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Influence of water on fast hydrogenation reactions with monolithic and slurry catalysts

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Abstract

The influence of water on the hydrogenation of α-methyl styrene (AMS) with Ni–Al_2O_3 slurry and monolithic catalysts was investigated. Addition of water to this liquid-phase hydrogenation results in a four-phase system, as applied industrially for the partial hydrogenation of benzene. Addition of already a limited amount of water to AMS reaction mixture resulted in a strong decrease in activity. This could not be explained by a poisoning effect of water.

It has been made plausible that the reaction changes from diffusion limited in hydrogen to diffusion limited in AMS in the presence of free water. The formation of a water layer around the catalyst introduces an external mass transfer resistance for AMS. Two mechanisms are proposed to explain the trend of decreasing activity upon increasing the amount of water. Both the slurry and the monolithic catalyst show the same behaviour. The water layer is formed on monoliths as easily as on slurry catalysts. As the formation of a water layer is a prerequisite for high selectivity in the partial hydrogenation of benzene, the application of monoliths in this reaction is promising. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Hydrogenation; α-Methyl styrene; Monoliths; Four-phase system

1. Introduction

The application of four-phase systems in chemical reactors is becoming of increasing importance. A few well-known examples of four-phase reaction systems are: the catalytic hydrogenation of benzonitrile (Greenfield [1]), the catalytic partial hydrogenation of benzene (Struijk et al. [2,3]) and the hydrogenolysis for deprotection of amino acids (Yamada et al. [4]).

The liquid-phase hydrogenation of benzene with ruthenium as a catalyst, is a fast reaction which yields almost 100% cyclohexane. Addition of a fourth phase, a salty water solution, can increase the selectivity towards cyclohexene resulting in a yield of 20–60%. This process is industrially being carried out by Asahi (Nagahara and Konishi [5]).

The selectivity of the reaction towards cyclohexene is highly dependent on the presence of the catalyst in the water phase (Struijk et al. [2]). The water layer has two effects. It will decrease the hydrogen concentration at the catalyst thus lowering the cyclohexene hydrogenation rate. Because of a difference in solubility of cyclohexene and cyclohexane in water, the water layer promotes the desorption of cyclohexene. In a slurry system it is very well possible for the catalyst particles to be present at the gas–liquid or the liquid–liquid interface. This will result in a loss of selectivity. A structured catalyst like the monolithic catalyst could improve this situation.

The addition of water changes the course of the reaction drastically resulting in changing the selectivity.

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Nomenclature

a	specific surface area (m^2/m^3)
C	concentration (mol/m^3)
Ca	Carberry number (–)
d_p	particle diameter (m)
d_t	channel diameter (m)
D_A	diffusion coefficient of species A (m/s^2)
g	acceleration due to gravity (m/s^2)
k_{LS}	liquid–solid mass transfer coefficient (m/s)
L_t	channel length (m)
R_{AMS}	reaction rate of AMS ($mol/(s\,m^3)$)
R_{obs}	reaction rate observed ($mol/(s\,m^3)$)
Re	Reynolds number (–)
Sc	Schmidt number (–)
Sh	Sherwood number (–)

Greek symbols

μ	viscosity ($kg/(m\,s)$)
ρ	density (kg/m^3)

Subscripts and superscripts

a	apparent
A	species A
b	bulk
f	fluid
L	liquid
S	solid

Therefore, it is hard to compare the system with and without water and to find out whether kinetics or mass transfer are governing the reaction. The hydrogenation of α-methyl styrene (AMS) was chosen as a model reaction. This is a very fast reaction, zero order in AMS, for sufficiently high concentrations of AMS, and first order in hydrogen. The apparent first order is caused by the external mass transfer limitation of hydrogen (Germain et al. [6]). AMS is irreversibly converted to cumene with no by-products from side reactions. Addition of water to the AMS system cannot change the selectivity of the reaction. The effect of water as an inhibitor or as an extra mass transfer barrier can be researched with this reaction, for both the slurry and the monolithic catalyst. The better insight in the mass transfer properties of the four-phase system can then be utilised to gain a better understanding into the cyclohexane reaction system.

