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Suppression of catalyst deactivation by means of acoustic irradiation—Application on fine and specialty chemicals

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Abstract

The effect of acoustic irradiation has been studied in several hydrogenation reactions (1-phenyl-1,2-propanedione, ethyl-pyruvate and D-fructose hydrogenation) as well as in an esterification reaction over various heterogeneous catalysts. The reaction rate and selectivity were significantly improved under sonification in 1-phenyl-1,2-propanedione hydrogenation over Pt/SF (silica fiber) catalyst. Acoustic irradiation enhanced the reaction rate in esterification of propionic acid with ethyl alcohol over functionalized polymer fiber Smopex-101 catalyst compared to identical silent conditions. Furthermore, ultrasound remarkably suppressed catalyst deactivation in D-fructose hydrogenation over Raney-Ni catalyst. The spent catalysts used in the hydrogenation reactions either in presence or absence of acoustic irradiation were intensively studied by means of scanning electron microscopy (SEM) and transmission electron microscopy (TEM).

Keywords: Ultrasound; Heterogeneous catalyst; Fine and specialty chemicals

1. Introduction

Heterogeneously catalyzed reactions are the most important class of industrial reactions. A larger number of products ranging from bulk chemicals to alimentary and pharmaceutical substances are produced by means of heterogeneous catalysis with easy handling, separation and low costs being the clear benefits. One of the major problems related to the use of heterogeneous catalysts is the loss of catalyst activity and/or selectivity with time-on-stream, i.e. "deactivation". These deactivation processes are both of chemical and physical nature. These are commonly divided into four classes, namely poisoning, coking, sintering and phase transformation. Deactivation is inevitable, but it can be retarded or prevented and some of its consequences can be avoided [1] with clever process design. An elegant way to promote catalyst durability, activity and selectivity is to apply on-line acoustic irradiation during the course of reaction [2].

Ultrasound can retard catalyst deactivation by (catalyst) surface cleaning and exposing fresh, highly active surface as well as by the reduction of diffusion length in the catalyst pores by deformation of catalyst surface. Furthermore, strongly absorbed organic impurities that block active sites can be removed by sonification.

The sonic treatment can change the catalyst morphology and particle size [3] and when applied on-line, it can improve mass and heat transfer as well.

Acoustic irradiation can alter the reactivity of heterogeneous catalysts in a variety of reactions [4–13] as well as suppress the catalyst deactivation [14].

Two different modes of action of ultrasound can exist at different reaction conditions (intensity, pressure, etc.): cavitating and non-cavitating ultrasound (acoustic streaming). Cavitating ultrasound forms cavitation bubbles, which violently collapse on or near the catalyst surface and direct jets of liquids towards it. These shock waves cause localized deformation of catalyst surface involving intensive cleaning. Acoustic streaming is the movement of liquid induced by the sonic wave, which can be considered to be simply the conversion of sound to the kinetic energy, and is not a cavitation effect [15].

Four different model reactions were investigated and will be discussed in this paper: hydrogenation of 1-phenyl-1,2-propanedione, ethyl pyruvate and D-fructose and esterification of propionic acid with ethyl alcohol.

Enantioselective hydrogenation of activated ketones over cinchonidine-modified Pt catalyst has been intensively studied in recent years [16] and it has a vast potential for cheaper and more efficient pharmaceutical production. Ethyl pyruvate hydro-

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genation is the most studied model reaction and the reaction mechanism is fairly well known. In the present study, ethyl pyruvate was hydrogenated in the absence of cinchonidine modifier, as more severe catalyst deactivation could be anticipated. The main product of enantioselective 1-phenyl-1,2-propanedione hydrogenation, (*R*)-1-hydroxy-1-phenylpropanone which is an optically active hydroxyketone, is used as an intermediate in the synthesis of several drugs [17]. Previously, it has been reported [18,19] that during continuous hydrogenation of ethyl pyruvate and 1-phenyl-1,2-propanedione, a notable catalyst deactivation takes place. Therefore, it is important to study if ultrasound can prevent or, at least, retard this deactivation.

Selective hydrogenation of D-fructose to D-mannitol, is an interesting reaction, since the product is a low caloric sweetener [20]. D-mannitol is a sweet-tasting hexavalent sugar alcohol widely distributed in nature, found in olive trees, plane trees, fruits and vegetables. However, production of mannitol by extraction of plant raw materials is no longer economical. Instead, three phase catalytic hydrogenation of fructose or glucose–fructose syrups is the industrially dominating procedure [21].

An esterification reaction is a reaction between an alcohol and a carboxylic acid, leading to the formation of an ester and water. Organic esters are, e.g. a very important class of chemicals having applications in a variety of areas in chemical industry, such as perfumes, flavors, pharmaceuticals, plasticizers, solvents and intermediates [22].

2. Experimental

2.1. Reactor set-up

Two different types of ultrasonic equipment were used to carry out the experiments: high intensity horn system and high intensity transducer system. In case of enantioselective hydrogenation of 1-phenyl-1,2-propanedione and D-fructose hydrogenation, ultrasonic irradiation was obtained by an ultrasonic horn (AEA Technologies Inc.). The apparatus consisted of a generator (nominal operational frequency 20 kHz, adjustable power output 0–100 W), a piezoelectric stack transducer and a titanium horn (displacement 12 μm ± 1 μm peak to peak) with a tailor-made connection to the bottom of laboratory-scale pressure autoclave. In sonochemistry two different domains exist, e.g. cavitating and non-cavitating ultrasound regimes. Bath systems (low intensity ultrasound) are usually non-cavitating whereas probe systems can be either cavitating or non-cavitating [7]. In case of D-fructose hydrogenation, we assume that non-cavitating ultrasound regime persists since high H_2 pressures (30 bar) were applied. An increase of H_2 pressure leads to increase of the cavitation threshold and, thus, cavitation bubbles cannot be created [15].

