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Three-phase catalytic hydrogenation of xylose to xylitol — prolonging the catalyst activity by means of on-line ultrasonic treatment

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Abstract

A novel concept for improvement of the activity of recirculated Raney nickel catalyst by means of on-line ultrasonic irradiation was studied. Qualitatively, acoustic irradiation was clearly found to retard the catalyst deactivation in the three-phase hydrogenation of xylose to xylitol. Two different intensities of the ultrasonic field were utilized in the experiments. The hydrogenation kinetics was modeled with a semi-competitive reaction–adsorption model accounting for interstitital adsorption sites for hydrogen located between larger organic molecules.

The deactivation of the Raney nickel catalyst was found to diminish notably upon the use of on-line acoustic irradiation. Also, the selectivity of the system was found to be improved by the use of ultrasound in comparison to the case when no acoustic energy was dispatched to the system. The kinetic model used in the fitting of the data was able to explain the experimental concentrations fairly well.

Keywords: Raney nickel catalyst; Ultrasonic treatment; Catalytic hydrogenation of xylose; Xylitol

1. Introduction

Hydrogenation kinetics of xylose to xylitol was investigated in a three-phase laboratory autoclave. Xylitol, a sugar alcohol with interesting properties, has a high sweetening capacity and its crystals resemble those of normal sugar. Besides, xylitol possesses non-diabetic and anti-caries properties. The most common catalysts used for the hydrogenations of sugars to the corresponding sugar alcohols are of Raney nickel type. The catalyst is rather inexpensive, it is easy to use as suspended slurry in typical industrial batch reactors and it has a good activity and selectivity. Anyhow, there exists drawbacks: rather rapid catalyst deactivation and difficult separation from the reaction medium.

Ultrasonic irradiation enhances heterogeneous catalysis on Ni. It has been found that ultrasound has multiple effects on the morphology and surface characteristics of inorganic solids: in solid–liquid systems, acoustic cavitation causes surface damage, increased surface area and increased particle aggregation due to high velocity interparticle collisions [1]. A tailor-made, high intensity ultrasonic liquid processing system was integrated to the reactor autoclave in hope for enhanced reaction and extended catalyst lifetime. A schematic illustration of the experimental setup is illustrated in Fig. 1.

The question is, of course, why the catalyst deactivation is retarded by the use of acoustic irradiation, since catalyst characterization studies (SEM, ESCA, BET) as well as kinetic experiments indicated that the deactivation rate of the catalyst clearly diminished by the use of ultrasonic irradiation: we propose that

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Nomenclature

A	D-arabinitol
c_i	concentration
F	furfural
H	hydrogen
K_d	deactivation rate parameter
K_i	adsorption constant
k_i	reaction rate constant
Q	objective function in non-linear regression analysis
R_i	reaction rate
RDS	rate-determining step
S	D-xylose
t_d	total time the catalyst has been in use in all batches
w_j	weight factor of component j
X	xylitol
Xy	D-xylulose

Greek symbols

α	relative activity of the catalyst
β	asymptotic activity of the catalyst (0–1): no ultrasonic treatment: 1.0, 0.85, 0.5; with ultrasonic treatment: 1.0, 0.9, 0.9, 0.9
Θ	fraction of sites covered by organic species (0–1)
Σ	a collection of terms $[(K_S + K_{Xy}k_{isom})c_S + K_Ac_A + K_Xc_X + K_Fc_F]$

Subscripts and superscripts

A	index referring to the RDS (xylulose to arabinitol)
i,j	general index
iset	index indicating the batch
XI	index refering to the RDS (xylose to xylitol)
XII	index referring to the RDS (xylulose to xylitol)

the primary reason for catalyst deactivation is the loss of active sites on the catalyst surface due to the leaching of the promoter metal, Mo, surface restructuring and adsorbed organic residues. The acoustic irradiation "grinds" the catalyst into smaller particles, thus revealing new, previously unexposed surface and therefore, de facto, creates new active sites for the hydrogenation reaction [2].