2. Experimental

2.1. Chemicals

Monoliths consisting of pure γ-alumina were used as obtained from Corning, USA. $Ni(II)(NO_3)_2{\cdot}6H_2O$ and AMS were supplied by Merck–Schuchardt, Germany. Toluene was obtained from Acros organics. Hydrogen, purity 99.95% was obtained from Air Products, the Netherlands and was used without further purification.

2.2. Catalyst preparation

Monolithic catalysts were prepared by homogeneous deposition precipitation, according to Geus et al. [7]. The dimensions of the monoliths used were 1 cm diameter, 5 cm long and a channel density of 400 cells per square inch.

The 11.64 g of $Ni(NO_3)_2$ and 24.02 g of urea were dissolved in 200 ml of demineralised water. γ-Alumina monoliths with a total weight of 45 g were added to the solution. The temperature was increased to 353 K and kept at this temperature until the solution turned colourless. The monoliths were then washed with demineralised water and dried. Calcination at 673 K was followed by reduction at 823 K. The nickel loading thus achieved was 5 wt.%, as determined with X-ray fluorescence.

For preparation of the slurry catalysts, γ-alumina monoliths were ground and sieved to obtain a particle size range 35–75 μm. With this powder the same procedure as with the monoliths was followed. Only in this case the nickel salt solution was stirred during heating.

2.3. Hydrogenation apparatus

Hydrogenation experiments with monoliths were performed in a 700 cm^3 turbine autoclave from Premex reactor AG Switzerland. In this reactor up to seven 1 cm diameter monoliths can be placed. The monoliths are placed in the centre of the reactor, the turbine stirrer is located surrounding the monoliths. The autoclave is constructed of Nimonic and equipped with a magnedrive, a thermowell, a heating jacket, and a cooling coil located in the reactor wall. The temperature was regulated with a controller actuating the heating jacket and cooling water. The pressure was regulated with a Brooks forward pressure controller.

Hydrogenation experiments with slurry catalyst were performed in a 500 cm^3 titanium autoclave from Premex reactor AG Switzerland. This reactor was equipped with a gas inducing Rushton turbine stirrer, and also with a magnedrive, a thermowell, a heating jacket, and a cooling coil located in the reactor wall. The temperature was regulated with a controller actuating the heating jacket and cooling water. The pressure was regulated with a Brooks forward pressure controller.

2.4. Experimental procedure

The experimental procedure is almost identical for both reactors. For the monolithic reactor 300 ml of AMS was added to an injection vessel. For the slurry reactor 100 ml of AMS and 200 ml of toluene was added to an injection vessel. The catalyst was placed in the autoclave and reduced in situ under 5 bar hydrogen at 543 K for 2 h. The reactor was cooled down to room temperature. The solution containing the reactant was added to the autoclave and the experiments were performed at 373 K and 10 bar total pressure. To follow the course of the reaction, liquid samples were taken and analysed with a gas chromatograph with FID equipped with a CP-Sil 8CB column. Varying amounts of demineralised water were added to the solution with reactants, while keeping the total liquid volume constant.

3. Mass transfer in a four-phase system

The hydrogenation of AMS is mass transfer limited in hydrogen [6]. Assuming the liquid–solid mass transfer is rate limiting, the equation for the reaction rate can be written as

$$R_{\mathrm{AMS}} = k_{\mathrm{LS}} a (C_{\mathrm{H_2\,Organic}} - C_{\mathrm{cat}}) \tag{1}$$

in which $C_{\mathrm{H_2\,Organic}}$ is the concentration of hydrogen in the liquid surrounding the catalyst surface, C_{cat} the concentration of hydrogen on the catalyst surface and, a the interfacial area.

Introducing a second liquid phase could induce an increase in the resistance to mass transfer. If the solid phase has a preference for the second liquid phase, a layer of this second phase will be created around the solid phase.

To quantitatively determine whether the liquid–solid transfer is indeed controlling the reaction rate, a theoretical value for the mass transfer rate can be estimated with Eq. (1). Upon comparison of this rate with the experimentally determined rate, conclusions on the rate determining step can be drawn. This comparison is built into the Carberry number, *Ca*:

$$Ca = \frac{R_{\mathrm{obs}}}{a k_{\mathrm{LS}} C_{\mathrm{b}}} \tag{2}$$

For a first order reaction, a value of *Ca* smaller than 0.05 indicates that the rate of diffusion of a reagent at the liquid–solid interface does not limit the reaction rate [8].