Fig. 1. Multi-transducer set-up.

For ethyl pyruvate hydrogenation and esterification of propionic acid with ethyl alcohol, e.g. systems which do not require elevated pressures, high intensity transducer system was applied. The transducer system consisted of six transducers and a generator with adjustable power output 0–600 W and operating frequency of 20 kHz. The system operated on time variable on/off cycles and the reactor vessel was placed in the middle of the transducers (Fig. 1). With this ultrasound system it can be safely assumed that cavitating regime per-

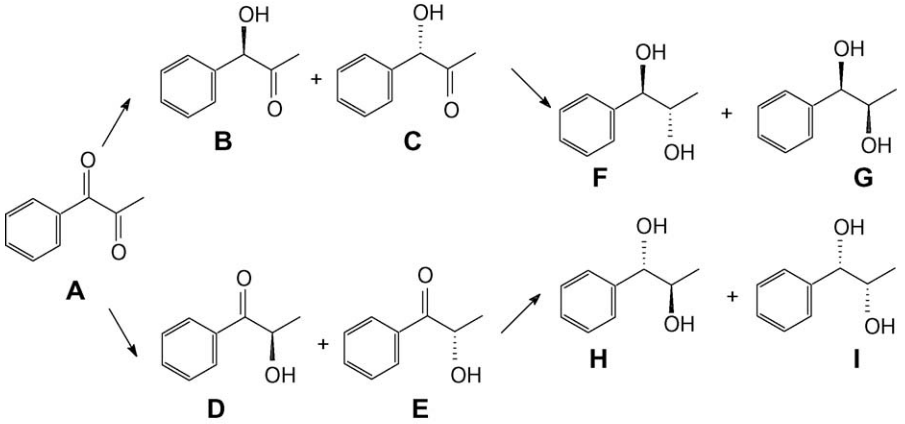

Fig. 2. Reaction scheme of 1-phenyl-1,2-propanedione. *Symbols*: **A**, 1-phenyl-1,2-propanedione; **B**, (*R*)-1-hydroxy-1-phenylpropanone; **C**, (*S*)-1-hydroxy-1-phenylpropanone; **D**, (*R*)-2-hydroxy-1-phenylpropanone; **E**, (*S*)-2-hydroxy-1-phenylpropanone; **F**, (1*R*, 2*S*)-1-phenyl-1,2-propanediol; **G**, (1*R*, 2*R*)-1-phenyl-1,2-propanediol; **H**, (1*S*, 2*R*)-1-phenyl-1,2-propanediol; **I**, (1*S*, 2*S*)-1-phenyl-1,2-propanediol.

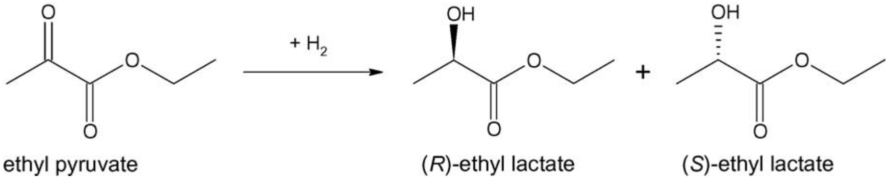

Fig. 3. Reaction scheme of ethyl pyruvate hydrogenation.

sists since high power outputs and low ambient pressures were applied.

2.2. Experimental conditions

1-Phenyl-1,2-propanedione was hydrogenated (Fig. 2) in a 300 ml pressurized reactor (Parr Co.) over 150 mg of 5 wt.% Pt/SF (silica fiber) catalyst in methyl acetate, toluene and mesitylene as solvents. The preparation of the 5 wt.% Pt/SF crushed silica fiber catalyst is described elsewhere [23]. The catalyst was activated under hydrogen flow at 400 °C for 2 h and cooled down to reaction temperature. The deoxygenated solvent, reactant and modifier, (−)-cinchonidine (Aldrich, C8040-7, 96%) were injected into the reactor after which the reaction was commenced. The initial reactant and modifier concentrations were 0.019 and 1.7×10^{-4} mol/l, respectively. The applied hydrogen pressure was 10 bar and the reaction temperature 15 °C. The stirring rate was 2000 rpm to exclude any effects of external mass transfer. The experiments were carried under acoustic irradiation with a nominal intensity input of 78 W/cm^2 as well as under comparative silent conditions. The samples drawn from the reactor were analyzed by a gas chromatograph (GC) equipped with a FI detector and with a β-dex 225 chiral column (length 30 m, diameter 0.25 mm, film thickness 0.25 μm). The enantiomeric excess (ee) of B is defined as follows ee = ([B] − [C])/([B] + [C]), where [B] and [C] are the concentrations of (*R*)- and (*S*)-1-hydroxy-1-phenylpropanone, respectively.

The 5 wt.% Pt/Al_2O_3 (Strem) catalyst deactivation was investigated in ethyl pyruvate (Fluka, 97%) hydrogenation (Fig. 3) in toluene. The catalyst deactivation study was conducted by recycling the catalyst (100 mg) in the presence or absence of acoustic irradiation. In case of sonic reaction, the nominal power input to the system was 500 W. The experiments were carried out in the absence of catalyst modifier and the initial reactant concentration was 0.1 mol/l. The reactant, ethyl pyruvate was vacuum distilled prior to use in hydrogenation. The partial pressure of hydrogen was 3 bar and reaction temperature 20 °C. The stirring rate of 2000 rpm and catalyst particles below 20 μm were utilised to ensure operation in absence of external and internal mass transfer limitations. The samples drawn from the reactor were analyzed by means of a gas chromatograph equipped with β-dex 225 (Supelco) chiral column. The peaks in the chromatograms were identified and the calibration was carried out by using EtPy and (−)-ethyl lactate (Fluka 77367, >99%).

