements. At the same time the absolute conversion rate was about the same.

Another worthy example is catalytic enantioselective hydrogenation of ketones, namely reaction network in 1-phenyl-1,2-propanedione hydrogenation. Over a non-modified, conventional catalyst, the diketone readily adsorbs in a planar position, where carbonyl group in α position and the phenyl ring are in the same catalyst plane, and the reaction is regioselective in this C=O group. The regioselectivity changes, if small amounts of catalyst modifier are added. The aromatic ring hydrogenation is no longer possible (as indicated by the disappearance of the cyclohexyl products) since the adsorbed modifier occupies the surface in such a way that the planar adsorption of the reactant is not favoured. This implies that the carbonyl groups are adsorbed on somewhat tilted orientation and that the adsorption mode of the reactant depends on the modifier coverage of the catalyst surface [51].

In hydrogenation of cinnamaldehyde removal of adsorbed reactants was not achieved (as it follows from characterisation data) and accumulated adsorbate would cause observed behaviour, i.e. considerably increased selectivity (25%) between the first and the second run. More specifically, on the surface adsorbed species can cause the self-assembling effect as described above, thus improving the selectivity towards cinnamylalcohol. Correspondingly, since adsorbate (coke) content does not increase extensively between the second and third run (Table 1) further major selectivity increase would not be expected. Indeed, the observed minor selectivity increase confirms this prediction.

Following characterisation results, properties of the 1-butene gas-phase deactivated catalysts are comparable to the catalyst after second or third liquid-phase run. It can be concluded (Tables 1 and 2) that fast gas-phase deactivation of Y-zeolite (12-membered ring) in flow of 1-butene led to deposition of maximum coke content (16–17%) in about 10 minutes or less. Hydrogenation experiments confirmed this conclusion, since selectivity as well as activity were similar no matter if the catalyst was deactivated for 10 minutes or 2 hours.

Comparing the selectivity and activity of corresponding catalysts (Figs. 2 and 3) the apparent conclusion is that gas-phase deactivated catalysts exhibited about the same activity and lower selectivity than the liquid-phase deactivated catalyst.

In the gas-phase deactivation skeletal isomerisation of 1-butene the Y-zeolite with 12-membered ring system do not suppress the formation of carbonaceous deposits and the pores get quickly blocked [52]. On a fresh HFER zeolite at 623 K coke formed during the skeletal isomerization of 1-butene was found to be composed of slightly condensed (2–4-membered ring) aromatics [53]. Coke molecules resulted from the transformation of secondary benzenic products. Less then 5% of the coke was recovered by soxhlet extraction indicating the deactivation during the reaction was due to the growth of the coke molecules in the zeolite pores [54].

In context of characterisation data the main difference between the differently pretreated catalysts in this study seems to be the character of coke, i.e. aromatic coke in case of gas-phase deactivation and non-desorbed reaction products in case of liquid-phase reaction.

Although the presented concepts are reasonably supported by the observed reaction behaviour, characterisation methods, and by literature data it was not possible to distinguish which of these two concepts prevails. Moreover the observed catalytic behaviour can be probably more complex and combination of the presented concepts as well as some other effects should be taken into account and applied. For instance, the steric aspects are reported to play an important role in hydrogenation of cinnamaldehyde over microporous zeolites [8,55]. The influence of such effects might contribute to higher yields of cinnamylalcohol over Ru/Y compared to Ru/MCM-41.

5. Conclusions

The properties of 2.5% Ru/Y, 2.5% Pt/Y and 2.5% Ru/MCM-41 were tested in the liquid-phase hydrogenation of cinnamaldehyde. Three consecutive runs with the same catalyst batches were performed in order to evaluate the deactivation.

Catalyst activity in repeated experiments was influenced by the support and by the active metal used. No activity changes were observed over the Ru/Y catalyst, while moderate and strong activity decrease was obtained over Ru/MCM-41 and Pt/Y catalyst.

Typically an increase of selectivity towards cinnamylalcohol during the experiments was visible. Considerable selectivity increase (ca. 20–30%) was noticed after the first reaction during the second run, further less pronounced selectivity increase (ca. 10%) was obtained in the third run. The microporous Ru/Y catalyst exhibited higher yields of cinnamylalcohol than mesoporous Ru/MCM-41.