3.1. Estimation of k_{LS} slurry catalyst

To be able to calculate the theoretical rate, an estimation of k_{LS} has to be made. For slurry catalysts the following correlation is suggested [9]:

$$\left(\frac{k_{\mathrm{LS}} d_{\mathrm{p}}}{D_{\mathrm{A}}}\right)^2 = 4.0 + 1.21 \left(\frac{g d_{\mathrm{p}}^3 (\rho_{\mathrm{a}} - \rho_{\mathrm{L}})}{18 \mu D_{\mathrm{A}}}\right)^{2/3} \tag{3}$$

Thus from the rates measured in a system with water added, if present, the change in mass transfer resistance can be calculated, as the surface area is equal for both systems.

3.2. Estimation of k_{LS} monolithic catalyst

Hatziantoniou and Andersson [10] developed an empirical model for mass transfer between the liquid phase and the wall in a monolith

$$Sh = 3.51 \times \left(\frac{Re\,Sc}{L_t/d_t}\right)^{0.44} \left(\frac{L_t}{d_t}\right)^{-0.09} \tag{4}$$

with L_t is the channel length, d_t the channel diameter and *Sh* the Sherwood number. Although this model assumes Taylor flow, it can also be used as an indication for the value of k_{LS} for this system.

4. Results and discussion

4.1. Activity measurement

In Fig. 1, a typical result of a hydrogenation run without water added, is shown. The conversion rate remains constant until approximately 70% conversion. The trend is the same for slurry and monolithic catalysts. It is clear that the system without water shows a zero order dependence on AMS.

From the concentration vs. time plots the activities of the systems were determined. In Fig. 2, the activities of monolithic catalysts vs. the amount of water per gram catalyst and, vs. the volume of the separate water phase, are shown.

Addition of a small amount of water results in a large decrease in activity. Readily, an activity loss of over 90% is reached. For the slurry catalysts (Fig. 3), a similar trend can be observed but more water per gram catalyst is needed.

4.2. Water mass balance

The reactants and solvents used are not predried. However, the solubility of water at room temperature in the organic liquid results in a total dissolution of only 0.08 ml in the reaction system before water is added. This amount is a maximum, in practice the amount dissolved will be less. Moreover, the quantity of water added in the experiments exceeds this volume at least 12 times. The contribution of the already dissolved water can therefore be neglected. When water is added to the reaction mixture, some water will dissolve in the organic phase, some water will be in the vapour phase. The remaining part will be present as liquid water, forming a separate phase.

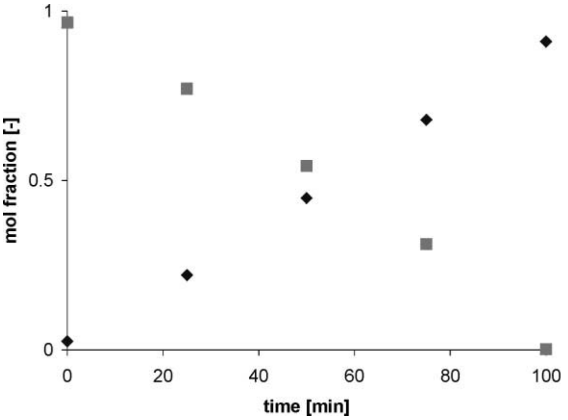

Fig. 1. Typical result of an AMS hydrogenation run showing the mole fraction of AMS (■), and the mole fraction of cumene (◆), vs. time in minutes. Pressure: 10 bar, temperature: 373 K, 4 g Ni on Al_2O_3 monolithic catalyst, 0 ml H_2O, 300 ml AMS.

