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Ethyl pyruvate hydrogenation under microwave irradiation

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Abstract

Enantioselective and racemic hydrogenation of ethyl pyruvate over Pt/Al_2O_3 catalyst was investigated under conventional and microwave dielectric heating. Experiments were carried out in a single-mode microwave loop reactor, equipped with a heating band, to directly compare the efficiency of the conventional convective/conductive heating and microwave dielectric heating. A sequence of kinetic experiments was performed, varying the microwave power input and the solvent. A catalyst deactivation study was conducted by recycling the catalyst. The choice of solvent significantly affected reaction rate and enantioselectivity. The highest reaction rate and enantioselectivity (75%) was achieved in toluene. In this solvent, the kinetics and enantioselectivity was unaffected by the mode of heating. In case of ethyl alcohol as solvent, the reaction rate remained the same for conventional and dielectric heating. However, the enantioselectivity dramatically decreased under microwave irradiation. The spent and fresh catalysts were characterized by scanning electron microscopy (SEM), nitrogen physisorption and direct current plasma (DCP) technique. Based on the SEM images and nitrogen physisorption analyses, slight sintering of catalyst surface was observed under microwave irradiation.

Keywords: Microwave irradiation; Heterogeneous catalyst; Hydrogenation; Ethyl pyruvate

1. Introduction

In the production of fine chemicals, the current trend is to develop new, more profitable and environmentally sustainable production technologies, which utilize heterogeneous catalysis and also focus more on reactor engineering aspects. Traditionally, fine chemicals have been produced via stoichiometric organic synthesis, which produces a large amount of waste and comprises of several reaction steps. The replacement of stoichiometric synthesis routes with catalytic reaction routes is one way to process intensification by reducing the number of reaction steps and minimizing the amount of waste and increasing the product yield [1,2]. The other way is to utilize instead of the most commonly used batch- and semi-batch reactors, other reactor alternatives or different forms of energy.

The rate acceleration by microwave irradiation has been observed for a wide range of organic reactions [3–9], but only the minority of them describes effects of microwaves on catalysed reactions. However, the rate enhancement in several cases, which is claimed to result from athermal effects, can be due to a higher reaction temperature in the dielectric field. Many of these prejudices have arisen from inaccurate knowledge of the temperature distribution due to the difficulty in measuring temperature in irradiated media [10]. This clearly demonstrates that it is very important to carefully monitor the reaction temperature directly in the electromagnetic field. Therefore, in the present work optical fiber technology was applied to monitor the temperature in the reaction zone. Several articles list examples of an increased selectivity, i.e. the chemo- or regioselectivity can be increased under the microwave dielectric heating compared to conventional heating [11,12]. However, in some cases the selectivity of the reaction could be affected in a negative way by microwaves due to the local superheating effect. Recently, two studies dedicated to homogenously catalysed asymmetric synthesis under microwave irradiation were reported claiming improvement of reaction rate while maintaining the selectivity constant [13,14]. However, to the best of our knowledge there are no examples of microwave enhanced heterogeneous asymmetric catalysis. Ethyl pyruvate hydrogenation is well studied under conventional heating [15–17] which makes it an interesting model reaction for microwaves studies.

The advantage of microwave irradiation as an energy source for heterogeneously catalysed systems is that microwaves do not substantially heat up the adsorbed organic layers, but interact

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directly with the metal sites on the catalyst surface thus creating hot spots. This is particularly interesting in heterogeneous catalysis where high temperatures diminish selectivity. Nevertheless, significant temperature gradients between a catalyst bed and a bulk liquid can be established. This concept is expected to be beneficial in carrying out chemical reactions, for which competitive or consecutive side reactions lead to by-products deteriorating selectivity.

