Trickle bed reactors: Effect of liquid flow modulation on catalytic activity

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ABSTRACT

The effect of slow ON–OFF liquid flow modulation on the oxidation of aqueous solutions of ethanol using a 0.5% Pd/Al$_2$O$_3$ commercial egg-shell catalyst was investigated in a laboratory trickle bed reactor (TBR). In this mode of operation, the catalyst was cyclically exposed to oxidative and reductive environments. The study was carried out under different gas and liquid flow rates, cycle periods and splits. Cycling results have been compared with the steady-state experiments performed at the corresponding average liquid flow rate. Significant improvements over the continuous operation were obtained when the catalyst was exposed to a short surplus of oxygen (to minimize deactivation by overoxidation in the kinetic regime) after a longer time of working in the mass transfer limited regime. According to the results presented here, it is recommended to work with high liquid flow rates and moderate gas flow rates to ensure complete wetting of the catalyst during the ON cycle and to minimize the overoxidation process during the OFF cycle.

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1. Introduction

The aqueous catalyzed alcohol oxidation with molecular oxygen can provide useful products and intermediates for various applications in fine chemistry. This process is quite attractive and, compared with traditional stoichiometric oxidations presents economical and environmental advantages. Reaction conditions are mild, and typically temperatures below 90 °C at atmospheric pressure in neutral or slightly alkaline aqueous media are used.

The intrinsic kinetics of noble metal catalyzed alcohol oxidation has been extensively studied in the last decade (Mallat and Baiker, 1994; Horányi, 1994; Markusse et al., 2001). The most accepted reaction scheme for the transformation of alcohols on Pd/Al$_2$O$_3$ states that aldehydes are formed via the oxidative dehydrogenation of the alcohol. Then, the aldehydes are further oxidized to carboxylic acids (via hydration–dehydrogenation reactions) or may decompose to produce strongly adsorbed carbon monoxide (CO) and hydrocarbon residues (decarbonylation) (Keresszegi et al., 2005; Mallat and Baiker, 2004).

As in most heterogeneous systems, proper treatment of the kinetics has to take into account oxygen mass transport and diffusion considerations (Kluytmans et al., 2000). Particularly, when oxygen mass transport is limiting, the dehydrogenation activity of noble metal catalysts is usually low because the active sites are covered by coproduct hydrogen. According to Keresszegi et al. (2002), the role of oxygen is to oxidize the adsorbed hydrogen to water, therefore increasing reaction rates. So, in order to carry out the reaction at appropriate rates, oxygen mass transport has to be enhanced.

Deactivation may occur for several reasons but its nature is largely influenced by the amount of oxygen present at the catalyst surface. In reducing conditions, the catalyst may be slowly deactivated by adsorption of hydrocarbon intermediate products and CO. The relevance of this process depends on the type of reactants used (Kluytmans et al., 2000). This deactivation mechanism is reversible and the removal of CO can be achieved exposing the catalyst to oxygen, while the remotion of the hydrocarbon intermediate products is achieved in strong reducing conditions (Keresszegi et al., 2002).

When the oxygen mass transfer rate is enhanced, the rate of dehydrogenation increases, and an optimum alcohol dehydrogenation rate can be obtained. However, this situation is not easy to achieve since the rate of oxygen supply easily exceeds the rate of oxygen consumption (Gangwal et al., 2005). So, in the intrinsic kinetic regime, the catalyst surface is rapidly oxidized, inactive surface oxides are formed and the catalyst deactivates due to overoxidation.

Particularly, for noble metal catalyzed alcohol oxidation carried out in continuous reactors, the relative importance of kinetics and mass transfer steps can switch as reaction time is extended. When the reaction is carried out with fresh catalyst, mass transport of oxygen is likely to be the rate-determining step. As reaction proceeds, the presence of strongly adsorbed alcohol oxidation

products may deactivate the catalyst. Then, as catalyst activity decays, intrinsic kinetics could limit the rate of alcohol oxidation. In this regime, the catalyst surface is oxidized and the catalyst deactivates due to overoxidation.