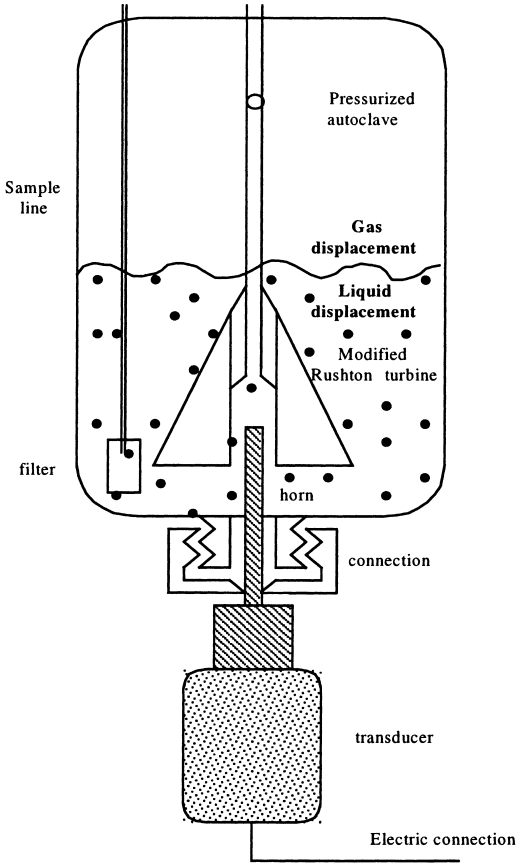

Fig. 1. The experimental apparatus for xylose hydrogenation with simultaneous acoustic irradiation.

Acoustic energy is mechanical by its nature, i.e. it is not adsorbed by molecules. In the liquid bulk of the reaction medium, cavitation bubbles are formed, provided that the intensity of ultrasonic field is sufficiently high. Cavitation close to the liquid–solid interface differs from that in pure liquid. Two mechanisms for the effects of cavitation in the vicinity to the surfaces have been proposed: microjet impact and shockwave damage. The existence of both mechanims has been established, but their relative importance is still a matter of debate [3]. Suslick [3] states that microjet formation cannot take place at ultrasonic frequencies of ≅20 kHz, in solid–liquid systems with solid particles smaller than ≅200 μm. However, in case of Ni powder, a considerable decrease in the thickness of the oxide coat after ultrasonic irradiation was found.

Thus, it is possible that even the most modest oxygen concentrations in the reactive liquid might contribute notably to the deactivation of Ni catalysts.

2. Experimental

Xylose hydrogenation experiments were performed in a pressure range of 40–70 bar, since the hydrogenation velocity is extremely low at an ambient hydrogen pressure. The temperature was varied between 80 and 130°C, in accordance to the temperature range of optimized operation. The concentration regime chosen for the majority of the hydrogenation experiments was 40–60 wt.% xylose in water [4]. The catalyst amount was 5 wt.% of the initial xylose mass. The effective volume of the autoclave (Parr Instrument) was 300 ml. The actual volume of the reaction medium used in the experiments was 250 ml. In these particular experiments the initial xylose concentration chosen was 50 wt.% (140 g).

Before each experiment, the catalyst and the reactor vessel were preheated under hydrogen atmosphere to the desired temperature. Simultaneously, the xylose–solvent mixture was heated under hydrogen flow (15 min) in a preheater. Also, bubbling with nitrogen was tested, thus confirming that presaturation of the reactive mixture with hydrogen does not affect the reaction rate measurably in our experimental conditions. The liquid reactant–solvent mixture was fed into the reactor rapidly, after which the pressure was immediately adjusted to the experimental conditions. Simultaneously, the stirrer was switched on. This moment was considered as the initial starting time of the experiment. The water used was always deionized. Hydrogen had a purity of 99.999% (Oy AGA Ab).

A commercial Raney nickel catalyst was used. The average particle size was found to be 22.3 μm. The reactor contents were analyzed off-line with a liquid chromatograph (HP 1100 LC Series) equipped with an HP 1047A RI-detector. The removal of the catalyst was avoided by placing a filter in the sampling line. In the beginning of the experiment, the samples were withdrawn more frequently (every 2–5 min) than during the main course of the reaction (every 20 min).

