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Short overview on the application of metal-modified molecular sieves in selective hydrogenation of cinnamaldehyde

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Abstract

This article shortly overviews our recent work on the application of metal supported molecular sieve catalysts in liquid-phase hydrogenation of cinnamaldehyde. The topic covers catalyst deactivation, influence of the support, active metals as well as the influence of reaction conditions on catalytic performance. Acquired results demonstrate superior performance of microporous supports (zeolites) compared to mesoporous MCM-41, which was relatively unselective and less active. At optimised conditions, selectivity towards cinnamylalcohol of about 60–70% and reasonable activity were achieved.

Keywords: Cinnamaldehyde hydrogenation; Cinnamylalcohol; Zeolite catalysts

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1. Introduction

Selective hydrogenation of α,β-unsaturated aldehydes yields unsaturated alcohols, industrially valuable products and intermediates for the synthesis of fine chemicals [1–3].

The desired product in hydrogenation of cinnamaldehyde is cinnamylalcohol, an important additive in food industry, perfumery and an intermediate in the production of certain pharmaceutics [4]. Despite economic drawbacks the conventional method used for many years for the reduction of cinnamaldehyde is based on the Meerwein–Ponndorf–Verley reaction giving after the purification the yield of cinnamylalcohol 85–90% [5]. It is apparent that the application of heterogeneous catalysis might be advantageous. At the same time the reaction might give a broad spectrum of by-products originating from undesired aromatic ring hydrogenation, hydrogenolytic and condensation reactions [6], and therefore selectivity aspects are crucial.

Molecular sieves represent attractive catalysts or supports for a broad spectrum of reactions. Their particular properties such as tunable microstructure, acidity, shape selectivity make them essentially important in crude oil refining [7]. Surprisingly there are only few reports on the application of metal-modified molecular sieves in hydrogenation of unsaturated aldehydes.

The main aim of this short paper is to briefly overview our recent work on the application of metal-modified molecular sieve catalysts in liquid-phase hydrogenation of 3-phenyl-2-propenal (cinnamaldehyde).

2. Experimental

The synthesis of mesoporous Na-MCM-41 support was based on well-known procedures [8,9] with some minor modifications. The NH_4-Y, NH_4-Beta and NH_4-Mordenite supports (Zeolyst International, CBV 712, CP 814E, CBV 21A) and 5 wt.% Pt/C (Johnson & Matthey, 5R18/264), 5 wt.% Ru/C (Johnson & Matthey, 5R97/6) catalysts were obtained from commercial sources. The NH_4-Beta, NH_4-Y and NH_4-Mordenite zeolite were transformed to H-form by calcination in a muffle oven and wet-impregnated by an aqueous solution of H_2PtCl_6 (40% Pt, Degussa) or $RuCl_3{\cdot}xH_2O$ ($x \leq 1$, Sigma Aldrich). The impregnation was carried out in a rotary evaporator (Buchi Rotavapor R114) for a period of 24 h. Impregnated catalysts were dried in an oven at 383 K for 12 h.

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Hydrogenation of cinnamaldehyde (98%, Aldrich) was performed in a stirred batch reactor (500 ml, Autoclave Engineers) under kinetic region conditions. Reactions were typically carried out at 373 K under the total pressure of 5 MPa. Prior hydrogenation, catalysts were activated in hydrogen flow at 473–573 K for 2 h. 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). Initial catalysts activities were calculated as TOFs. The overall activity was determined from the conversion achieved after 4 or 6 h of hydrogenation, respectively. Selectivity was calculated as molar ratio of the formed product to the reacted substrate.

3. Discussion

In case of the catalysts used the present study, the reaction network can be represented by the simplified scheme on Fig. 1.

3.1. Support and metal effect

The evaluation of support effect was based on results obtained by comparing Pt-modified catalysts [10]. Due to observed deactivation the catalysts activities were related to conversion achieved after 4 h of hydrogenation (373 K, 5 MPa, cyclohexane).

Catalyst activity decreased in the order Pt/Mordenite $\gg$ Pt/C (Pt/NH$_4$-Y $\geq$ Pt/Y $\approx$ Pt/Beta $>$ Pt/MCM-41 while selectivity increased in the following order Pt/Beta $>$ Pt/Y $>$ Pt/NH$_4$-Y $\approx$ Pt/Mordenite $>$ Pt/C (Pt/MCM-41. The highest selectivity of ca. 40% was obtained at 67% substrate conversion over Pt/Beta. Pt/Y, Pt/NH$_4$-Y and Pt/Beta exhibited relatively high overall activity and selectivity that increased with conversion. Mesoporous Pt/MCM-41 catalyst was unselective. Commercial Pt/C exhibited constant selectivity about 10–12% up to high degree of conversion. Reaction rate over Pt/Mordenite catalyst was exceptionally high and selectivity decreased with conversion.