In brief, catalyst deactivation can be caused by overoxidation (in the intrinsic kinetic regime) and/or by catalyst poisoning in a longer time scale. Therefore, the major drawback for the large-scale operation of this process is the limited lifetime of the catalyst under typical reaction conditions.

Then, in the last few years, several researchers have reported different procedures to enhance catalyst stability (Markusse et al., 2001; Gangwal et al., 2005). From experiments in CSTRs performed under intrinsic kinetics control, Kluytmans et al. (2000) suggested that, if overoxidation is responsible for catalyst deactivation, catalyst activity could be restored by regular interruption of the oxygen flow to the reactor for a sufficient long time in order to let the alcohol reduce the surface. So, the use of a redox-cycle bubble column loop reactor is proposed in which the slurry catalyst could be switched through aerobic (in which reaction and deactivation processes take place) and anaerobic (in which the catalyst is regenerated) zones. That is, the catalyst is cyclically exposed to oxidative and reductive environments. They found that deactivation by overoxidation can be reversed by a brief exposure (typically 4–10 min) of the catalyst to a reductive environment, e.g. oxygen-free reactant solution. If oxygen was not purged from the solution, it has to be removed completely by reaction, which will take longer time.

These results are in good agreement with those reported by Markusse et al. (2001) and Gangwal et al. (2002).

Another important issue was recently addressed by Gangwal et al. (2005). They studied the oxidation of a polyol in a semi-batch reactor using Pt catalysts and molecular oxygen as oxidant. The influence of three different start-up procedures (reductive, oxidative and inert) was investigated under oxygen rich conditions. The reductive start up resulted in the highest initial catalysts activity, compared with the other procedures. These researchers recommend pretreating the catalyst before use, since inert start up resulted in no catalytic activity at all. The formation of inactive Pt oxides was the main cause of catalyst deactivation under oxygen rich conditions, when a weak reducing compound is used. This fact was independent of the start-up procedure.

Catalytic oxidation of organic solutions is frequently carried out in TBRs operated at steady state. However, the attainment of viable reaction rates is determined by the low solubility of oxygen in water at atmospheric pressures and the wetting of the catalyst that limits the access of oxygen to the particle. So, reactor performance may be enhanced by directly pulsing the liquid loading, i.e. switching the liquid flow rate between a minimum (usually zero) and a maximum value (or ON–OFF cycling) while the gas flow is kept constant. In this way, the external surface coverage of the catalyst particles varies periodically, so the supply of oxygen is improved. Not only mass transfer rates to the surface of the catalyst are enhanced but also internal concentration profiles change accordingly (Ayude et al., 2005). Performance enhancements achieved with liquid flow modulation have been reported by several investigators (Silveston and Hanika, 2002). Recently, Muzen et al. (2005) studied the oxidation of ethanol and benzyl alcohol solutions in a continuous mini-pilot scale TBR packed with 1% Pt/Al$_2$O$_3$ uniform catalyst. Conversion improvements over steady-state operation and a maximum in the enhancement vs. split curve were observed for certain conditions. They also observed that forced liquid cycling could modify the product distribution.

Besides the well-known effect of liquid flow interruption on mass transport, there is some evidence that ON–OFF periodic operation may enhance the activity of semi-conductor catalysts. Their surface has a dynamic character that depends on the properties of the reactants. Therefore, activity may be enhanced when catalysts are exposed to richer oxygen environments (Pintar et al., 1997; Massa et al., 2005).

The present work explored the effect of slow ON–OFF liquid flow modulation on the oxidation of aqueous solutions of ethanol using a 0.5% Pd/Al$_2$O$_3$ commercial egg-shell catalyst. The reaction is carried out in a laboratory TBR. As mass transfer of the gaseous reactant is the limiting step, ON–OFF modulation of the liquid flow may lead to a substantial increase in the conversion and/or reaction rate. Additionally, by alternating oxygen and alcohol solution through the catalyst, the TBR will behave as a redox cycle reactor. This concept is similar to that proposed by Kluytmans et al. (2000), but applied for the case of mass transport controlled reactions typically found in fixed bed reactors.