After completed batch hydrogenation experiment the autoclave contents were discarded and the catalyst was allowed to sedimentate at the bottom of the autoclave. Before reinsertion into the autoclave the catalyst was washed with pure water and filtrated. Care was taken to avoid catalyst contact with air, since Raney nickel catalyst is pyroforic and easily oxidized.

The experiments with on-line acoustic irradiation were performed at 110°C, 50 bar (Fig. 2) and 100°C, 40 bar (Fig. 3). The power supplied in the first series was the maximally attainable 100 W [2], whereas in the second one half of this, i.e. 50 W. The apparatus consisted of a generator (20 kHz, 0–100 W), a piezoelectric transducer and a titanium horn (12 ± 1 μ peak to peak) with a tailor-made connection to the bottom of the autoclave. The total input of acoustic energy supplied to the system was 0.4–0.2 W/ml, or related to the tip area (1.54 cm^2) of the probe 65–32.5 W/cm^2. A picture introducing the vibrating probe tip in the

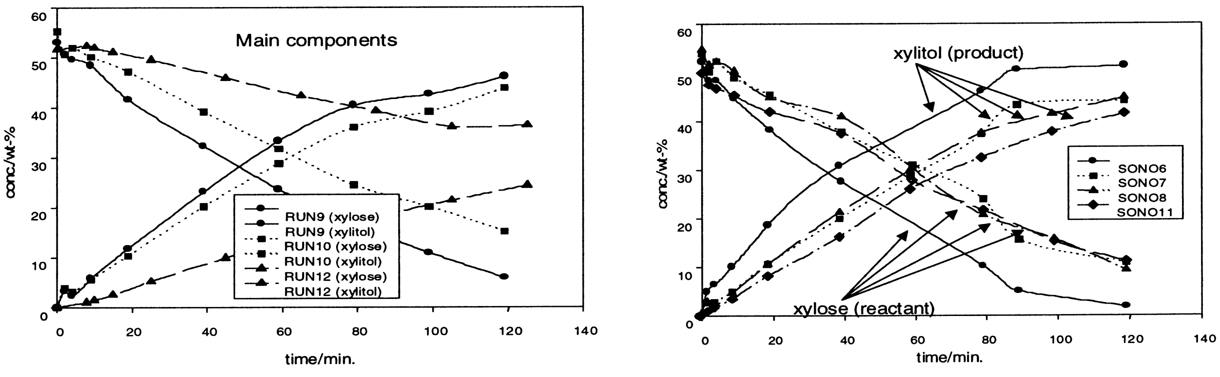

Fig. 2. The concentration profiles of xylose and xylitol without (left) and with (right) on-line acoustic irradiation (batches with recycled catalyst). Acoustic field 100 W, 110°C, 50 bar.