2. Experimental

2.1. Experimental conditions

Ethyl pyruvate (Fig. 1) hydrogenation was studied in a single-mode microwave loop reactor over Pt/Al_2O_3 catalyst by using toluene (Baker, >99.5%) and ethyl alcohol (Altia, 99.5%) as solvents. The reactions were studied in the absence and presence of a catalyst modifier (cinchonidine, Fluka 27350, >98.0%) (Fig. 2). The Pt/Al_2O_3 catalyst was prepared by impregnating a commercial alumina spheres (La Roche A-201, $d \sim 2.2$ mm) with an aqueous solution of hexachloroplatinic acid (H_2PtCl_6). The metal content on the support was determined by DCP and was found to be ca. 3 wt.%. After the impregnation, the catalyst was washed with deionized water, calcinated and reduced ex situ at 290 °C under H_2 flow (0.05 dm^3/min) and prior to the reaction in situ at 290 °C under H_2 flow (1 bar). The catalyst mass was 5 g and the amount of solvent was 1.1 dm^3. The mass ratio of substrate-(ethyl pyruvate)-to-Pt was 85. The hydrogenations were carried out at 23 and 36 °C and 7 bar of H_2. The loop flow velocity was 1.2 dm^3/min. The concentrations of EtPy and CD were 0.1 and 6.2×10^{-4} mol dm^{-3}. The samples drawn from the reactor were analysed by means of a gas chromatograph (GC) 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%). The enantiomeric excess of (*R*)-ethyl lactate is defined as $ee = (R - S)/(R + S) \times 100$ (%), where *R* and *S* are concentrations of (*R*)- and (*S*)-ethyl lactate, respectively.

2.2. The reactor set-up

A flexible, multipurpose system (Fig. 3a and b) was used, which allows studying various gas-, liquid- and multiphase systems, with or without a stagnant catalyst bed residing in the microwave field. Single-mode units have a smaller cavity, higher energy efficiency and a more even temperature distribution in the reaction vessel than multi-mode units (such as domestic MW ovens). Since it is interesting to compare the efficiency of traditional convective/conductive and MW dielectric heating, the reactor set-up is equipped with conventional heating band and necessary control units for accurate temperature adjustment as well. Furthermore, the actual temperature in cavity (reaction zone) is measured by means of optical fiber technology (Fiso Technologies Inc.).

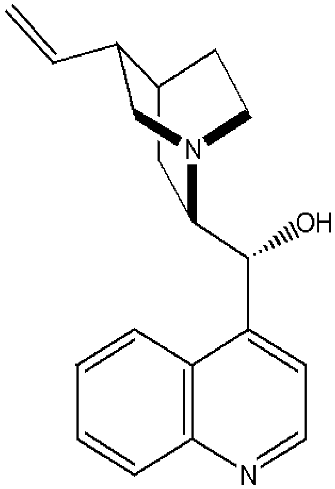

Fig. 2. Chiral catalyst modifier cinchonidine CD.

The catalyst bed was located in the quartz tube placed into the reactor set-up and reduced in situ at 290 °C under H_2 flow (1 bar). After the reduction, the catalyst bed was cooled down to room temperature (23 °C) and placed by adjusting the level of the generator and the surrounding appliances to the cavity. The catalyst bed was heated by microwave irradiation and cold liquid (solvent + reactant) was circulated in the loop anti-clockwise passing the cooler. Since the solvent (toluene) was transparent to microwave irradiation, no dramatic heating was observed. Due to safety aspects, it is very important to ensure that cavity contains material; i.e. in case of loop configuration the control of flow is crucial, otherwise microwave-reflected power sensor might be burnt due to excessive reflected power or even worse, a meltdown or/and explosion might take place in the catalyst bed residing in the cavity. Therefore, an emergency switch as well as a limit switch of microwave irradiation were inbuilt to switch off the microwave source in case the flow rate decreases below the set-point of 0.2 dm^3/min. Furthermore, a metal jacket with nitrogen flow was installed around the quartz tube to ensure that in case of tube cracking no hydrogen explosion will take place.