A catalyst deactivation study was conducted in D-fructose hydrogenation by recycling the Raney-Ni (Acticat) catalyst (3 g). Four experiments under silent and sonic conditions were performed. In case of sonic reaction, the nominal ultrasound intensity input of 130 W/cm^2 was applied. Fructose (Danisco Sweeteners) was hydrogenated (Fig. 4) over Raney-Ni catalyst in a pressurized autoclave reactor (600 ml). The effective liquid volume of the reactor was 250 ml. The set-up was equipped with a Rushton turbine. The stirring rate was 1800 rpm in all of the experiments to operate at the kinetically controlled regime. The partial pressure of hydrogen was 30 bar and the reaction temperature 110 °C. The samples drawn out from the reactor were analyzed by high-performance liquid chromatograph (HP 1100 LC series), equipped with an RI detector HP 1047 A, a Biorad Aminex HPX-87C carbohydrate column, a precolumn, a degasser, a binary pump with two channels and an autosampler.

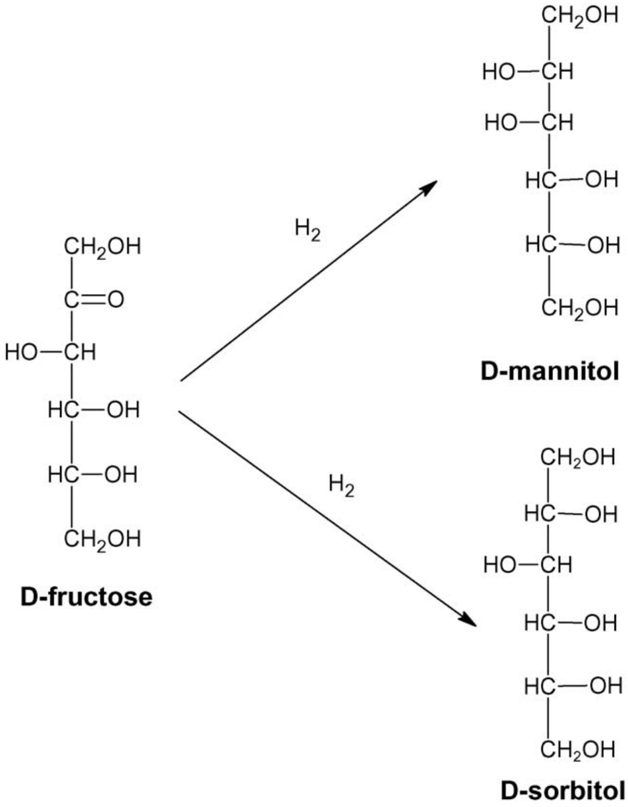

Fig. 4. Simplified reaction scheme of D-fructose hydrogenation.

Esterification of propionic acid with ethyl alcohol (Fig. 5) over 6 g of Smopex-101 (Smoptech, J. M.) catalyst was carried

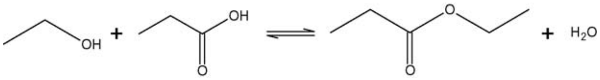

Fig. 5. Reaction scheme for esterification reaction of propionic acid with ethyl alcohol.

out in glass reactor under silent and sonic conditions. Fibrous catalyst (Smopex-101) was manufactured by supporting sulphonic acid on poly(ethylene-*graft*-polystyrene). The detailed specification of the catalyst (Smopex-101) preparation and characterization is described elsewhere [24]. In case of sonic reaction, the nominal power input to the system was 500 W. Propionic acid and ethyl alcohol were pre-heated separately and reaction initiated by pouring propionic acid into the reactor. The studies were carried out at 70 °C with an initial molar ratio of 1:1 between propionic acid to ethyl alcohol and the total liquid volume was 0.75 l. The stirring rate was varied from 185 to 1000 rpm. The samples drawn from the reactor were analyzed by means of a gas chromatograph equipped with FID detector and DB-1 (100% dimethylpolysiloxane) column (length 30 m, diameter 0.25 mm and thickness 0.5 μm).

2.3. Catalyst characterization

The catalyst particles were characterized by scanning electron microscopy (SEM). A 360 (LEO Electron Microscopy LTD) scanning electron microscope equipped with a secondary and backscattered electron detector was used for imaging of spent catalysts treated either in presence or absence of ultrasound.

The Pt particle size of Pt/SF (silica fiber) catalyst was determined by transmission electron microscopy (TEM). TEM was performed using Philips CM30T electron microscope with a LaB_6 filament as the source of electrons operated at 300 kV. Samples were mounted on Quantifoil microgrid carbon polymer supported on a copper grid by placing a few droplets of a suspension of ground sample in ethanol on the grid, followed by drying at ambient conditions.

The BET specific surface areas of Raney-Ni catalysts were determined by nitrogen adsorption (Sorptometic 1900, Carlo Erba Instruments).

3. Results and discussion

3.1. Enantioselective hydrogenation of 1-phenyl-1,2-propanedione

In enantioselective hydrogenation of 1-phenyl-1,2-propanedione over 5 wt.% Pt/SF catalyst a notable enhancement of reaction rate, ee and rs (defined as (B + C)/(D + E)) was observed under ultrasound compared to silent conditions. Over four-fold higher reaction rate was observed under ultrasound ($r = 1.3 \times 10^{-3}$ mol/l × g_{cat} min) in mesitylene compared to identical silent conditions ($r = 0.3 \times 10^{-3}$ mol/l × g_{cat} min). Also, in methyl acetate and in toluene a slight rate enhancement under ultrasound was observed (Fig. 6a). Ultrasound had a major impact on selectivity as well (Fig. 6b): the highest, two-fold, improvement of enantioselectivity under ultrasound was observed in toluene (ee = 34%) compared to silent reaction (ee = 17%) under identical conditions. However, in the case of methyl acetate and mesitylene no significant enhancement of ee and rs was obtained by sonification.