2. Experimental

The catalytic oxidation of aqueous solutions of ethanol was studied in a liquid batch-recycled differential TBR operated at 1 atm and 70 °C. Catalyst specifications are given in Table 1.

The experimental apparatus is shown in Fig. 1. It is essentially similar to that described by Castellari and Haure (1995), modified to minimize the loss of volatile compounds. The liquid phase was placed in a reservoir where it was contacted with oxygen leaving the reactor. After that, it flowed concurrently with the gas phase (pure oxygen) through the reactor. At the reactor outlet it was separated from the gas and returned to the reservoir. The gas was cooled in a vertical gas condenser kept at 273 K. Remaining gas leaving the condenser was bubbled into a cold trap with 80 ml of distilled water (not shown in the figure).

The catalytic bed has 2.54 cm internal diameter and 40 cm height and was packed with 120 g of a 0.5% Pd/γ-Al$_2$O$_3$ egg-shell catalyst, supported by a screen. Three hundred ml of ethanol solution (0.25 M) was fed to the reactor by a variable speed peristaltic pump, commanded by a programmable logic controller (PLC). The reservoir and

Table 1
Catalyst specifications

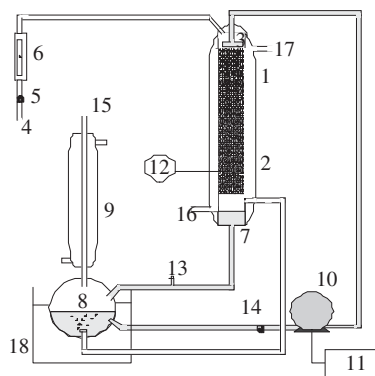|	
Palladium content	0.5% wt
Active layer thickness	250 μm
Particle size	2–3.2 mm
Mean diameter	2.7 mm
Particle porosity	0.60
Catalyst mass	120 g
BET surface area	70 m^2/g

Fig. 1. Schematic experimental setup. 1—prepacking; 2—catalyst bed; 3—liquid distributor; 4—oxygen inlet; 5—needle valve; 6—rotameter; 7—gas liquid separator; 8—absorber; 9—refrigerant; 10— liquid pump; 11—programmable logic controller; 12—temperature thermocouple; 13—liquid sampler; 14—liquid sampler; 15—gaseous stream outlet; 16,17—hot water; 18—thermostatic bath.

pipes were kept constant at 344 K. A sheathed thermocouple was inserted axially in the middle of the catalytic bed. Under the experimental conditions explored temperature remained approximately constant (± 1 K) during continuous and cycling experiments. In most runs, a constant flow rate of 200 ml/min of oxygen was used.

Ethanol, acetaldehyde and acetic acid were effectively separated with a capillary column ECONO-CAP EC-WAX. A temperature program (30 °C: 3 min; 30 °C per minute ramp; 150 °C: 3 min) was used, to improve separation.

For all the runs presented here, the catalyst bed was always flooded overnight with fresh ethanol solution. To start an experiment, the liquid was circulated through the bed for about 20 min in the absence of oxygen. An initial liquid sample was withdrawn and analyzed by GC to get the reference ethanol concentration. Then, the bed was flooded again and preheated up to the operating temperature. This reductive start-up procedure ensures complete internal wetting of the catalyst and a higher initial catalyst activity.

After the start-up procedure was completed, gas and liquid flows were introduced to the reactor. As the experiment progressed, small samples of liquid obtained from the absorber and the cool trap were withdrawn. With this procedure and taking into account that the variation of the liquid volume in the cool trap was negligible, the total liquid volume in the experimental setup changed approximately by 1%.