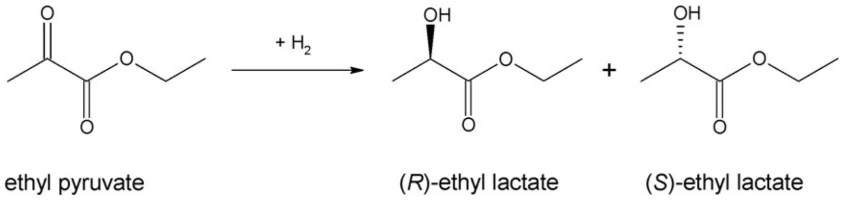

Fig. 1. Reaction scheme of ethyl pyruvate hydrogenation.

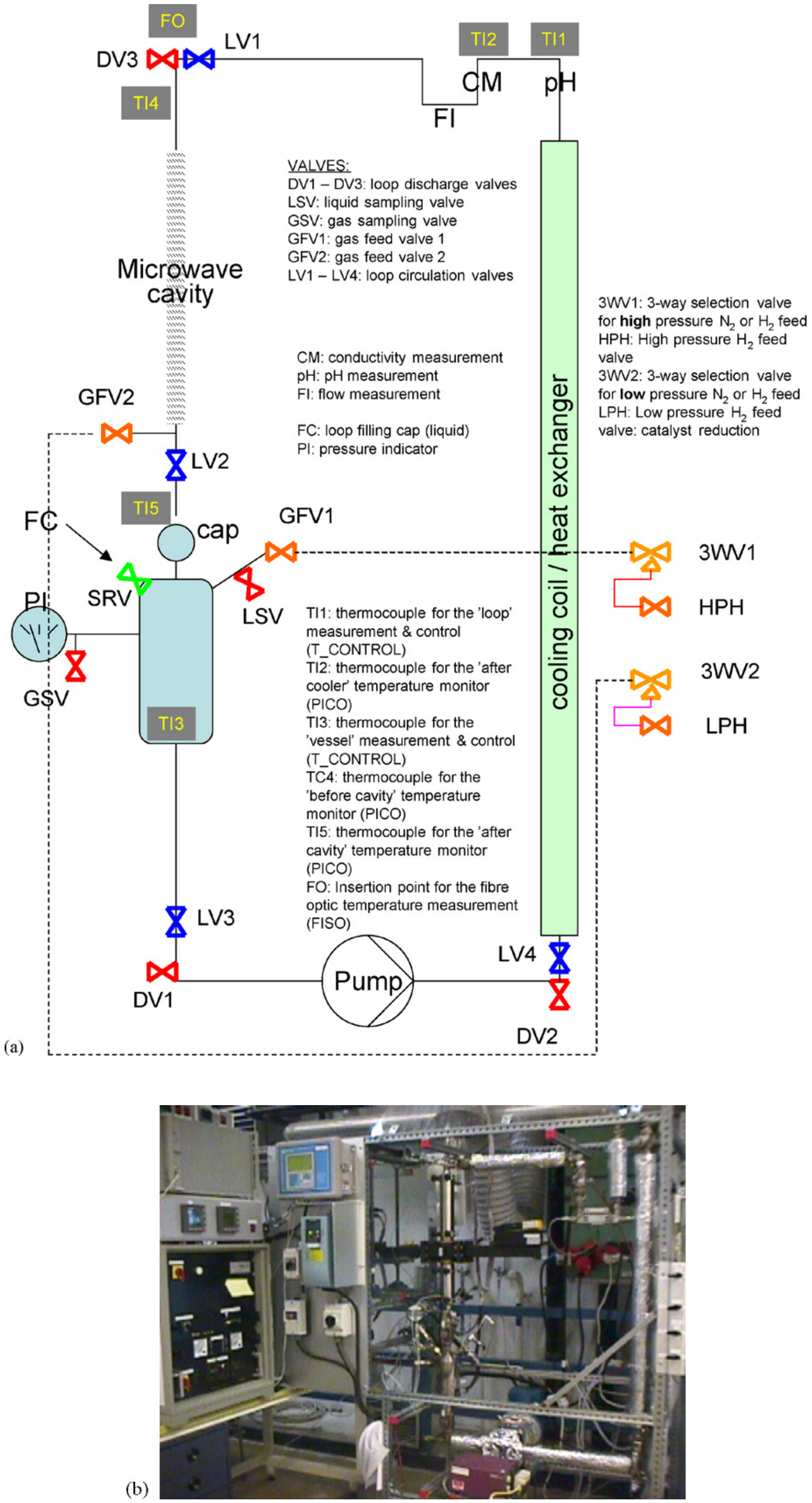

Fig. 3. (a) Schematic flow sheet of single-mode microwave loop reactor. (b) Single-mode microwave loop reactor.

2.3. *Catalyst characterization*

The catalyst particles were characterized by SEM. A 360 (LEO Electron Microscopy LTD) scanning electron microscope equipped with a secondary and backscattered electron detector was used for imaging the fresh Pt/Al_2O_3 catalysts, catalyst exposed to conventional heating as well as catalyst exposed to microwave irradiation.

The BET specific surface area of the catalysts was determined by nitrogen adsorption (Sorptometic 1900, Carlo Erba Instruments). The catalysts were degassed for 4 h at 200 °C in vacuo prior to measurements.

The metal content on the Al_2O_3 support was determined by direct current plasma (DCP) technique.

3. Results and discussion

3.1. *Solvent effect*

Microwave effects have to be considered according to reaction medium, as solvent effects are of particular importance. If polar solvents are involved, (e.g. alcohols, water) the main absorption of microwave irradiation occurs by the polar molecules of the solvent. In this case, energy is transferred from the solvent to the reactants and the catalyst. Consequently, the results should be similar to those obtained by conventional heating. This case was observed in several esterification reactions [18,19]. A more promising approach to observe microwave specific effects upon use of non-polar solvents (e.g. hydrocarbons) since there will exist very weak solvent–microwave interactions allowing specific absorption of microwaves by catalyst and reactants. Energy is transferred then from reactants to the solvent and the results might be different under microwave and conventional heating [20].