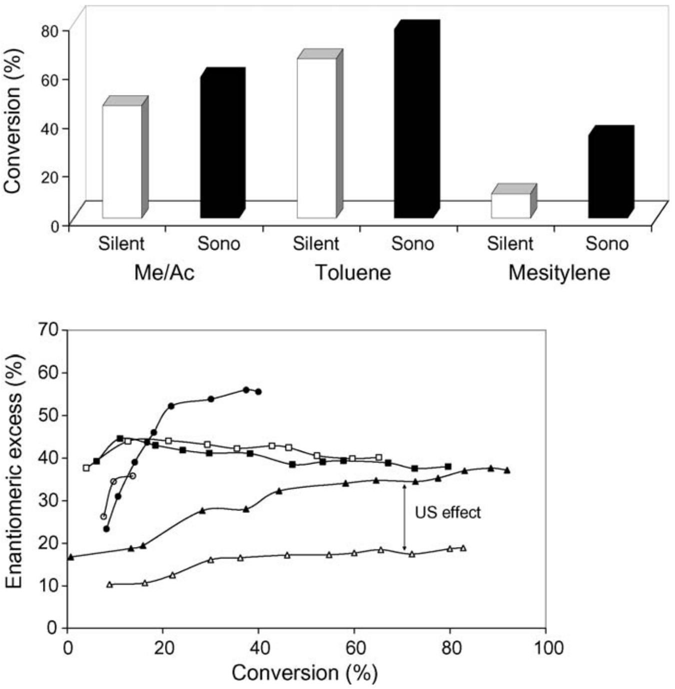

Fig. 6. The effect of different solvents (Me/Ac—methyl acetate, toluene and mesitylene) in enantioselective hydrogenation of 1-phenyl-1,2-propanedione) in presence and absence of acoustic irradiation over Pt/SF catalyst at 15 °C and 10 bar on (a) conversion after 60 min conversion and (b) enantiomeric excess as a function of conversion: (□—MeAc, Silent; ■ —MeAc, Sono; △—Toluene, Silent; ▲—Toluene, Sono; ○—Mesitylene, Silent; ●—Mesitylene, Sono).

Pt/SF catalyst surface smoothening and cleaning was obtained under acoustic irradiation (Figs. 7 and 8). This observation can be the explanation for the observed improvement of catalyst activity in the presence of ultrasound compared to experiments carried out under identical silent conditions.

However, no significant differences on Pt particle size distribution between sonic and silent treated catalysts were observed by TEM (Figs. 9 and 10). Furthermore, the Pt particle size distribution is extremely broad (3–35 nm) and some of the large Pt particles do not seem to have much contact with the support material.

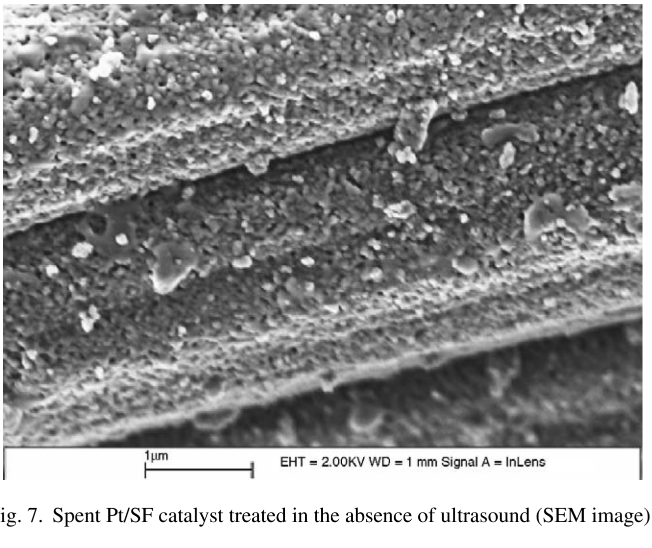

Fig. 7. Spent Pt/SF catalyst treated in the absence of ultrasound (SEM image).

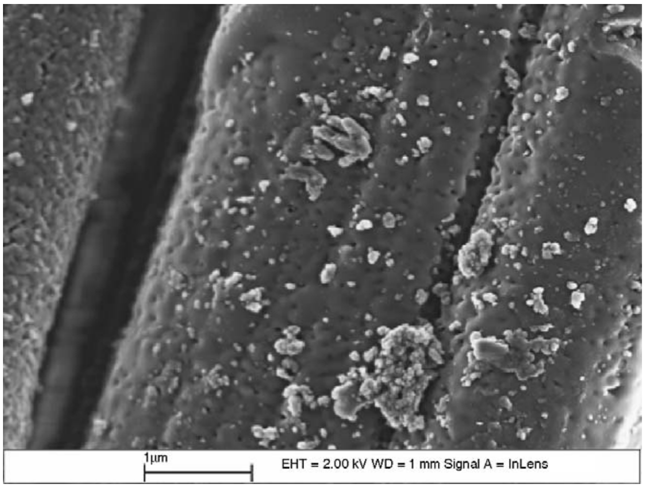

Fig. 8. The ultrasonic treated spent Pt/SF catalyst (SEM image).