It can be concluded that catalysts activity generally increased with support acidity (concentration of Brønsted sites) while selectivity in unsaturated alcohol decreased (Fig. 2A1 and B1).

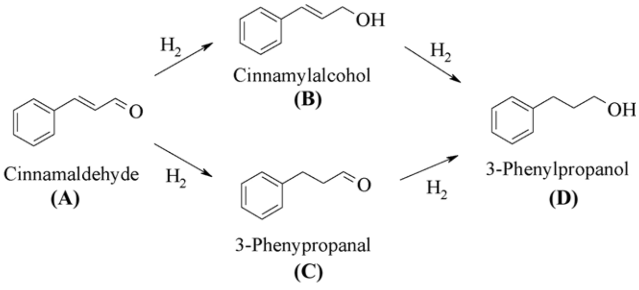

Fig. 1. Cinnamaldehyde hydrogenation network.

Comparison of Pt/C, Pt/Y and Pt/MCM-41 with analogous Ru catalysts showed that platinum ones were more active and slightly less selective.

3.2. Deactivation

Deactivation is generally of utmost importance for long-term performance of catalysts. In a number of catalytic processes carbonaceous deposits are formed from the reaction mixture. The process is referred as fouling or coking. In low-temperature reactions ($\leq$400 K), hydrocarbon transformation does not occur and the carbonaceous deposits are mostly the non-desorbed reaction products and reactants. Depending on molecular size deposition may not be uniform, starting either within the inner or the outer surface of the catalyst [11].

During previous experiments carried out in cyclohexane considerable deactivation of catalysts was observed. In order to study the deactivation three consecutive runs for each of tested catalysts (5% Ru/Y, 5% Ru/MCM-41, 5% Pt/Y) were performed [12].

Repeated experiments carried out over the Ru/Y catalyst indicated an increase of selectivity towards cinnamylalcohol, however, activity remained constant. 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 (Fig. 2A2 and B2).

Deactivation of Ru/MCM-41 catalyst was more profound. The lowest activity was observed during the third run, along with (as in case of Ru/Y) the highest selectivity. 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, 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. Similar to previous cases, the selectivity towards cinnamylalcohol increased from one run to the following one.

Characterisation data confirmed fast coke deposition in the microporous Y-zeolite catalysts, while slower coking has been observed over the mesoporous MCM-41 catalyst. The maximum content of carbonaceous deposits in Y-zeolite reached about 16–17%. Following conclusions of Guisnet [11], we infer that coke deposition during hydrogenation of cinnamaldehyde most probably starts within inner surface of the support and after the pores are more or less filled the deposition takes place on the outer surface. This correlates well with characterisation data, e.g. amount of coke and surface area decrease. On the basis of experimental data, two mechanistic concepts were invoked.