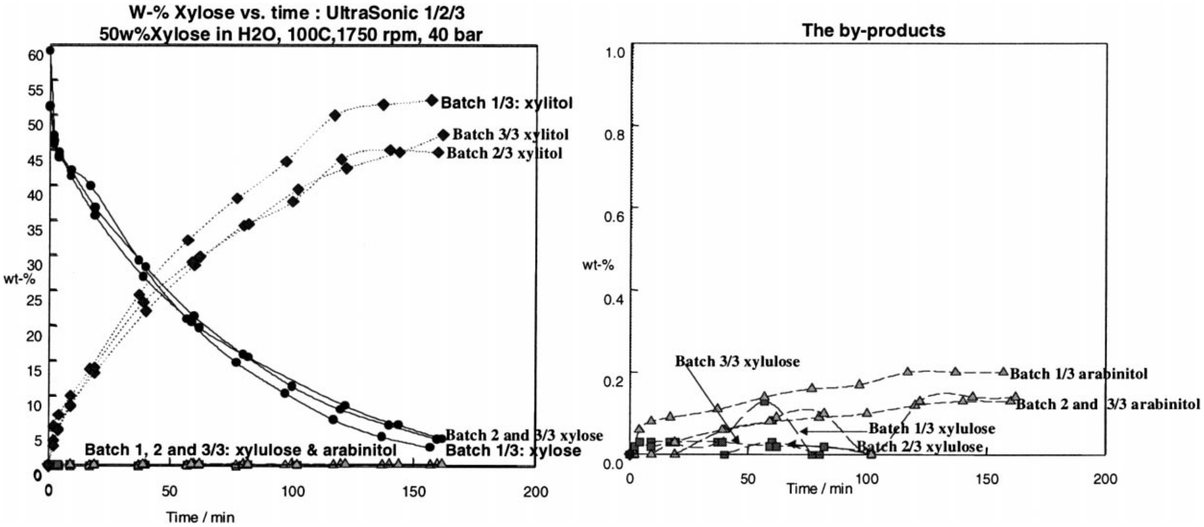

Fig. 3. The concentration profiles of xylose and xylitol and the by-products with on-line acoustic irradiation (batches with recycled catalyst). Acoustic field 50 W, 100°C, 40 bar.

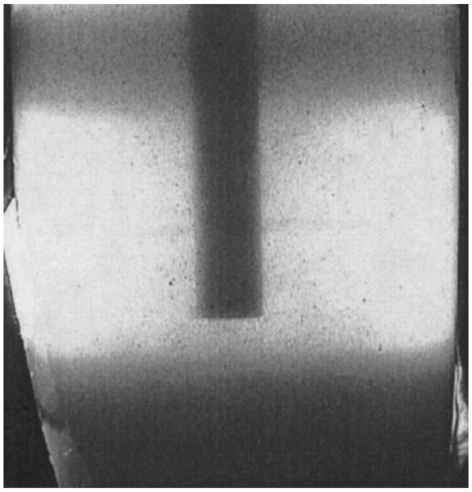

Fig. 4. The sonoprobe.

reactive medium with suspended Raney nickel solids is displayed in Fig. 4.

3. Catalyst deactivation and kinetic model

The hydrogenation kinetics was modeled with a new semi-competitive adsorption–surface reaction model, which was tested with the experimental kinetic data. The developed semi-competitive adsorption–desorption model is especially useful for systems containing reaction between hydrogen and large-sized organic molecules. Since the organic molecules taking part in the reaction are much larger than hydrogen atoms, it would be rather unrealistic to assume a complete competitive adsorption of hydrogen and the organic molecules: between the organic molecules, there always remain interstitial adsorption sites accessible for hydrogen. Typically the adsorption and desorption steps are assumed to be rapid, whereas the hydrogenation steps on the surface are presumed to be rate controlling. The hydrogenation steps are regarded as irreversible. After a standard treatment of the surface rate equations and application of adsorption–desorption quasi-equilibria, the following rate equations were obtained for the semi-competitive model [5,6]:

$$R_{\mathrm{XI}} = \frac{k_{\mathrm{RDS,XI}} K_{\mathrm{S}} K_{\mathrm{H}}^{2/i} \Theta[1+(1-\Theta)\Sigma]^2 c_{\mathrm{S}} c_{\mathrm{H}}^{2/i}}{[1+(K_{\mathrm{H}}c_{\mathrm{H}})^{1/i}+\Sigma+(1-\Theta)(K_{\mathrm{H}}c_{\mathrm{H}})^{1/i}\Sigma]^{i+1}} \tag{1}$$

$$R_{\mathrm{XII}} = \frac{k_{\mathrm{RDS,XII}} K_{\mathrm{Xy}} K_{\mathrm{H}}^{2/i} \Theta[1+(1-\Theta)\Sigma]^2 c_{\mathrm{S}} c_{\mathrm{H}}^{2/i}}{[1+(K_{\mathrm{H}}c_{\mathrm{H}})^{1/i}+\Sigma+(1-\Theta)(K_{\mathrm{H}}c_{\mathrm{H}})^{1/i}\Sigma]^{i+1}} \tag{2}$$

$$R_F = \frac{k_{RDS,F}\Theta c_S}{[1+(K_H c_H)^{1/i} + \Sigma + (1-\Theta)(K_H c_H)^{1/i}]} \tag{3}$$

$$\Sigma = (K_S + K_{Xy}k_{isom})c_S + K_A c_A + K_X c_X + K_F c_F \tag{4}$$

$$R_A = \frac{k_{RDS,A}K_{Xy}K_H^{2/i}\Theta[1+(1-\Theta)\Sigma]^2 c_S c_H^{2/i}}{[1+(K_H c_H)^{1/i} + \Sigma + (1-\Theta)(K_H c_H)^{1/i}\Sigma]^{i+1}} \tag{5}$$

the complete set of plausible surface steps are presented in Fig. 5.