3.2. Ethyl pyruvate hydrogenation

A catalyst deactivation study was conducted by recycling the Pt/Al_2O_3 catalyst in racemic ethyl pyruvate hydrogenation in the absence of chiral catalyst modifiers. The catalyst was reused three times in the presence and absence of ultrasound. However, no major effect of acoustic irradiation on catalyst activity was observed compared to identical comparative experiments under silent conditions (Fig. 11). As can be expected, due to lack of any chiral catalyst modifiers, the enantiomeric excess was 0% in all experiments.

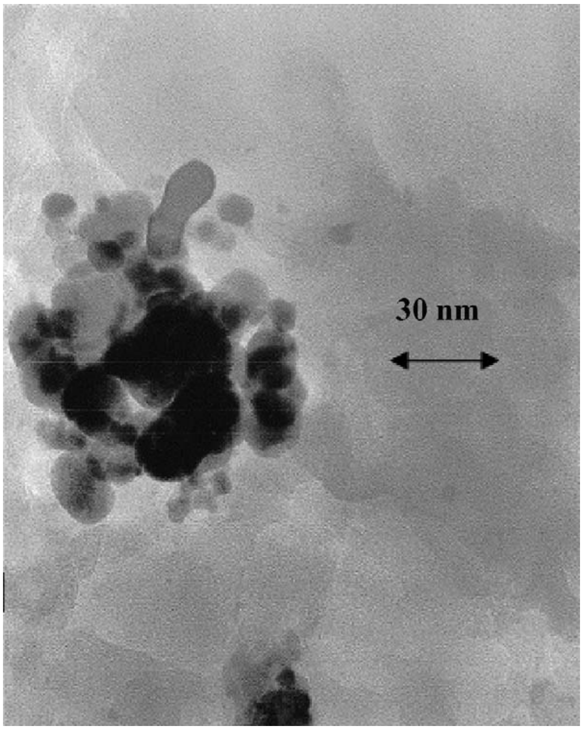

Fig. 9. Spent Pt/SF catalyst treated in the absence of ultrasound (TEM image).

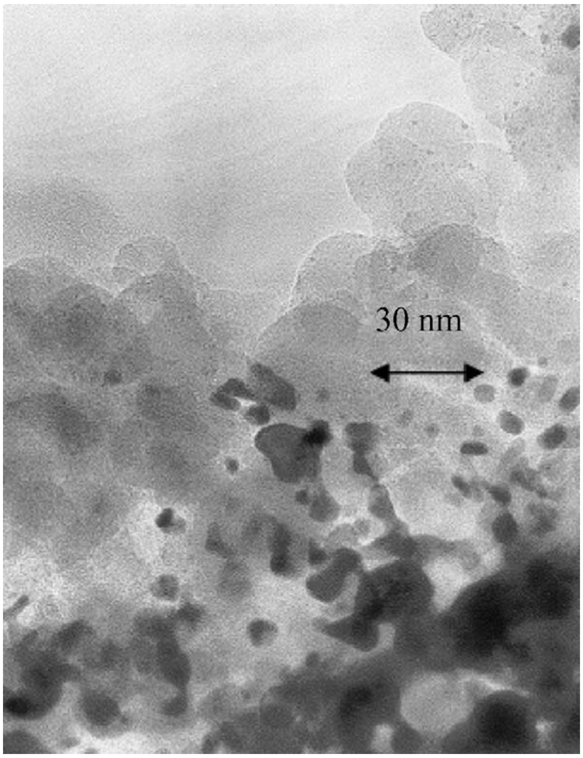

Fig. 10. The ultrasonic treated spent Pt/SF catalyst (TEM image).

Based on the SEM analysis, no significant differences in Pt/Al_2O_3 catalyst particles were obtained due to the ultrasonic treatment.

3.3. D-fructose hydrogenation

Sonification during the reaction had a significant effect on Raney-Ni catalyst deactivation in D-fructose hydrogenation. In experiments carried out under silent conditions, notable catalyst deactivation was observed, however, acoustic irradiation was found to retard deactivation significantly (Fig. 12). The selectivity to target product D-mannitol was essentially unaffected by catalyst deactivation and sonification and remained in all experiments between 47 and 51%.

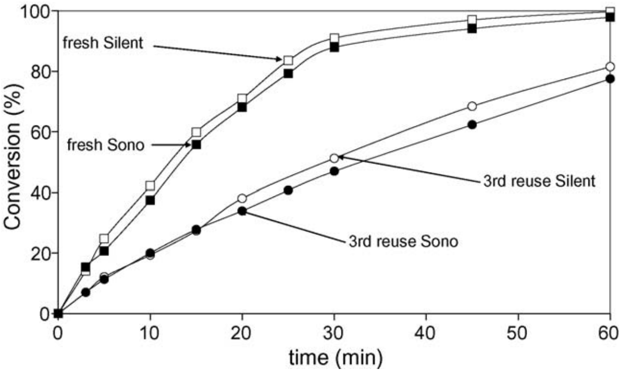

Fig. 11. Pt/Al_2O_3 catalyst deactivation series in ethyl pyruvate hydrogenation at 20 °C and 3 bar.

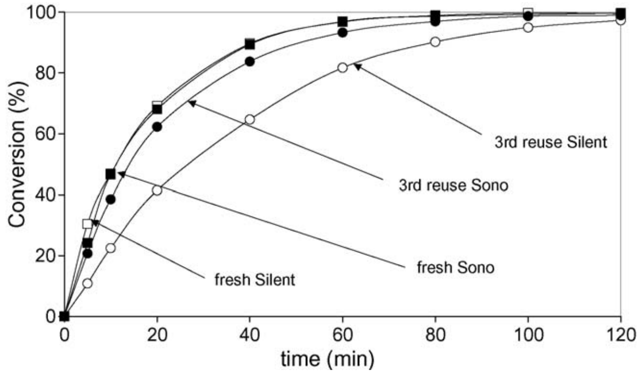

Fig. 12. Raney-Ni catalyst deactivation series in D-fructose hydrogenation at 110 °C and 30 bar.