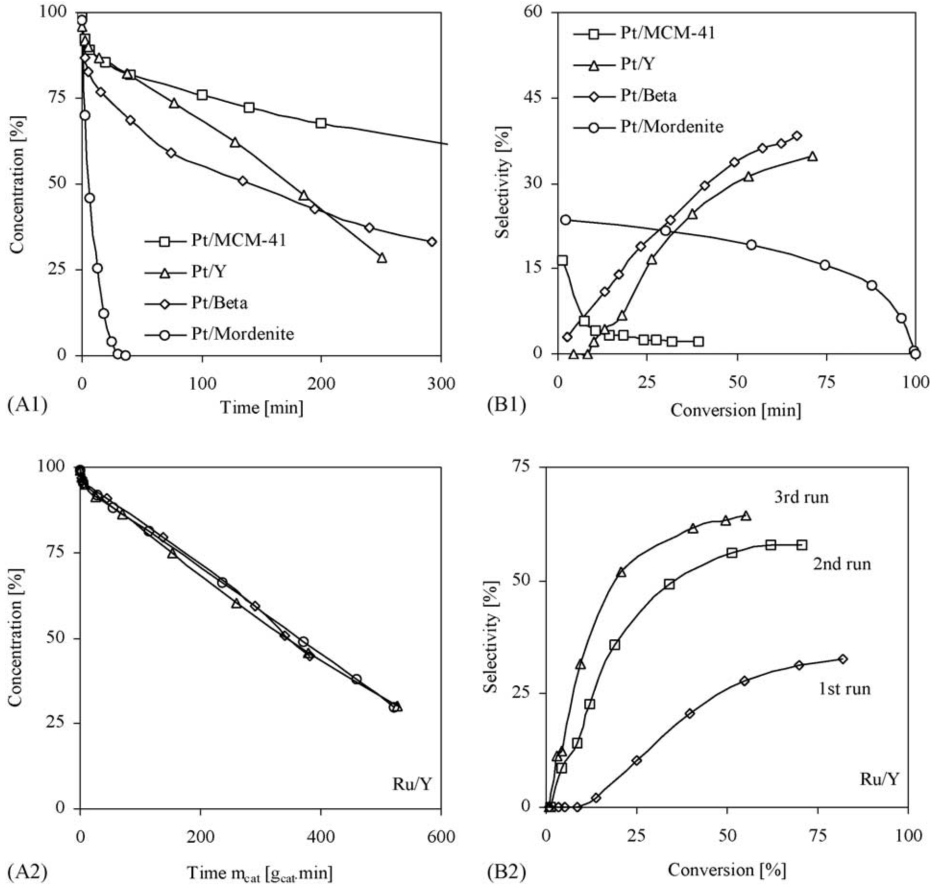

Fig. 2. Support effect (A1, activity; B1, selectivity towards cinnamylalcohol) and deactivation (A2, activity; B2, selectivity towards cinnamylalcohol).

3.2.1. Particle size effect concept

Due to adsorption on the inner surface the small metal particles inside pores may become inaccessible and the only free active sites (relatively large particles) will remain at the outer catalyst surface. The observed selectivity increase during the reaction thus might be associated to reaction progress in which the small metal particles, found inside pores are stepwise blocked.

The fact that formation of cinnamylalcohol is favoured on larger particles was previously noticed in several studies [13–15]. The minor deactivation in repeated runs will then correspond with the fact that majority of active sites is located on the outer catalyst surface. Presented concept cannot explain, however, more pronounced deactivation over the Pt/Y catalyst.

3.2.2. Concentration dependent mode of the adsorption concept

Concentration dependent mode of cinnamaldehyde adsorption and increased selectivity towards (**B**) at higher (**A**) concentrations was recently demonstrated [16]. In particular, cinnamaldehyde at higher concentrations was thought to adsorb perpendicular to the catalyst surface with the aromatic rings in parallel arrangements. Concurrently the absolute conversion rate remained at the same level.

The analysed deposits were only the reaction products and the removal of adsorbed reactants was not achieved (as it follows from characterisation data). Such accumulated adsorbate would cause observed selectivity increase in the repeated runs.

Although the presented concepts are feasible it is not yet possible to distinguish which of these two concepts prevails. 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. For instance, the steric aspects are reported to play an important role in hydrogenation of cinnamaldehyde over microporous zeolites [17,18].

3.3. Optimisation

To improve catalytic performance, several reaction parameters were systematically varied [19]. The tested 5% Ru/Y catalyst was prepared according to procedure described in Section 2 and deactivated by one run (6 h) in cyclohexane.

The solvent effect was evaluated using 14 common solvents. Typically, the effect of solvent varies with the whole set of its properties [20,21] and it has been shown that it is hardly possible to abridge the results [22]. The solvent