The effect of polar and non-polar solvent on enantioselective hydrogenation of ethyl pyruvate was studied in toluene and ethyl alcohol. From the literature it is known that ee values of 81 and 77% are observed in toluene and ethyl alcohol, respectively [21]. Typically, ee decreases with increasing solvent polarity. The highest ee (>95%), in ethyl pyruvate hydrogenation is observed in acetic acid [22]. The microwave power input in the experiments was 300 W, the bulk reaction temperatures in toluene and ethyl alcohol were 23 and 36 °C, respectively, at H_2 pressure of 7 bar. In case of toluene, which is transparent to microwaves, no change in reaction rate and enantioselectivity was observed under dielectric (MW) and conventional heating (CH) (Figs. 4 and 5). In case of ethyl alcohol, the reaction rate remained the same (Fig. 6), however, the enantioselectivity dramatically decreased from 60 to 40% under microwave heating (Fig. 7). This observation was probably obtained due to the local superheating of the polar solvent ethyl alcohol in the cavity, which cannot take place in the case of non-polar toluene. High reaction temperatures are not feasible for the cinchona alkaloid systems, as enantioselectivity is known to rapidly decrease at higher temperatures (<50 °C) [23–27]. This temperature dependence of enantioselectivity has been proposed to originate either from desorption of the modifier at higher temperatures [24] or

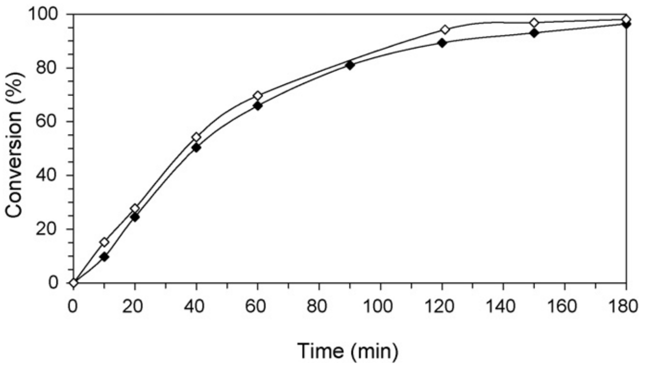

Fig. 4. Conversion vs. time in toluene over Pt/Al_2O_3 at 23 °C, 7 bar and in presence of CD: (◊) CH and (♦) MW (300 W).