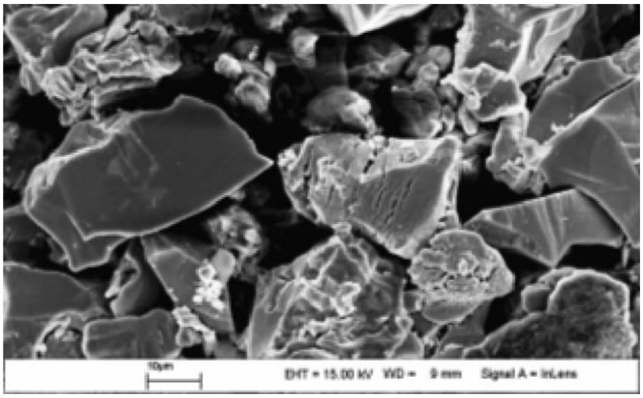

Fig. 13. Spent Raney-Ni catalyst treated in the absence of ultrasound (SEM image).

In case of Raney-Ni catalyst, acoustic irradiation seems to provide additional deformation of the catalyst surface, exposing fresh, highly active surface (Figs. 13 and 14). However, nitrogen adsorption analyses did not provide more evidences for this proposal since specific surface area of Raney-Ni catalyst treated under sonic conditions was determined 65 m^2/g, under silent conditions 66 m^2/g and for the fresh catalyst 91 m^2/g.

3.4. Esterification of propionoic acid with ethyl alcohol

Utilization of acoustic irradiation in esterification reaction of propionic acid with ethyl alcohol notably enhanced the activity of Smopex-101 catalyst. The initial catalyst activity was the same in the presence and absence of ultrasound. However, at longer reaction times (between 2 and 12 h), sonification clearly retards deactivation and maintains a higher catalytic activity, at higher conversions (Fig. 15). Nevertheless, by increasing the reaction time, the reactants and products are reaching equilibrium (see Fig. 15) which remained unaffected by acoustic irradiation. Variation of the stirring rate (rpm) had a major impact on ultrasonic effect. At lower stirring rates, 185–300 rpm, significant enhancements of catalyst activity were obtained by sonification. However, at higher stirring rates (1000 rpm) no improvement of reaction rate was observed under ultrasound (Fig. 16). This observation can be explained by disturbances of cavitation by intensive mechanical stirring in which bubbles and foams are formed and suppressing acoustic cavitation. Nevertheless, reaction rate was independent on the stirring rate under silent or sonic conditions, which indicates operation in the absence of mass transfer limitations.

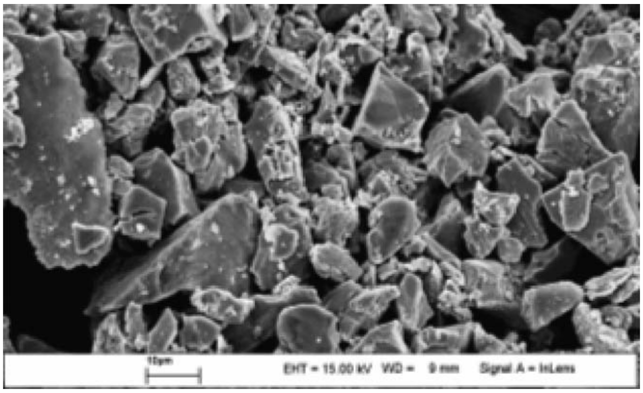

Fig. 14. The ultrasonic treated spent Raney-Ni catalyst (SEM image).

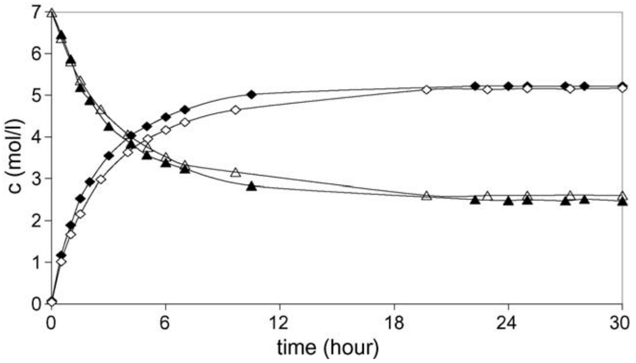

Fig. 15. Esterification of propionic acid with ethyl alcohol over Smopex–101 catalyst (◇—ethyl propionate, Silent; ◆—ethyl propionate, Sono; △—ethyl alcohol, Silent; ▲—ethyl alcohol, Sono) at 70 °C and 1 bar.

Acoustic irradiation seems to smoothen and clean Smopex-101 catalyst surface (Figs. 17–20), which can be one of the reasons why reaction proceeds faster in presence of ultrasound.

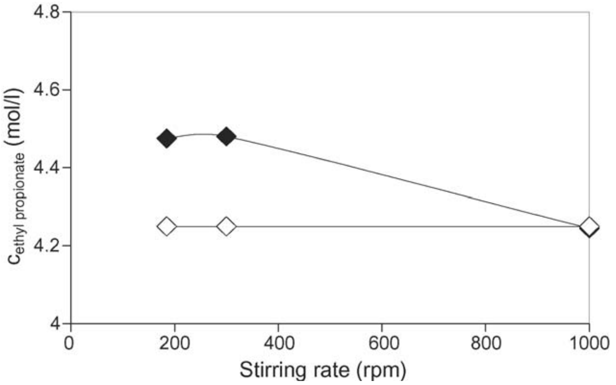

Fig. 16. Effect of the stirring rate on concentration of ethyl propionate in esterification reaction of propionic acid with ethyl alcohol over Smopex-101 catalyst (concentration after 6 h, ◇—Silent; ◆—Sono) at 70 °C and 1 bar.