A deactivation model was also coupled to the rate equations: the relative activity of the catalyst is proportional to the number of accessible active sites, and for the disappearance of the sites obeys a first-order kinetic model [7]. On the other hand, the experiments revealed that the catalyst decay is not complete; some hydrogenation activity always remains after successive experiments. This can partly be explained by reversible adsorption of organics. Therefore we complete the conventional deactivation model with a term accounting for the reversibility. The following differential equation describes the change of the relative activity (α) of the catalyst:

$$\frac{d\alpha}{dt} = -k_d(\alpha - \beta) \tag{6}$$

where β is the asymptotic activity and k_d the rate constant of the activity decay. Solution of the differential equation with the initial condition $t = 0,\ \alpha = 1$ gives

$$\alpha = \beta + (1-\beta)\,e^{-k_d t_d} \tag{7}$$

where t_d is the total time for which the catalyst has been exposed to reaction conditions. The deactivation model is treated in more detail in our previous publication [7].

$$S + * \xleftrightarrow{k_S} S*$$
$$H_2 + 2* \xleftrightarrow{k_H} 2(H*)$$
$$S \xrightarrow{k_{isom}} X_Y$$
$$X_Y + * \xleftrightarrow{k_{XY}} X_y*$$
$$S* + 2(H*) \xrightarrow{k_{RDS,XT}} X* + 2*$$
$$X_Y* + 2(H*) \xrightarrow{k_{RDS,XYT}} X* + 2*$$
$$X_Y* + 2(H*) \xrightarrow{k_{RDS,A}} A* + 2*$$
$$X* \xleftrightarrow{k_X} X + *$$
$$A* \xleftrightarrow{k_A} A + *$$
$$S* \xleftrightarrow{k_{RDS,F}} F* + 3H_2O$$
$$F* \xleftrightarrow{k_F} F + *$$

Fig. 5. The reaction and adsorption on Ni surface: $i = 1$ or 2; S: D-xylose; Xy: D-xylulose; X: xylitol; A: D-arabinitol; F: furfural.

4. Results

The catalyst deactivation was notable from first to the second batch, after which the activity was found to remain essentially constant (Figs. 2 and 3). On the other hand, in the second series (S40–S42) the catalyst activity seemed to remain closer to the original level of the first batch even in the successive second and third hydrogenation batch. The reason for this observation is not totally resolved: however, since the recirculation of the catalyst in the first series was performed by means of filtration with a vacuum pump, whereas in the second series by means of sedimentation, it is probable that the catalyst oxidation by air contributed to the loss of activity during the first series. Also, the somewhat lower hydrogenation temperature and the lower intensity of the acoustic irradiation might be favorable. For both series, the catalyst was also washed with deionized water a priori to the re-insertion to the reactor vessel.

The value of the deactivation constant, k_{d0}, was found to be $4.5 \times 10^{-3}\,\text{min}^{-1}$ for the series with half effect of acoustic irradiation, 100°C and 40 bar, compared with the value, $6 \times 10^{-3}\,\text{min}^{-1}$ (Fig. 6) that was found to apply for a system without acoustic irradiation [8]. This implies that the catalyst deactivation has been considerably diminished by application of ultrasonic field into the reactive media with suspended solids. It is also interesting to observe that the amount of by-products diminishes at the successive batches with recycled catalyst. It is probable that the minor