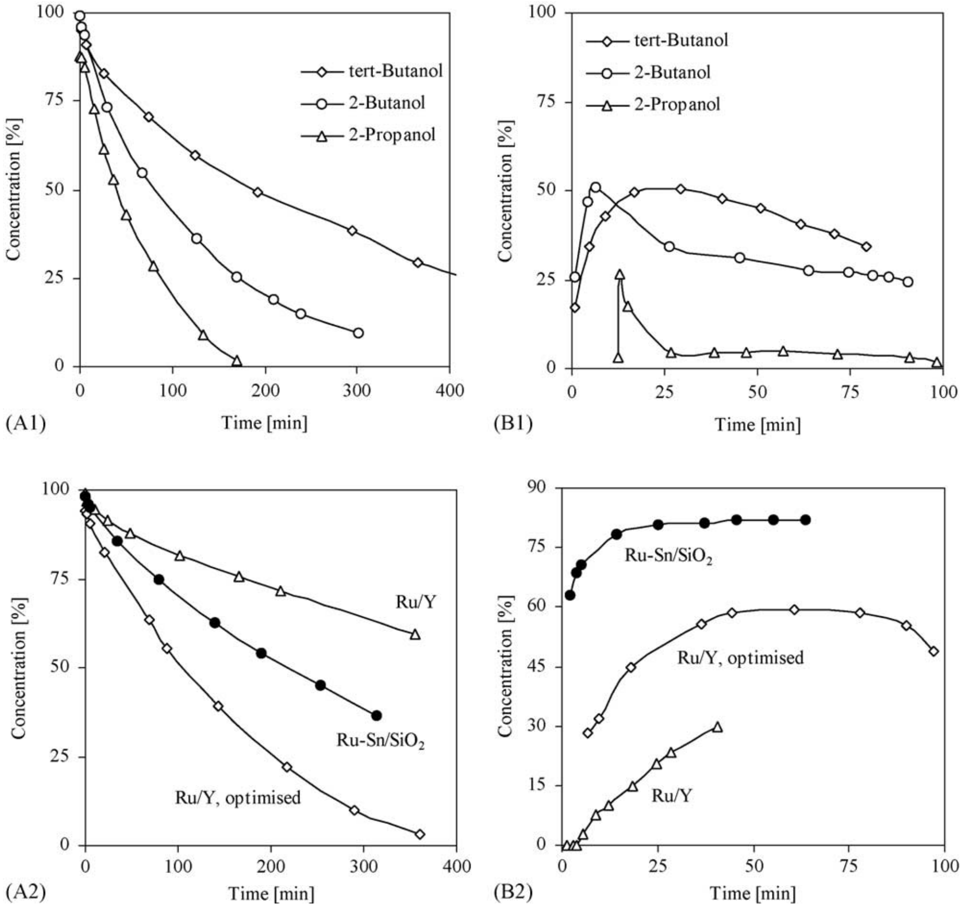

Fig. 3. Solvent effect (A1, activity; B1, selectivity towards cinnamylalcohol) and improved catalytic performance (A2, activity; B2, selectivity towards cinnamylalcohol).

effect in catalytic hydrogenations within the kinetic region comprises mainly its interactions with a substrate and a catalyst.

Typically for solvents within a particular group classified according to Parker [23], catalyst activity increased with polarity of the solvent, whereas selectivity decreased. Fig. 3A1 and B1 show such trend within polar solvents. Generally, the highest conversions were achieved in alcohols while highest selectivities were obtained in apolar solvents. Formation of condensation products particular for hydrogenations carried out in lower alcohols was avoided by using higher (less reactive) alcohols starting from *tert*-butanol.

In some cases, the substrate/catalyst ratio may affect catalyst activity and selectivity. Reaction in cyclohexane was very fast at the ratio of 3 but the selectivity was lost. At the highest ratio (24) large activity decrease and negligible selectivity improvement was indicated.

Selectivity towards (**B**) might be sensitive also to reaction temperature, as shown for Ru–Sn sol–gel catalyst [24]. However, current experiments did not prove it. The decrease of reaction temperature from 373 to 293 K demonstrated certain minor selectivity enhancement counterbalanced by massive decrease of the Ru/Y catalyst activity.

In the case of bimetallic Ru–Sn catalyst the improvement of activity was achieved by chemical reduction using $NaBH_4$ [25]. Comparison of $NaBH_4$ and N_2H_4 reduced Ru/Y with the non-reduced catalyst showed that the activity in the former case was increased by two to three times. Additionally, reduction by $NaBH_4$ did not affect the selectivity. Graphs on Fig. 3A2 and B2 demonstrate the improved performance over Ru/Y; data for Ru–Sn/SiO_2 [23] are given for comparison.

4. Conclusions

Presented results indicate that the activity of Pt-modified molecular sieves increased with support acidity while selectivity decreased. Obtained results also demonstrate better performance of microporous zeolites compared to mesoporous M41S representative (MCM-41) that was unselective towards unsaturated alcohol and less active. Platinum catalysts were more active and slightly less selective that ruthenium ones.

The reaction behaviour during repeated runs in cyclohexane indicated considerable deactivation of catalysts accompanied with substantial selectivity increase and typically with less significant activity decrease.

The activity of Ru/Y catalyst commonly increased with polarity of the solvent while the highest selectivities were obtained in apolar solvents. The highest selectivity of 70% at the conversion of 30% was achieved in toluene. Higher substrate/catalyst ratios (6–24) as well as decreased reaction temperature (373–293 K) had minor effect on selectivity. Chemical reduction by $NaBH_4$ increased catalyst activity by two to three times without lowering the selectivity. Improved selectivity from ca. 30 to 60% and significantly enhanced activity under optimised reaction conditions (373 K, 5 MPa, cyclohexane) were achieved.

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