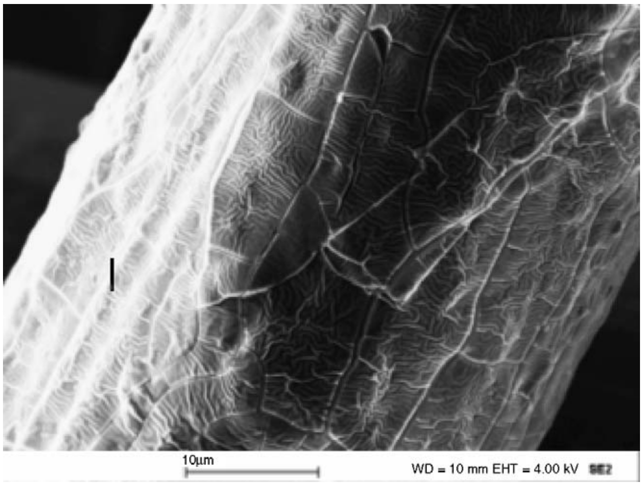

Fig. 17. Spent Smopex-101 catalyst treated in the absence of ultrasound (SEM image).

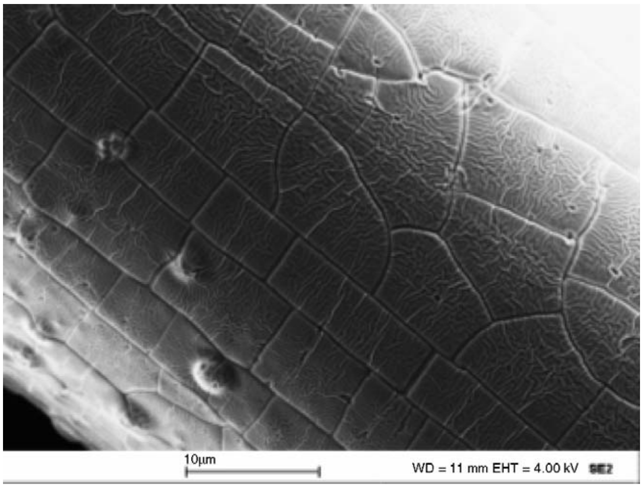

Fig. 18. Spent Smopex-101 catalyst treated in the presence of ultrasound (SEM image).

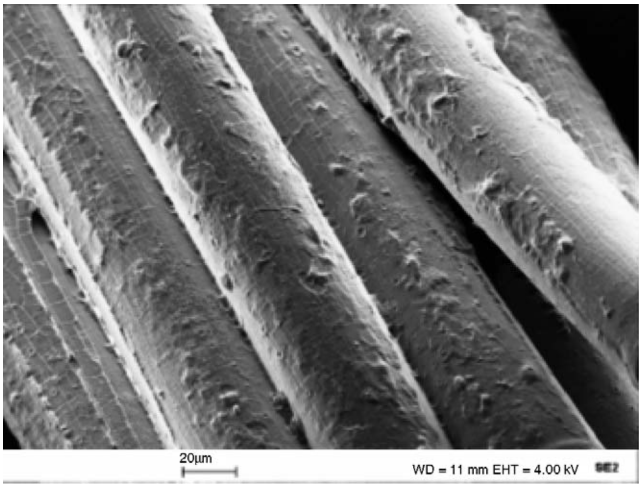

Fig. 19. Spent Smopex-101 catalyst treated in the absence of ultrasound (SEM image).

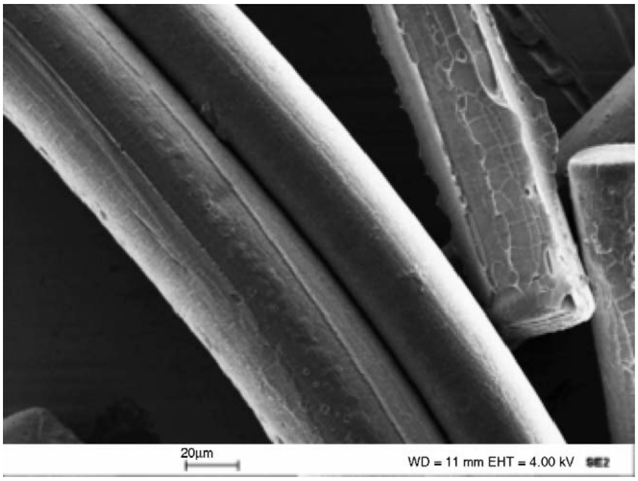

Fig. 20. Spent Smopex-101 catalyst treated in the presence of ultrasound (SEM image).

4. Conclusions

The effect of acoustic irradiation on heterogeneous catalyst activity was studied in several hydrogenation reactions (1-phenyl-1,2-propanedione, ethyl pyruvate and D-fructose hydrogenation) as well as in esterification of propionic acid with ethyl alcohol. On-line acoustic irradiation was found to counter-effect catalyst deactivation, increase the reaction rate and improve selectivity.

Ultrasound notably enhanced reaction rate, ee and rs in enantioselective hydrogenation of 1-phenyl-1,2-propanedione over Pt/SF catalyst. Sonic effects seem to be solvent dependent, the highest enhancement of reaction velocity was observed in mesitylene, which is solvent with the lowest vapor pressure, i.e. solvent in which the most violent cavity collapse takes place, resulting into higher collapse pressure and temperature compared to toluene and methyl acetate. On the other hand, the highest improvement of enantioselectivity by means of ultrasound was achieved in toluene.