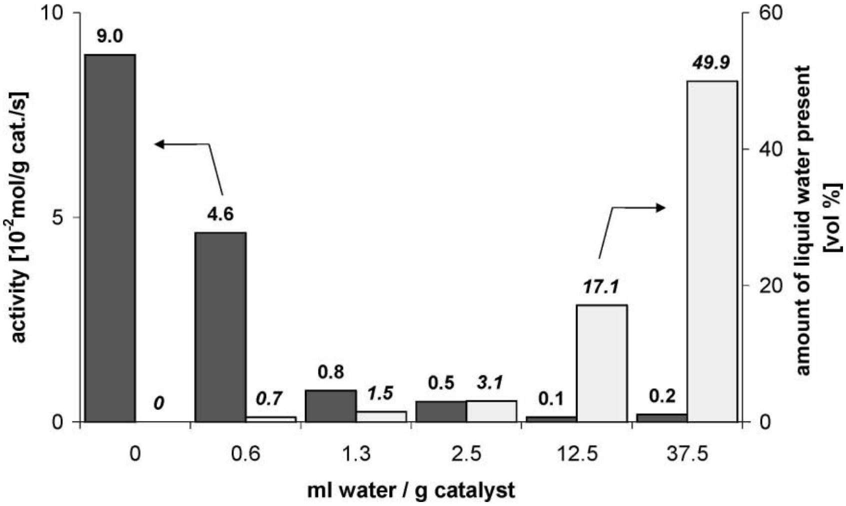

Fig. 2. Activity of monolithic catalyst in the hydrogenation of AMS vs. the amount of water added. Pressure: 10 bar, temperature: 373 K, 4 g of Ni on Al_2O_3 monolithic catalyst, 150–300 ml AMS, 2.5–150 ml H_2O.

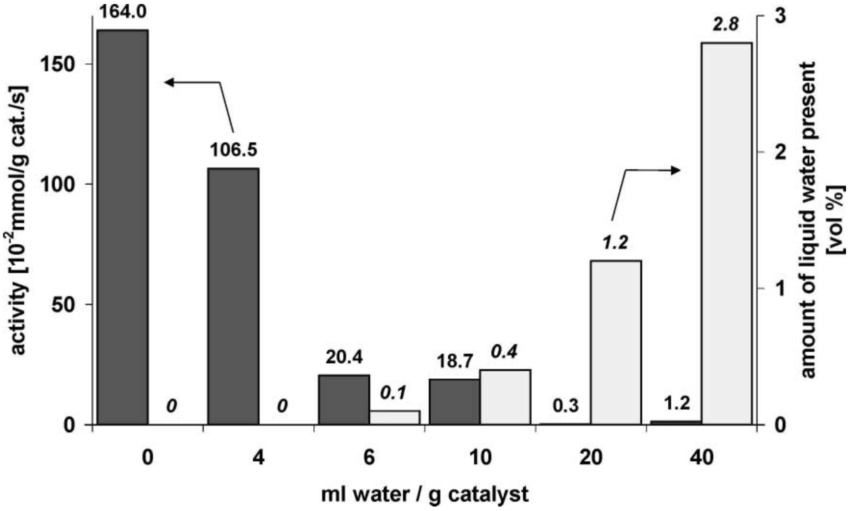

Fig. 3. Activity of slurry catalyst in the hydrogenation of AMS vs. the amount of water added. Pressure: 10 bar, temperature: 373 K, 0.25 g Ni on Al_2O_3 slurry catalyst, 100 ml AMS, 200 ml toluene, 1–10 ml H_2O.

In the experiments performed in the monolithic reactor, there is 0.1 g present as water vapour [11]. Taking into account the solubility of water in the organic phase at 100°C, a maximum of 0.5 ml water is dissolved [12,13]. As shown in Fig. 2, a separate water phase is present in each experiment with water added.

In the case of the slurry experiments there is also 0.1 g present as water vapour. However, as the organic phase is diluted with toluene, the solubility is different. Approximately, 1.2 ml water can dissolve in the organic phase. As is also shown in Fig. 2, with 4 ml water per gram catalyst, there is no free water present. In this case, the vapour pressure is estimated to be not higher than one time the partial pressure of the pure component. A maximum of 0.2 g water will be present as vapour. The presence of a separate water phase in the remaining cases is confirmed by visual observation.

4.3. Poisoning

The loss of activity could be the result of water adsorbing irreversibly on the active sites. However, if this would be the case, only a limited amount of water would be needed, with a maximum of the pore volume of the catalyst. Furthermore, increasing the amount of water above the pore volume would have no further effect.