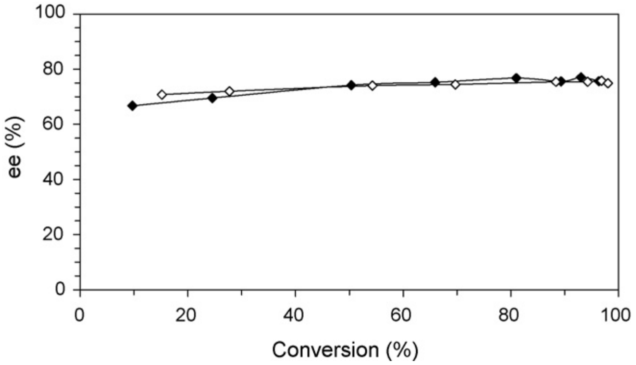

Fig. 5. Enantiomeric excess vs. conversion in toluene over Pt/Al_2O_3 at 23 °C, 7 bar and in presence of CD: (◊) CH and (♦) MW (300 W).

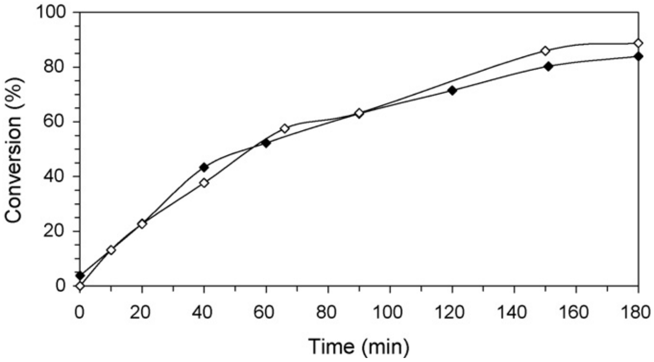

Fig. 6. Conversion vs. time in ethyl alcohol over Pt/Al_2O_3 at 36 °C, 7 bar and in presence of CD: (◊) CH and (♦) MW (300 W).

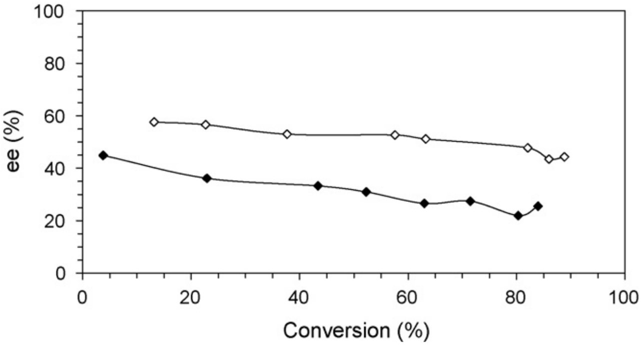

Fig. 7. Enantiomeric excess vs. conversion in ethyl alcohol over Pt/Al_2O_3 at 36 °C, 7 bar and in presence of CD: (◊) CH and (♦) MW (300 W).

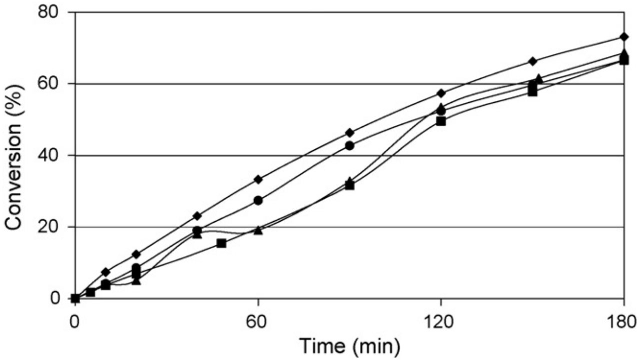

Fig. 8. Conversion vs. time in toluene over Pt/Al_2O_3 at 23–38 °C, 7 bar and in absence of CD: (♦) 100 W, (●) 300 W, (▲) 500 W and (■) 700/500 W.

