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Intensification of the solvent-free catalytic hydroformylation of cyclododecatriene: Comparison of a stirred batch reactor and a heat-exchange reactor

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Abstract

The potential of heat-exchange reactors with mm-scale channels to provide process intensification for homogeneously catalysed gas–liquid reactions was explored. The solvent-free hydroformylation of cyclododecatriene using a homogeneous catalyst was carried out in a heat-exchange (HEx) reactor with mm-scale thin channels, and in a stirred batch autoclave for comparative purposes. The reaction was carried out using generally a concentration of 0.3 mol% catalyst from 50–85 °C temperatures and between 12 and 40 bar pressure. This channel flow is expected to provide increases in mass transfer while high heat transfer capability will accommodate the increased heat transfer duty resulting from increased reaction rates and the absence of the solvent. A simple kinetic model of the data obtained using both reactor types is derived allowing a comparison based on apparent turn-over frequencies. Operation in the HEx reactor was free of mass transfer limitations and the observed turnover frequency was independent of catalyst concentration. By contrast the catalyst productivity in the autoclave was a function of its concentration indicating mass transfer limitations. The observed reaction rate, in terms of apparent turnover frequency was 10–15 times higher in the heat-exchange reactor than the laboratory scale stirred tank. The selectivity to the desired monoaldehyde product was also higher in the HEx reactor. The temperature, pressure and catalyst concentration appear to have little influence of reaction selectivity (for the monoaldehyde) and the product distribution, this being dependent only on the concentration of cyclododecatriene and monoaldehyde. The reasons for this behaviour are discussed in detail.

Keywords: Process intensification; Micro-structured reactor; Hydroformylation

1. Introduction

The reaction of hydroformylation of olefins to aldehydes and/or alcohols is a reaction used for the manufacture of high tonnage products, such as detergents, soaps, surfactants and plasticizers, with an annual production up to several millions of tonnes worldwide [1], as well as the industrial production of fragrances, perfumes, flavours, pharmaceuticals and synthetic building blocks [2–5]. This reaction consists of a CO-insertion, which takes place in a gas–liquid system, and depending on the substrate used, can lead to the synthesis of highly valuable oxygen-containing compounds, which, otherwise, would be hardly accessible. Generally, the catalysts used in this reaction are organometallic compounds of transitional metals. For small-scale reactions, the most commonly used are the Rh-based catalysts, which are both active and selective [6]. For large-scale production, cheaper Co-based catalysts are usually preferred [1]. These catalysts are usually dissolved in an appropriate organic compound, commonly toluene, which serves also as the reaction solvent. A major problem arising from this approach is the toxicity of these solvents. As a consequence, for the hydroformylation reaction, a step change is needed in the way the process and reactions are carried out, in order to replace them with a more environmentally friendly hydroformylation processes. That could mean the use of solvent-free conditions for the reaction, as well as enhanced

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gas-to-liquid mass transfer [1]. Reaction kinetics and reactor design are strongly dependant on gas solubilities, since the reaction takes place in the liquid phase, either in the bulk of the liquid, or in the liquid film adjacent to the gas–liquid interface. For rapid reactions the liquid-phase diffusion pushes the reaction inside the film and towards the phase boundary [7].

There have been many investigations and innovations in catalytic multiphase reactors in the last 10–20 years [8], with significant attention to reactor and catalyst structuration [9]. An important subset of this is integration of the reactor with the heat exchange required by so many chemical transformations. Intensification of reaction also increases monotonically the heat transfer duty required by the reactor system. In stirred tank reactors, not only do the heat and mass transfer coefficients decrease with scale but also, especially those heated by a jacket, the heat transfer area declines with increasing scale. This means that reactions with significant thermochemistry risk becoming heat exchange limited with scale up. This notwithstanding there are relatively few reports of concomitant intensification of multiphase reaction and heat transfer in a multifunctional, integrated reactor, such as a heat-exchange reactor; catalysed monolith reactors are inherently adiabatic and any heat exchange is carried out external to the reactor shell. Researchers at BHR Group, in collaboration with Chart Energy & Chemicals among others, have explored the used of heat-exchange reactors, featuring mm-scale channels for strongly exothermic liquid phase [10,11] and liquid–liquid [12] reactions. Experimental and modelling work, while ostensibly focussed on the catalysed wall reactor has demonstrated that high gas–liquid mass transfer coefficients can be achieved in mm-scale capillary flow [13,14]. For catalysed gas–liquid reaction examples also exist of micro-structured reactors with the catalyst coated onto the wall [15] or in the form of a packed bed [16]. There appears however to be little or no literature on the use of mm-scale heat-exchange reactors for multiphase reaction. Exceptions to this are the work of Plucinski and co-workers [17–19] who have used a packed bed of 150 μm catalyst in 2–5 mm channels in a heat-exchange reactor, and Enache and co-workers who use a 1–3 mm channels with the catalyst in suspended form, and thus as a downflow structured slurry bubble column, initially in single and multiple capillary reactors [20,21] and subsequently in a uncatalysed honeycomb monolith to provide the flow structuration [20,22] and a heat-exchange reactor of with 1–2 mm channel dimensions [23]. Both of these design approaches appear to give productivity gains.