The γ-alumina carrier material used has a porosity of approximately 0.5. The density of the material is 1700 kg/m^3. Thus for the slurry system 0.07 ml and for the monolithic system 1.17 ml water could fill the total pore volume. Adding 1.5 ml to the slurry system and 2.5 ml to the monolithic system would be more than sufficient. However, from Figs. 2 and 3, it can be seen that the effect of adding this amount is limited in reducing the activity. Increasing the amount of water further has a pronounced effect. Therefore, it can be concluded that water does not have a poisoning effect on the nickel catalyst.

4.4. Mass transfer limitation slurry system

It is assumed that the system without water is liquid–solid, mass transfer limited in hydrogen. Evaluation of the Carberry number can clarify this. The k_{LS} and the theoretical mass transfer rate calculated for the slurry system are shown in Table 1. The diffusivities necessary for the calculation of k_{LS} were estimated with [14]. The Carberry number indicates that liquid–solid mass transfer is most probably the rate-limiting step. As the concentration of AMS does not influence the conversion rate, it is not mass

Table 1
Calculated values for mass transfer in slurry and monolithic system with organic or water layer surrounding the catalyst

Solute	Solvent	Solubility (mol/m^3)	$k_{LS}a$[a] (s^{-1})	$k_{LS}a$[b] (s^{-1})	Activity[c] ($mol\,g^{-1}\,s^{-1}$)	Activity observed ($mol\,g^{-1}\,s^{-1}$)	Carberry (–)
Slurry catalyst							
H_2	Organic	40	78	1.14E−03	1.85E−03	1.64E−03	0.89
	Water	10	123	7.20E−04	7.33E−04[d]	2.19E−04	0.30[d]
AMS	Water	2	33	3.08E−04	3.50E−05[e]	1.22E−05	0.35[e]
Monolithic catalyst							
H_2	Organic	40	6.6	1.99	1.57E−04	8.97E−05	0.57
	Water	10	8.7	2.60	5.10E−05	4.62E−05[f]	0.91[f]
AMS	Water	2	9.1	2.72	9.45E−06	1.80E−06[g]	0.19[g]

[a] Estimated from Eqs. (3) and (4) based on m^3 catalyst.

[b] Estimated from Eqs. (3) and (4) based on m^3 reaction volume.

[c] Estimated from Eq. (1).

[d] Activity measured with 0.1 vol.% of water.

[e] Activity measured with 2.8 vol.% of water.

[f] Activity measured with 0.7 vol.% of water.

[g] Activity measured with 50 vol.% of water.

transfer limited in AMS. The assumption that the system without water is mass transfer limited in hydrogen is therefore confirmed.

Addition of water to the system lowers the activity. If poisoning is not the reason for the loss of activity, diffusion limitation could be the cause. Forming a physical layer around the catalyst particles, water introduces a resistance to mass transfer for both hydrogen and AMS. Furthermore, the solubility of hydrogen and AMS in water is rather low [15].

Suppose the reaction remains mass transfer limited in hydrogen. The k_{LS} for hydrogen when the catalyst particle is surrounded by a water layer can be calculated. The resulting mass transfer rate, using the solubility of hydrogen in water, is indeed lowered. The rate is half of the mass transfer rate in the organic system (Table 1).

The activity measured, however, is lowered much more upon increasing the volume of water added. In the system without water, there is no mass transfer limitation in AMS. But addition of water may change this situation. Because of the low solubility of AMS in water, the concentration of AMS near the catalyst surface is reduced with a factor 1000. The k_{LS} for AMS in water is also less than the k_{LS} for hydrogen. Suppose the reaction becomes mass transfer limited in AMS. In that case a first order plot should show a straight line. In Fig. 4, it can be seen that this transition takes place. D shows a clear first order dependence on AMS. The calculated mass transfer rate is of the same order of magnitude as the lowest activity measured (Table 1). This supports the observation that provided enough water has been added, the reaction becomes mass transfer limited in AMS.

The intermediate region could point towards two mechanisms. The first one assumes incomplete coverage of the catalyst particles with water. The activity of the uncovered particles is an order of a magnitude higher than of the covered particles. The contribution of these uncovered particles to the total reaction rate is relatively high. As the amount of water is increased, the percentage of partly covered particles is expected to decrease until all particles are covered and the reaction rate is equal to the mass transfer limited rate of AMS in water.