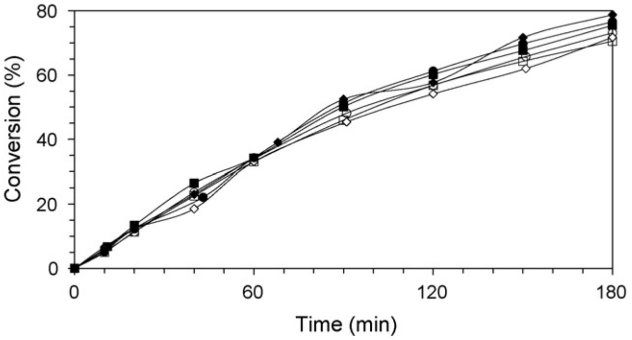

Fig. 9. Conversion vs. time in toluene over Pt/Al_2O_3 at 23 °C, 7 bar and in absence of CD: (♦) MW (fresh, 300 W), (■) MW (first re-use, 300 W), (●) MW (second re-use, 300 W), (◇) CH (fresh), (□) CH (first re-use) and (○) CH (second re-use).

from changes in the adsorption mode of cinchonidine [27]. The significantly lower value of ee was observed in experiments carried out in ethyl alcohol (40–60%) compared to experiments carried out in toluene (80%). This might be due to combined effect of higher reaction temperature (36 °C) and solvent ethyl alcohol, as generally lower values of ee are observed in ethyl alcohol compared to toluene [21].

3.2. Power effect

The effect of microwave power input (100, 300, 500, 700/500 W) was studied in the absence of the catalyst modifier (CD), in toluene at 23–38 °C and 7 bar of H_2.

No enhancement of the reaction rate with increasing microwave power input was observed. This is due to the inability of the reaction medium to absorb higher intensities of microwave irradiation (500 W, 700 W). It was very challenging to carry out experiments with a high power input (500 W, 700 W), since the amount of reflected power fluctuated from 20 to 100%. As the reaction was carried out initially at the microwave power input 700 W the power had to be decreased to 500 W during the reaction since due to the high amount of reflected power the temperature profile was extremely unstable. The reaction rate was affected by this initial instability of electromagnetic field and the conversion was moderately lower at the beginning of the reaction compared to experiments carried out at 100 and 300 W (Fig. 8). However, at a higher power (500 W) the bulk reaction temperature was increased to over 30 °C compared to reaction temperature of 23 °C at a power input 100 and 300 W in the end of the experiment and the reaction rate was increased moderately (Fig. 8). The reaction was carried out at racemic conditions (in the absence of catalyst modifier) and, therefore the ee was 0% and no major effect of microwave power input on ee was observed. Furthermore, the reaction rate was nearly 50% lower for the reaction carried out without the catalyst modifier compared to an experiment with CD, due to the well documented rate acceleration effect in ethyl pyruvate hydrogenation caused by presence of cinchona alkaloid modifiers [28].

3.3. Catalyst recycling

Catalyst (Pt/Al_2O_3) deactivation was studied under microwave and conventional heating at a reaction temperature of 23 °C, H_2 pressure of 7 bar and in the absence of catalyst modifier, CD. The catalyst was re-used three times under dielectric and conventional heating.

Neither catalyst deactivation nor significant enhancement of the reaction rate (Fig. 9) was observed in these consecutive experiments. Moreover, these data indicate good reproducibility of the reaction conditions and accurate temperature control. The enantioselectivity was 0% since the reaction was carried in the absence of CD.