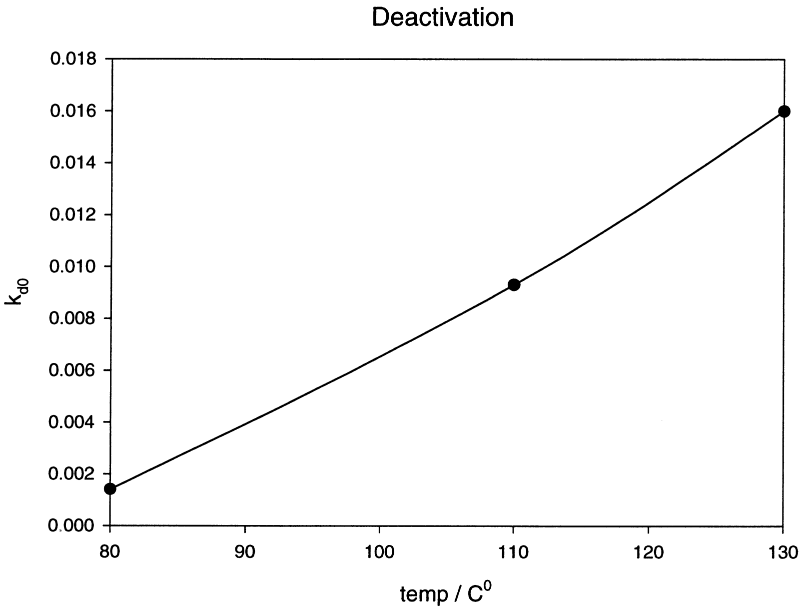

Fig. 6. The deactivation constant, k_{d0}, as a function of temperature for a system without acoustic irradiation.

amounts of aqueous sodium hydroxide (storage liquid for Raney nickel) left in the pores of the fresh catalyst contribute to the lower selectivity of the catalyst during the first batch.

The fitting of the hydrogenation experiments was performed with Modest software [9] using a combined Simplex Levenberg–Marquardt method. The following objective function was used in data

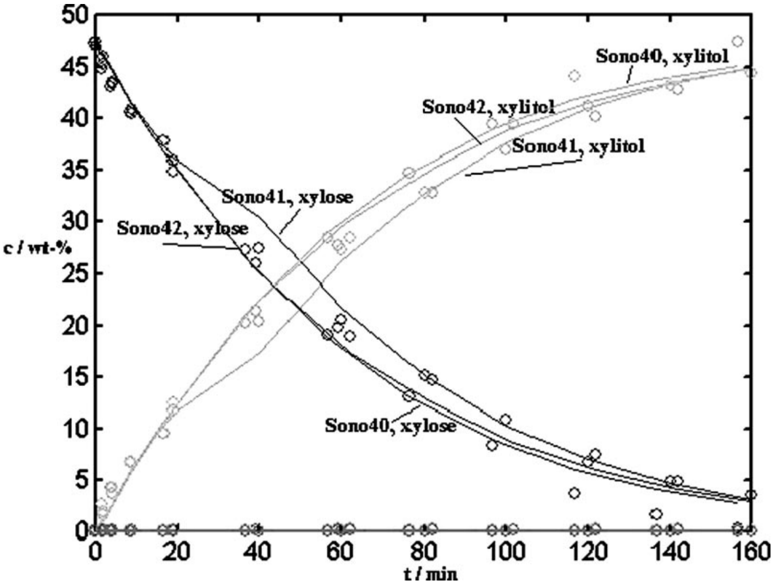

Fig. 7. A sample model fit for the hydrogenation experiments (100°C, 40 bar).

fitting,

$$Q = \sum (c_{i,\mathrm{exp}} - c_{i,\mathrm{calc}})^2 w_i \tag{8}$$

where the weight factors were chosen as follows: $w = 1$ for xylose and xylitol, whereas $w = 5$ for the by-products. Weighting was necessary to give some influence to the by-products in data fitting. Since the concentrations of the by-products was much lower (typically below 1 wt.%; D-xylulose, D-arabinitol, furfural) compared to the concentrations of the main components (D-xylose, xylitol), the use of weighting was clearly beneficial. The model was able to predict the experimental concentrations fairly well. The obtained degree of explanation for the series performed at 100°C and 40 bar was 99.7%. The amount of experimental points used in the regression analysis was 37. A sample model fit is displayed in Fig. 7.

Acknowledgements

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