The second one presumes a gradual increase of the thickness of the water layer. The calculation of the mass transfer rate of AMS in water assumes a fully developed water layer. In this case the thickness of that layer is approximately 700 μm as can be calculated from the Sherwood number. A layer of this thickness can only be formed with 3.2 vol.% water.

The preference of the catalyst particles for either phase could elucidate which mechanism prevails. From visual observations it was clear that in case of a four-phase system, the catalyst was located in the

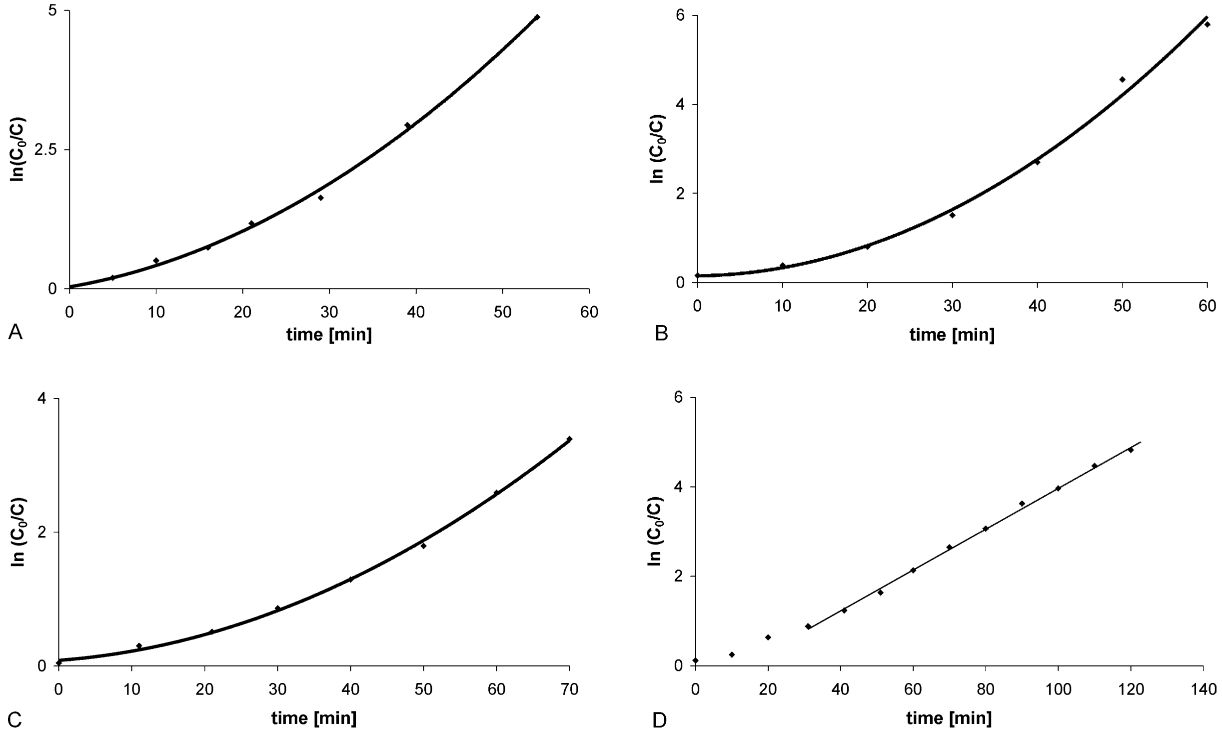

Fig. 4. First order plots of AMS hydrogenation experiments with different amounts of water added in slurry reactor. Pressure: 10 bar, temperature: 373 K, 0.25 g Ni on Al_2O_3 slurry catalyst, 100 ml AMS, 200 ml toluene. Amount of water added: (A) 0 ml; (B) 1 ml; (C) 1.5 ml; (D) 2.5 ml.

water phase. So, what is seen to be happening is the transfer of the catalyst from the organic phase to an increasing volume of the water phase. It may be clear that at the same stirrer speed, the droplet size will enlarge upon expansion of the water volume. This will also increase the effective film thickness around the catalyst particles. Thus the decrease in activity upon increasing the amount of free water can be explained.

In the absence of free water (as is the case with 4 ml/g slurry catalyst) there is still a pronounced effect. This can be caused by the adsorption of water on the catalyst surface.