4. Catalyst characterization

The catalyst surface areas (fresh, treated under microwave irradiation 100, 300, 500 W and conventional heating) determined by nitrogen adsorption are listed in Table 1. No significant changes of the specific surface areas were observed between the fresh catalyst and catalysts exposed to conventional or microwave heating (Table 1). On the other hand, a decrease of the specific pore volume was observed under conventional and microwave heating during the recycling series compared to fresh catalyst. A more dramatic decrease of the specific pore

Table 1
BET specific surface area and specific pore volume of Pt/Al_2O_3 catalyst

Catalyst Pt/Al_2O_3	Fresh	CH (CR)	MW 300 W (CR)	MW 100 W	MW 300 W	MW 500 W
Specific surface area (m^2/g)	202	205	190	233	248	218
Specific pore volume (cm^3/g)	0.75	0.50	0.40	0.80	0.48	0.48

CR, catalyst recycling series, the catalyst re-used three times.

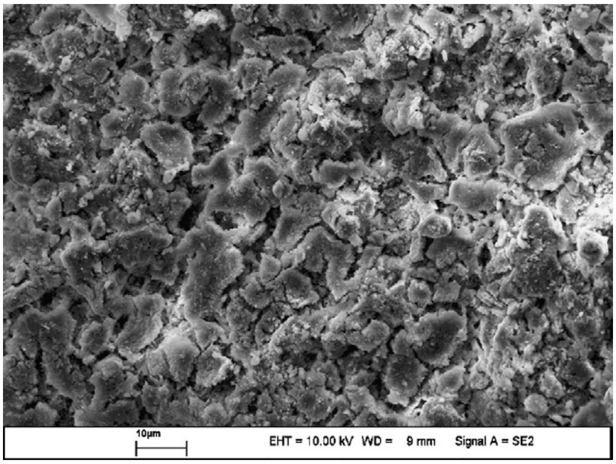

Fig. 10. SEM image of Pt/Al_2O_3 catalyst exposed to microwave irradiation (300 W).

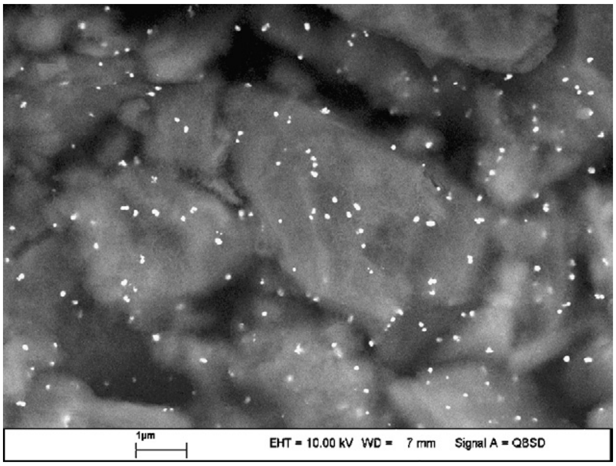

Fig. 11. SEM image of fresh Pt/Al_2O_3 catalyst.

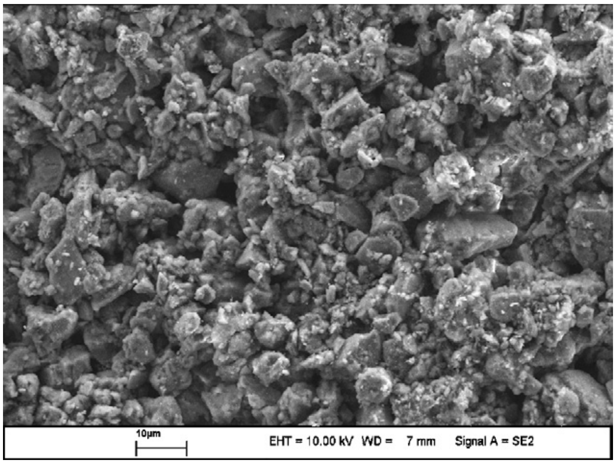

Fig. 12. SEM image of fresh Pt/Al_2O_3 catalyst.