The samples were properly refrigerated prior to analysis to minimize volatilization and ethanol was detected and quantified by GC/FID. For all the continuous and cycling tests performed, plots of the measured ethanol concentration against time were linear indicating a constant rate. As conversion per pass was very low, the reaction was allowed to proceed for a certain time meanwhile samples were taken. From these preliminary experiments, a reaction time of 180 min was fixed. Reaction rate was then evaluated from ethanol conversion at 180 min. After that time the liquid solution was discharged and fresh ethanol solution was fed and allowed to stay overnight before starting a new run.

For continuous and cycling experiments, total ethanol conversion (X) was evaluated from mass balances as

$$X = \frac{C_{et,0} \cdot V_0 - C_{et,R} \cdot V_R - C_{et,D} \cdot V_D}{C_{et,0} \cdot V_0}$$

where $C_{et,0}$, $C_{et,R}$ and $C_{et,D}$ indicate the initial ethanol concentration and the ethanol concentration in the residue (absorber) and in the distillate (cool trap), respectively. Also, V_0, V_R and V_D are the corresponding liquid volumes.

Overall reaction rate ($-r_{et}$) was then evaluated from ethanol conversion as follows:

$$-r_{et} = \frac{C_{et,0} \cdot X}{t}$$

where t is the total reaction time.

To compare results, the mean liquid flow rate during cycling runs was calculated as

$$u_{l_w} = u_{l_{ss}}(1/\sigma)$$

where σ is the split, defined as the ratio between the duration of the ON cycle and the total cycle period (P), and $u_{l_{ss}}$ and u_{l_w} are the liquid velocity for continuous operation and during the ON cycle of periodic operation, respectively.

The overall rate enhancement (ε) during cycling is defined as the relationship between the reaction rate obtained with liquid flow modulation and the continuous reaction rate obtained immediately before cycling, both evaluated at the same operation time.

Continuous and ON–OFF cycling experiments were performed in a similar way. Except otherwise specified, runs were arranged randomly, alternating continuous and cycling runs.

3. Results

Results obtained in continuous runs (in which mass transport of oxygen is the limiting step) are presented in Fig. 2. In each of these experiments, the reactor was charged with fresh ethanol solution and conversion was monitored up to 180 min. Then, the liquid was discharged and the reactor was loaded again with fresh ethanol solution. Runs were repeated (without changing the catalysts but following the reductive start up) up to 10 times, given a total of 30 h of operation. As shown in Fig. 2, reaction rate decreases approximately 16% during the first 24 h of operation, hence catalyst activity can be considered constant during this time period. For prolonged reaction times, rate decreases abruptly. Supported Pd-group metal catalyst may be deactivated during continuous aerobic oxidation of alcohols due to poisoning by CO and adsorbed products. However, this deactivation process usually depends on the type of reactant used and generally occurs at extended times (Kluytmans et al., 2000).

ON–OFF liquid flow experiments were performed randomly and repeated at least four times. Reproducibility was reasonable. The mean standard error was about 9% for conversion measurements.

Prior to each cycling run, the continuous reaction rate at the same mean liquid flow rate was evaluated in order to calculate the enhancement. Changes in measurements of continuous operation rates before and after a cycling experiment were taken as an evidence of variations in catalyst activity during periodic operation. Table 2 shows results obtained for two different sets of experiments. We observed that reaction rates obtained in continuous operation did not vary significantly after runs with relatively short OFF periods (Case A) while ethanol reaction rates clearly decreased after cycling runs in which the catalyst is exposed to oxygen for prolonged periods (Case B). This may indicate that the catalyst is being deactivated by overoxidation during the OFF cycle. When the continuous reaction rate dropped substantially (that is, values below 0.01 mol l^{-1} h^{-1}), a simple reactivation procedure was followed: the bed was contacted for several hours with the ethanol solution and nitrogen. After this reductive procedure, catalyst activity was fully recovered.
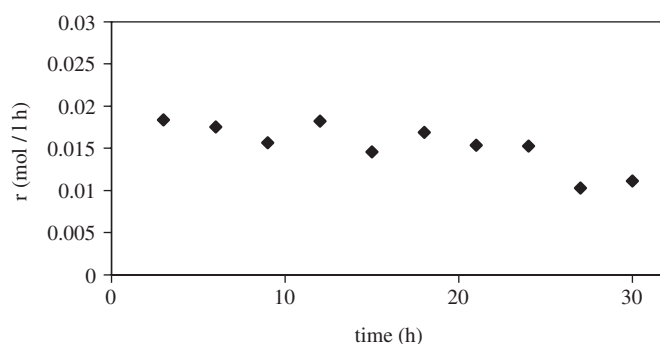