4.5. Mass transfer limitation monolithic system

Upon addition of water, in the monolithic system the same trend as in the slurry system can be observed (Fig. 5). Evaluation of the Carberry number (Table 1) shows that the reaction rate is indeed influenced by external mass transfer limitation in hydrogen.

As in the slurry system, the decrease in activity cannot be explained by the lower solubility of hydrogen in water. Moreover, from Fig. 5 it can be seen that above 1.3 ml water per gram catalyst the reaction rate shows a first order dependence on AMS. This strongly suggests external mass transfer limitation in AMS. If mass transfer resistance is caused by the presence of a water layer, calculation of the reaction rate with the solubility of AMS in water taken into account should confirm this. The calculated rate is indeed in the same order of magnitude as the lowest activity measured. Thus, provided enough water has been added, the reaction becomes mass transfer limited in AMS in the monolithic system.

4.6. Partial hydrogenation of benzene

The AMS reaction system shows a mass transfer limitation in the organic reactant. In the partial hydrogenation of benzene it has been found that the reaction

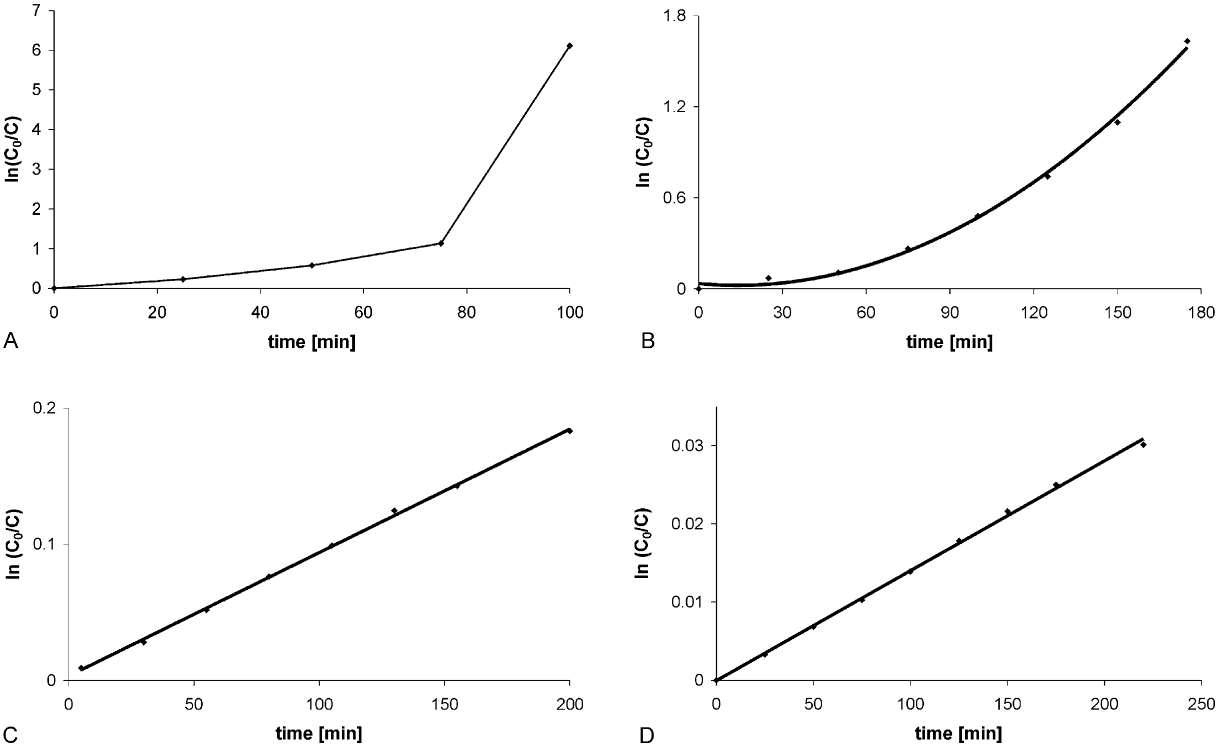

Fig. 5. First order plots of AMS hydrogenation experiments with different amounts of water added in monolithic reactor. Pressure: 10 bar, temperature: 373 K, 4 g of Ni on Al_2O_3 monolithic catalyst, 300 ml AMS. Amount of water added: (A) 0 ml; (B) 2.5 ml; (C) 5 ml; (D) 50 ml.

is mass transfer limited in both benzene and hydrogen [2,16]. However, this is mainly due to the rather high solubility of benzene in water at the reaction temperature compared to the solubility of AMS in water. The two reaction systems with water thus show a comparable behaviour.