Elementary analysis confirmed fast accumulation of carbonaceous deposits, namely within microporous Y zeolite, maximum content of deposits reached 16–17 wt.%. Soxhlet extraction proved the presence of reaction products and reactant as carbonaceous deposits.

Special deactivation experiments were performed by flowing 1-butene over Ru/Y catalyst. Characterisation data demonstrated similar properties of such gas-phase deactivated catalysts (carbon content, surface area decrease), however, lower selectivity towards cinnamylalcohol compared to liquid-phase deactivated catalyst were achieved.

Acknowledgement

This work is part of the activities at the Åbo Akademi University Process Chemistry Centre within the Finnish Academy Centre of Excellence Programme (2000–2005). Support given by the Grant Agency of the Czech Republic (grant number 104/03/0409) and the Finnish Graduate School of Chemical Engineering is greatly acknowledged.

References

[1] J.A. Moulijn, M. Makkee, A. van Diepen, Chemical Process Technology, Wiley, New York, 2001.
[2] R.A. Sheldon, Fine Chemicals Through Heterogeneous Catalysis, Wiley-VCH, Weinheim, 2001.
[3] H.F. Rase, Handbook of Commercial Catalysts: Heterogeneous Catalysts, CRC Press, Boca Raton, 2000.
[4] P.Z. Bedoukian, Perfumery Synthetics and Isolates, van Nostrand, Toronto, 1951.
[5] L.A. Greenberg, D. Lester, Handbook of Cosmetic Materials, Interscience, New York, 1954.
[6] Ullmann's Encyclopedia of Industrial Chemistry, vol. 14, Wiley-VCH, Weinheim, 2003.
[7] P.N. Rylander, D.R. Steele, Tetrahedron Lett. (1969) 1579.
[8] P. Gallezot, D. Richard, Cat. Rev.–Sci. Eng. 40 (1998) 81.
[9] B. Coq, A. Bittar, R. Dutartre, F. Figueras, J. Catal. 128 (1991) 275.
[10] G. Neri, L. Mercadante, C. Milone, R. Pietropaolo, S. Galvagno, J. Mol. Catal. A: Chem. 108 (1996) 41.
[11] V. Ponec, Appl. Catal. A 149 (1997) 27.
[12] J.P. Candy, B. Didillon, E.L. Smith, T.B. Shay, J.M. Basset, J. Mol. Catal. 86 (1994) 179.
[13] W.F. Tuley, R. Adams, J. Am. Chem. Soc. 47 (1925) 3061.
[14] P. Claus, Top. Catal. 5 (1998) 51.
[15] J.C. Van Der Waal, H. Van Bekkum, J. Porous Mater. 5 (1998) 289.
[16] C.R. Marcilly, Top. Catal. 13 (2000) 357.
[17] A. Corma, J. Catal. 216 (2003) 298.
[18] C.B. Dartt, M.E. Davis, Catal. Today 19 (1994) 151.
[19] S.J. Kulkarni, Stud. Surf. Sci. Catal. 113 (1998) 151.
[20] M.G. Clerici, Top. Catal. 13 (2000) 373.
[21] D. Wallenstein, R.H. Harding, J.R.D. Nee, L.T. Boock, Appl. Catal. A 204 (2000) 89.
[22] J.N. Beltramini, Chem. Ind. (Dekker) 61 (1995) 313.
[23] M.V. Twigg, M.S. Spencer, Top. Catal. 22 (2003) 191.
[24] N.M. Ostrovskii, Kinetics of Catalysts Deactivation, Nauka, Moscow, 2001.
[25] J. Edvardsson, P. Rautanen, A. Littorin, M. Larsson, J. Am. Oil Chem. Soc. 78 (2001) 319.