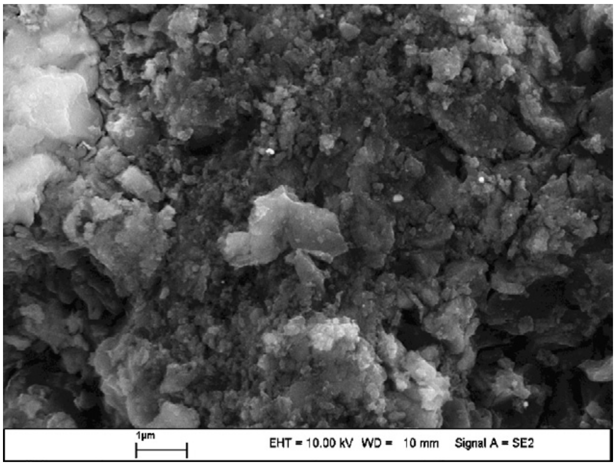

Fig. 13. SEM image of Pt/Al_2O_3 catalyst exposed to conventional conditions.

volume was observed under a higher microwave power inputs 300 and 500 W, compared to lower microwave power input 100 W (Table 1). This observation is possibly caused by a more intensive catalyst surface restructuring (migration, melting) at a higher intensity of the electromagnetic field as seen in the scanning electron micrographs.

Fresh Pt/Al_2O_3 catalyst, as well as samples exposed to conventional heating and microwave irradiation (300 W) were characterized by SEM. Slight sintering of the catalyst surface was observed under microwave irradiation (Fig. 10) compared to the fresh catalyst (Figs. 11 and 12 differing in magnification) as well as the catalyst exposed to conventional heating (Fig. 13). This observation was confirmed by BET surface analysis since the specific pore volume of catalyst exposed to the microwave irradiation was lower compared to the fresh catalyst and catalyst utilized under conventional conditions. However, based on the SEM results, only changes on the catalyst support Al_2O_3 can be revealed.

5. Conclusion

Enantioselective and racemic hydrogenation of ethyl pyruvate over Pt/Al_2O_3 catalyst was investigated under microwave dielectric and conventional heating. The tailor-made laboratory-scale microwave loop reactor set-up was capable to provide a good reproducibility of the reaction conditions and an accurate temperature control in the cavity. Furthermore, it enabled a realistic comparison of dielectric and conventional heating.

The effects of polar and non-polar solvents on enantioselective hydrogenation of ethyl pyruvate were studied in toluene and ethyl alcohol. In case of toluene, which is microwave transparent, no significant differences in the reaction rate and enantioselectivity were observed between dielectric and conventional heating. In case of ethyl alcohol, the reaction rate remained unaffected. However, the ee dramatically decreased from 60 to 40% under microwave heating. This observation was probably caused by the local superheating of the polar ethyl alcohol in the cavity, which is not possible in the non-polar toluene.

No significant improvement of the reaction rate with an increasing microwave power input was observed. However, due to the inability of the media to absorb higher intensities of electromagnetic field, it was very challenging to carry out experiments at higher power inputs.

No catalyst deactivation was observed in three consecutive experiments with re-used catalyst. Furthermore, no significant enhancement of reaction rate was observed under microwave irradiation in re-use experiments. These data indicate good reproducibility of the reaction conditions and accurate temperature control in the cavity.

Slight melting of catalyst surface under microwave irradiation was determined by SEM and confirmed by nitrogen adsorption.

It can be concluded that no athermal or beneficial specific microwave effects were obtained for this model reaction representing exothermal liquid-phase hydrogenation at room temperature over Pt supported on alumina. The reaction rate and the enantioselectivity were not enhanced by dielectric heating although the catalyst selective heating took place in this model reaction. However, the data indicate good reproducibility of the reaction conditions. The experimental set-up enables a direct comparison of microwave dielectric heating and conventional heating in the same reactor system thus diminishing experimental errors.

Acknowledgements

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