Fig. 2. Continuous experiments. $Q_{l,ss} = 70 \, cm^3 \, min^{-1}$; $Q_g = 200 \, cm^3 \, min^{-1}$.

Table 2
Representative outcomes

Case study	Type of operation	Reaction rate (mol l^{-1} h^{-1})
A	Previous continuous operation	0.0179
	Liquid flow modulation ($P = 9$ min, $\sigma = 0.7$)	0.0237
	Subsequent continuous operation	0.0164
B	Previous continuous operation	0.0196
	Liquid flow modulation ($P = 9$ min, $\sigma = 0.3$)	0.0186
	Subsequent continuous operation	0.0115

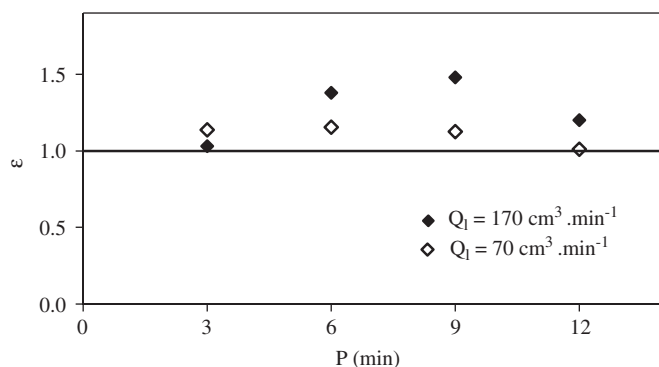$Q_l = 70 \, cm^3 \, min^{-1}$, $Q_g = 200 \, cm^3 \, min^{-1}$.

Fig. 3. Enhancement as a function of cycle period for different mean liquid velocities. $Q_g = 200 \, cm^3 \, min^{-1}$; $\sigma = 0.5$.

Fig. 4. Enhancement as a function of cycle period for different gas flow rates. $Q_{l,ss} = 70 \, cm^3 \, min^{-1}$, $\sigma = 0.5$.

Overall rate enhancements obtained with symmetrical liquid flow modulation for different periods at two different mean liquid velocities ($170 \, cm^3 \, min^{-1}$ and $70 \, cm^3 \, min^{-1}$) are presented in Fig. 3. With a mean liquid velocity of $170 \, cm^3 \, min^{-1}$, wetting is complete during the ON portion of the cycle as evaluated from the well-known correlation of Herzkowitz (1981) and confirmed by visual inspection of the bed. At $70 \, cm^3 \, min^{-1}$, the external surface of the catalyst particles is partially wetted.

Depending on cycling conditions, improvements over continuous operation can be achieved. For both operating conditions studied, a maximum is observed. Outcomes obtained with cycling are mainly influenced by the duration of ON and OFF cycles. Oxidation of ethanol takes place during the whole period, although rates for the wet and dry cycles may be different. During the wet cycle, ethanol oxidation takes place. Additionally, replenishment of liquid reactant and reactivation of the catalyst may also occur. So, the length of the ON cycle determines the mean concentration of ethanol inside the particle and is also relevant because reactivation takes place as the catalyst is exposed to the reductive ethanol solution. During the dry cycle, the surface oxygen concentration increases, the adsorbed hydrogen is oxidized to water and the reaction rate increases rapidly. Additionally, CO may be removed by oxidation during this cycle. However, if the duration of the dry cycle is not controlled, deactivation by overoxidation will take place. Moreover, for long dry cycles, depletion of the liquid reactant may also take place. So, the dry cycle has to be long enough as to allow the system to reach a state of enhanced mass transport of oxygen but if extended, overoxidation and depletion of the liquid reactant may also occur.