A water layer surrounding the catalyst is reported to be essential to a obtain a high selectivity in the partial hydrogenation of benzene. Large amounts of water, up to 50 vol.% were therefore added to the slurry reaction mixture [2,16]. Here, it has been shown that addition of only a limited amount of water is sufficient to form the necessary water layer. This is true for both the slurry and the monolithic system.

The water layer is formed on monoliths as easily as on slurry catalysts. The difference is that a monolithic reactor is much better defined. The monolithic catalyst is not likely to be exposed directly to the organic or the gas phase. Therefore, application of monoliths in the partial hydrogenation of benzene is promising.

5. Conclusions

Addition of a limited amount of water to AMS reaction mixture (1.6 vol.% for slurry, 3.6 vol.% for monoliths) resulted in a loss of activity of 90%. This trend was observed for both slurry and monolithic catalysts.

It is tentatively concluded that the reaction changes from diffusion limited in hydrogen to diffusion limited in AMS. The formation of a water layer around the catalyst introduces an external mass transfer resistance for AMS.

In principle, the water layer is formed on monoliths as easily as on slurry catalysts. However, the monolithic catalyst is not likely to be exposed directly to the organic or the gas phase and, as a consequence, is a much better defined system.

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References

[1] H. Greenfield, Ind. Eng. Chem. Prod. Res. Dev. 15 (1976) 156–158.

[2] J. Struijk, M. d'Angremond, W.J.M. Lucas-de-Regt, J.J.F. Scholten, Appl. Catal. A 83 (1992) 263.

[3] J. Struijk, R. Moene, T. van der Kamp, J.J.F. Scholten, Appl. Catal. A 89 (1992) 77.

[4] H. Yamada, T. Tagawa, S. Goto, J. Chem. Eng. Jpn. 29 (1996) 373–376.

[5] H. Nagahara, M. Konishi, US Patent 4 734 536 (1988).

[6] A. Germain, A. Lefebvre, G. L'Homme, in: H. Hulburt (Ed.), Chemical Reaction Engineering II, Advances in Chemistry Series 133, American Chemical Society, Washington, DC, 1974, pp. 164–180.

[7] J.W. Geus, L.M. Knijf, R.H. Bolt, R. van Ieperen, A.J. van Dillen, Stud. Surf. Catal. 63 (1991) 119–174.

[8] J.J. Carberry, in: J.R. Anderson, M. Boudart (Eds.), Catalysis: Science and Technology, Vol. 8, Springer, Berlin, 1987, p. 131.

[9] G.W. Roberts, in: P.N. Rylander, H. Greenfield (Eds.), Catalysis in Organic Synthesis, Academic Press, New York, 1976, pp. 1–48.

[10] V. Hatziantoniou, B. Andersson, Ind. Eng. Chem. Fund. 21 (1982) 451.

[11] R.C. Weast, CRC Handbook of Chemistry and Physics, 64th Edition, CRC Press, Boca Raton, FL, 1985.

[12] A.S. Kertes (Ed. in Chief), D.G. Shaw (Volume Ed.), Solubility Data Series, Vol. 37, Hydrocarbons with Water and Seawater, Part I: Hydrocarbons C5 to C7, Pergamon Press, Oxford, 1989.

[13] A.S. Kertes (Ed. in Chief), D.G. Shaw (Volume Ed.), Solubility Data Series, Vol. 38, Hydrocarbons with Water and Seawater, Part II: Hydrocarbons C8 to C36, Pergamon Press, Oxford, 1989.

[14] R.C. Reid, J.M. Prausnitz, B.E. Poling, The properties of gases and liquids, 4th Edition, McGraw-Hill, New York, 1988.

[15] C.L. Young (Ed.), Solubility Data Series, Vols. 5–6, Hydrogen and Deuterium, Pergamon Press, Oxford, 1981.

[16] L. Ronchin, L. Toniolo, Catal. Today 48 (1999) 255–264.