[26] M. Lindroos, P. Maki-Arvela, N. Kumar, T. Salmi, D.Yu. Murzin, T. Ollonqvist, J. Vayrynen, Chem. Ind. (Dekker) 89 (2003) 587.
[27] E.E. Petersen, A.T. Bell, Catalyst Deactivation, Marcel Dekker, New York, 1987.
[28] J.B. Butt, E.E. Petersen, Activation, Deactivation and Poisoning of Catalysts, Academic Press, San Diego, 1988.
[29] P. Forzatti, L. Lietti, Catal. Today 52 (1999) 165.
[30] M. Guisnet, in: G. Ertl, H. Knözinger, J. Weitkamp (Eds.), Handbook of Heterogeneous Catalysis, vol. 2, pp. 626–632.
[31] J.S. Beck, J.C. Vartuli, W.J. Roth, M.E. Leonowicz, C.T. Kresge, K.D. Schmitt, C.T.W. Chu, D.H. Olson, E.W. Sheppard, et al., J. Am. Chem. Soc. 114 (1992) 10834.
[32] K.M. Reddy, C. Song, Catal. Lett. 36 (1995) 103.
[33] R. Wickbold, Angew. Chem. 64 (1952) 133.
[34] M. Guisnet, P. Magnoux, Appl. Catal. 54 (1989) 1.
[35] W. Koo-amornpattana, J.M. Winterbottom, Proceedings of the Two-Day Symposium on IChemE Research Event, Newcastle upon Tyne, 7–8 April 1998, p. 1528.
[36] A.E. Newkirk, D.W. McKee, J. Catal. 11 (1968) 370.
[37] P.G.J. Koopman, A.P.G. Kieboom, H. Van Bekkum, React. Kinet. Catal. Lett. 8 (1978) 389.
[38] J. Hajek, N. Kumar, P. Maki-Arvela, T. Salmi, D.Y. Murzin, I. Paseka, T. Heikkila, E. Laine, P. Laukkanen, J. Vayrynen, Appl. Catal. A 251 (2003) 385.
[39] M. Lashdaf, A.O.I. Krause, M. Lindblad, M. Tiitta, T. Venalainen, Appl. Catal. A 241 (2003) 65.
[40] R. Ditchfield, W.J. Hehre, J.A. Pople, J. Chem. Phys. 54 (1971) 724.
[41] W.J. Hehre, R. Ditchfield, J.A. Pople, J. Chem. Phys. 56 (1972) 2257.
[42] T. Clark, J. Chandrasekhar, P.V.R. Schleyer, J. Comp. Chem. 4 (1983) 294.
[43] P.C. Hariharan, J.A. Pople, Theoret. Chim. Acta 28 (1973) 213.
[44] M.J. Frisch, G.W. Trucks, et al., Gaussian 98, Revision A.11.3, Gaussian Inc., Pittsburgh, PA, 2002.
[45] M.L. Connolly, J. Appl. Cryst. 16 (1983) 548.
[46] Ch. Baerlocher, W.M. Meier, D.H. Olson, Atlas of Zeolite Framework Types, Elsevier, Amsterdam, 2001.

[47] A. Giroir-Fendler, D. Richard, P. Gallezot, Catal. Lett. 5 (1990) 175.

[48] S. Galvagno, G. Capannelli, G. Neri, A. Donato, R. Pietropaolo, J. Mol. Catal. 64 (1991) 237.

[49] L. Mercadante, G. Neri, C. Milone, A. Donato, S. Galvagno, J. Mol. Catal. A 105 (1996) 93.

[50] R.J. Berger, E.H. Stitt, G.B. Marin, F. Kapteijn, J.A. Moulijn, CATTECH 5 (2001) 30.

[51] D.Yu. Murzin, Recent Res. Dev. Catal. 2 (2003) 143.

[52] J. Houzvicka, S. Hansildaar, J.G. Nienhuis, V. Ponec, Appl. Catal. A 176 (1999) 83.

[53] P. Andy, N.S. Gnep, M. Guisnet, E. Benazzi, C. Travers, J. Catal. 173 (1998) 322.

[54] F. Machado, C. Canaff, M. Guisnet, P. Magnoux, Rev. Soc. Venez. Catal. 4 (1990) 37.

[55] D.G. Blackmond, R. Oukaci, B. Blanc, P. Gallezot, J. Catal. 131 (1991) 401.