Enhancements are higher when conditions of complete external wetting are achieved during the ON portion of the cycle. This is in agreement with results presented in the literature (Ayude et al., 2005; Massa et al., 2005). However, for the case of noble metal catalysed oxidation of alcohols, additional issues should be considered. Both, the overoxidation process and the liquid reactant depletion can be overcome during the wet cycle provided that the liquid effectively washes the whole particle during a reasonable time. Therefore, the degree of wetting of the catalyst and the duration of the wet cycle play an important role on reaction enhancement.

Fig. 4 represents overall rate enhancements (ε) obtained for symmetrical ON–OFF cycling at different cycle periods. The mean liquid velocity is fixed at $70 \, cm^3 \, min^{-1}$ and the effect of two different gas flow rates is investigated. With $350 \, cm^3 \, min^{-1}$, no enhancement is attained at any period. Furthermore, enhancements slightly decrease as cycle period increases. At high gas flow rates the time required to drain the bed is shorter, and therefore a larger fraction of the catalyst is directly exposed to the gas phase. Then, oxygen mass transport is increased so, during the dry cycle, overoxidation will occur at
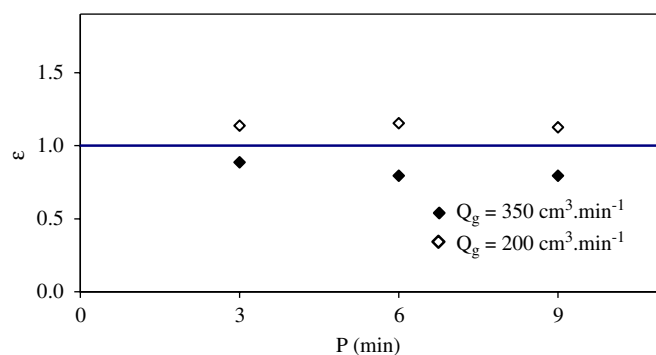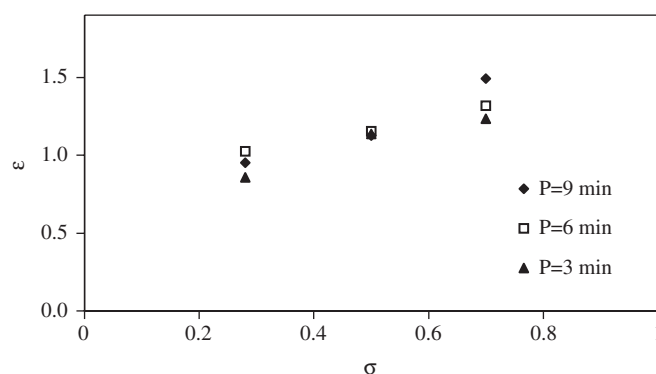

Fig. 5. Enhancement as a function of split for different periods. $Q_{l,ss} = 70 \, cm^3 \, min^{-1}$, $Q_g = 200 \, cm^3 \, min^{-1}$.

a higher extent. Reactivation during the wet cycle will take longer and may not be complete for the conditions studied.

To further investigate the influence of the extent of dry and wet cycles on reactor performance, additional experiments are performed at different splits (0.3, 0.5 and 0.7). For any given period considered, as shown in Fig. 5, significant improvements (30%) are found for the larger split, that is when the time of exposure to the gas phase is smaller and the duration of the wet cycle is larger. This result is not expected for gas limited reactions in which the catalyst activity remains constant during the dry cycle, where best improvements are usually attained at smaller splits, provided that no depletion of the liquid reactant occurs (Ayude et al., 2005). To explain this behavior, the role of oxygen on noble metal catalyst activity has to be taken into account. As the split increases, the duration of the dry cycle is shorter, and, as mentioned before, the effect of overoxidation becomes less important. During the wet cycle, the catalyst is reactivated by the ethanol solution and reaction proceeds under the mass transport regime. For the conditions studied in this reaction system, it is possible to neglect catalyst deactivation during the wet cycle because, as indicated in Fig. 1, poisoning by CO and adsorbed intermediate products occurs after several hours.