Sonification during the reaction noticeably suppressed Raney-Ni catalyst deactivation in D-fructose hydrogenation. However, no effect of ultrasound was obtained in ethyl pyruvate hydrogenation for Pt/Al_2O_3 catalyst. These observations infer that the effect of ultrasound on the catalyst performance strongly depends on the nature of the catalyst and catalyst deactivation cannot be suppressed in all heterogeneous catalytic reactions.

In the esterification reaction of propionic acid with ethyl alcohol acoustic irradiation enhanced activity, i.e. suppressed deactivation of functionalized polyethylene fiber catalyst. The ultrasonic effects were significantly dependent on the stirring speed.

It can be concluded that ultrasound effects are indeed strongly dependent on catalyst used as well as the solvent applied. Generally, positive ultrasonic effects were observed with the fiber catalyst where acoustic irradiation significantly increases the reaction rate by retarding catalyst deactivation. Significant suppression of catalyst deactivation was obtained in D-fructose hydrogenation over Raney-Ni catalyst and enantioselective hydrogenation of 1-phenyl-1,2-propanedione over Pt/SF catalyst. However, Pt/Al_2O_3 catalyst deactivation cannot be retarded in ethyl pyruvate hydrogenation by means of ultrasound, which indicates major influence of catalyst nature and structure on ultrasound effects. Furthermore, acoustic cavitation seems to improve catalyst activity, i.e. retard catalyst deactivation mainly in solvents with low vapor pressure and in systems under non-ideal operating conditions.

The plausible reasons for the beneficial effects of ultrasound in heterogeneous catalytic reactions are in general: ultrasonic smoothening and cleaning of solid surfaces that have been contaminated by sticky organic impurities, changes in surface morphology, catalyst particle size deterioration as well as sonic turbulences at microscopic level. The explanation for suppressed deactivation in the above presented model reactions is catalyst surface cleaning and smoothening provided by ultrasound during the course of reaction.

Acknowledgments

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References

[1] P. Forzatti, L. Leitti, Catal. Today 52 (1999) 165.
[2] B. Toukoniitty, J.-P. Mikkola, D.Yu. Murzin, T. Salmi, Appl. Catal. A Gen. 279 (2005) 1.
[3] K.S. Suslick, D.J. Casadonte, M.L. Green, M.E. Thompson, Ultrasonics 25 (1987) 56.
[4] I. Kun, B. Török, K. Felfödldi, M. Bartók, Appl. Catal. A Gen. 203 (2000) 71.
[5] A.L. Crum, Ultrason. Sonochem. 2 (1995) 147.
[6] P. Boudjouk, B.H. Han, J. Catal. 79 (1983) 489.
[7] R.S. Disselkamp, Y.-H. Chin, C.H.F. Peden, J. Catal. 227 (2004) 552.
[8] R.S. Disselkamp, T.R. Hart, A.M. Williams, J.F. White, C.H.F. Peden, Ultrason. Sonochem. 12 (2005) 319.
[9] J. Lindley, P.J. Lorimer, T.J. Mason, Ultrasonics 24 (1986) 292.
[10] J.-P. Mikkola, B. Toukoniitty, E. Toukoniitty, J. Aumo, T. Salmi, Ultrason. Sonochem. 11 (2004) 233.
[11] J. Gonzalo Rodríguez, A. Lafuente, Tetrahedron Lett. 43 (2002) 9581.
[12] R.S. Disselkamp, K.M. Judd, T.R. Hart, C.H.F. Peden, G.J. Posakony, L.J. Bond, J. Catal. 221 (2004) 347.
[13] A.N. Nikolopoulos, O. Igglessi-Markopoulou, N. Papayannakos, Ultrason. Sonochem. 13 (2006) 92.
[14] J.-P. Mikkola, T. Salmi, Chem. Eng. Sci. 54 (1999) 1583.
[15] T.J. Mason, J.P. Lorimer, Applied Sonochemistry, Wiley-VCH Verlag GmbH, Weinheim, 2002.
[16] D.Yu. Murzin, P. Mäki-Arvela, E. Toukoniitty, T. Salmi, Cat. Rev. Sci. Eng. 47 (2005) 175.
[17] P.M. Subramanian, S.K. Chatterjee, M.C. Bhatia, J. Chem. Technol. Biotechnol. 39 (1987) 215.
[18] E. Toukoniitty, D.Yu. Murzin, Catal. Lett. 93 (2004) 171.
[19] E. Toukoniitty, P. Mäki-Arvela, A. Kalantar Neyestanaki, T. Salmi, D.Yu. Murzin, Appl. Catal. A Gen. 235 (2002) 125.
[20] M. Makkee, A.P.G. Kieboom, H. van Bekkum, Starch 37 (1985) 136.
[21] M. Makkee, A.P.G. Kieboom, H. van Bekkum, Carbohydr. Res. 138 (1985) 225.
[22] K. Wessermel, H.-J. Arpe, Industrial Organic Chemistry, third ed., VCH, New York, 1997, pp. 289.
[23] A. Kalantar Neyestanaki, P. Mäki-Arvela, E. Toukoniitty, H. Backman, F. Klingstedt, T. Salmi, D.Yu. Murzin, Catalysis in Organic Reactions, Chemical Industries, vol. 89, DEKKER, 2003, pp. 33.
[24] J. Lilja, J. Aumo, T. Salmi, D.Yu. Murzin, P. Mäki-Arvela, M. Sundell, K. Ekman, R. Peltonen, H. Vainio, Appl. Catal. A Gen. 228 (2002) 253.