Finally, catalyst stability with liquid flow modulation is investigated at two different splits (0.3 and 0.7) and a cycle period of 9 min. Results are presented in Fig. 6. For each run, the reactor was charged with fresh ethanol solution and conversion was monitored up to 180 min. Then, the liquid was discharged and the reactor was loaded again with fresh ethanol solution before starting a new cycling run. For the larger split runs were repeated up to 8 times, given a total of 24 h of operation, with no continuous experiments between
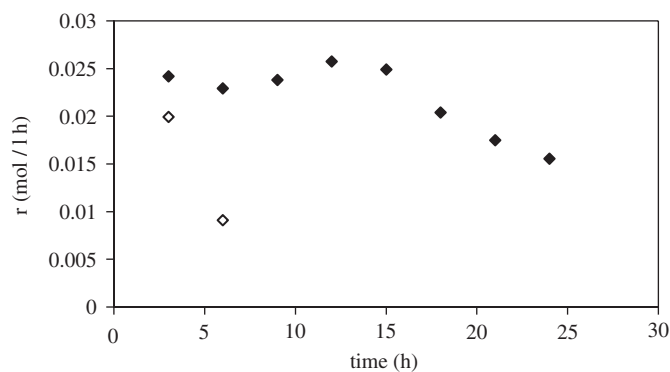
Fig. 6. Reaction rate as a function of cycle periods. $Q_{l,ss} = 70\,cm^3\,min^{-1}$, $Q_g = 200\,cm^3\,min^{-1}$. (◆) $P = 9$ min, $\sigma = 0.7$; (◇) $P = 9$ min, $\sigma = 0.3$.

liquid flow modulation runs. Ethanol reaction rates remain almost constant for the first 15 h.

When cycling is pursued with a smaller split (0.3), reaction rates drop significantly within 6 h, as catalyst is rapidly deactivated due to longer oxygen exposure time.

For both conditions studied, the catalyst was successfully reactivated following a reductive procedure. Even though at the conditions studied stability is not improved by ON–OFF cycling, experimental trends suggest that, for a given period, better results could be obtained at higher splits.

4. Conclusions

Slow ON–OFF liquid flow modulation is applied to the oxidation of aqueous solutions of ethanol using 0.5% Pd/Al_2O_3 commercial egg-shell catalyst in a laboratory trickle bed reactor. By alternating oxygen and alcohol solution through the catalyst, the TBR behaves as a redox cycle reactor.

The study is carried out under different gas and liquid flow rates, cycle periods and splits. Catalyst activity is monitored through continuous experiments. Certain degree of overoxidation is observed depending on the cycling conditions used. This deactivation mechanism is reversible and the activity is recovered by exposing the catalyst to flowing nitrogen and ethanol solution.

Significant improvements over the continuous operation are obtained when the catalyst is exposed to a short surplus of oxygen after a longer time of working in the mass transfer limited regime. Indeed, high liquid flow rates and moderate gas flow rates should be employed to ensure complete wetting of the catalyst during the ON cycle and to minimize the overoxidation process during the OFF cycle. Even though at the conditions studied, periodic operation did not improve catalyst stability, our work suggests that proper selection of cycle duration and an adequate start-up protocol are crucial to maintain long-term catalytic activity. Furthermore, cycling not only affects hydrodynamics and mass transfer resistances but also impacts on catalyst activity. To proper understand the performance under liquid flow modulation, the catalyst dynamic behavior has to be taken into account.

Notation

C	concentration
P	cycle period
Q	flow rate
r	reaction rate
t	total reaction time
V	volume
X	ethanol conversion

Greek letters

ε	rate enhancement
σ	split

Subscripts

D	distillate
et	ethanol
g	gas
l	liquid
0	initial
R	residue
ss	steady state
w	wet

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