In the present study attention is given to a gas–liquid reaction using a homogeneous catalyst, dissolved in the liquid phase. By careful selection of the catalyst, regarding its solubility in the substrate, and by using a heat-exchange reactor to accommodate the increased volumetric heat generation, the usual need for a solvent may be obviated. Process intensification therefore arises from a number of sources: omission of a solvent minimises the volume of the reacting liquid, the thin channel design will enable enhanced mass transfer rates and thus increased rate of reaction while the high heat transfer surface area and heat transfer coefficients are required to accommodate the increased heat transfer duty.

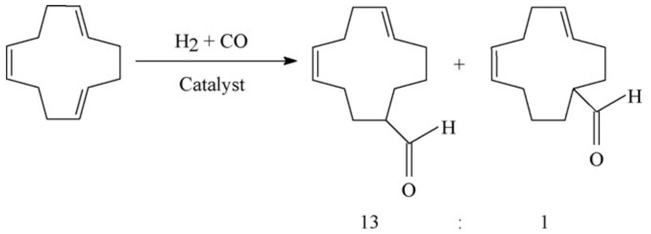

Fig. 1. Hydroformylation route.

In this study cyclododecatriene (CDDT) is used as the reaction substrate. The hydroformylation of CDDT is a potentially important reaction producing functionalised cyclo C-12 entities. In particular the selective mono-hydroformylated product is of interest as it provides synthetic pathways into a number of useful cyclo-C-12 derivatives. Fig. 1 presents the reaction studied. The reaction can continue and produce di- and tri-hydroformylated products (in a successive-reaction pathway). In this study, the reaction was performed in solvent-free conditions, using two different kinds of reactor: a stirred batch reactor and a micro-structured reactor. The results obtained in these two types of reactor were compared in terms of reaction rate and selectivity. These are the first data published for this reaction carried out in a micro-structured or heat-exchange reactor.

2. Experimental

2.1. Catalyst

The catalyst used in this study was obtained from Johnson–Matthey plc. and has the general formula $HRh(CO)(PPh_3)_3$. It consists of a yellow powder that can be dissolved in cyclododecatriene (CDDT). The maximum solubility at room temperature corresponds to a concentration of 0.3 mol%.

2.2. Batch reactor

For benchmarking and comparative purposes, hydroformylation reactions were carried out under different conditions at the 100 ml scale in a batch stirred reactor (Parr micro Autoclave). The operating procedure was as follows. The vessel was charged with 70 ml (0.384 mol) of *Trans*,*trans*,*cis*-1,5,9-cyclododecatriene (CDDT) and 1.06 g of catalyst (0.3 mol%). The vessel was purged three times with nitrogen gas and another three times with the carbon monoxide/hydrogen mixture, leaving the vessel under ca. 5 bar pressure. The stirrer was started (set at 2500 rpm), the vessel was heated to 80 °C and pressurised with the carbon monoxide/hydrogen mixture (1/1 ratio) to the working pressure. During the course of the reaction, the autoclave was maintained at this pressure by ‘‘topping up’’ with the gas mixture. The drop in pressure between restorations was typically 2 bar. Samples from the reactor were taken via the dip tube every hour (ensuring that the dip tube is cleared between samples) and analysed by GC. The pressure drop was recorded over the course of the reaction. When the reaction was complete, the vessel was allowed to cool to room temperature and then vented. The autoclave was purged three times with nitrogen and then opened to recover the product.

2.3. Heat-exchange reactor

The reaction was tested in a Chart Energy & Chemicals HEx reactor type KTS10437-38 reactor (Fig. 2). This reactor was chosen because in a previous study, it provided the highest reaction rate for Resorcinol hydrogenation [23] and is composed of 2 mm × 2 mm square section channels without splitter bars with the injection of the gas phase performed via a perforated separating plate along the length of the channels. A complex matrix of interconnected channels for heat transfer medium is embedded within the sold metal body, and it is the design of this that allows for high heat transfer rates.

The reactor was installed in a flow rig with a receiver vessel, recirculation of the cyclododecatriene reaction liquid. The gas is introduced within the reactor. The process fluid is depressurised at the reactor exit and degassed in the receiver vessel. This set up has been described in detail previously [20,23].

Unless otherwise stated, 1.5 g (0.3 mol%) of catalyst were dissolved in 100 ml of cyclododecatriene (CDDT) and introduced into the receiver of the reactor rig; the liquid flow rate was set at 15 ml/min, which was the optimum flow rate observed for the hydrogenation of Resorcinol [20], the gas flow rate ($CO:H_2 = 1:1$ in the reaction conditions) 440 N ml/min and pressure ca. 30 bar. The pressure was maintained using a backpressure regulator and monitored by a pressure transducer and a manometer with an accuracy of 0.1 bar. The readings of the pressure transducer have been logged into a computer (1 reading 30 s) and the recorded values were used to calculate the average pressure for the entire experiment. The accuracy in reading the temperature was 1 °C.

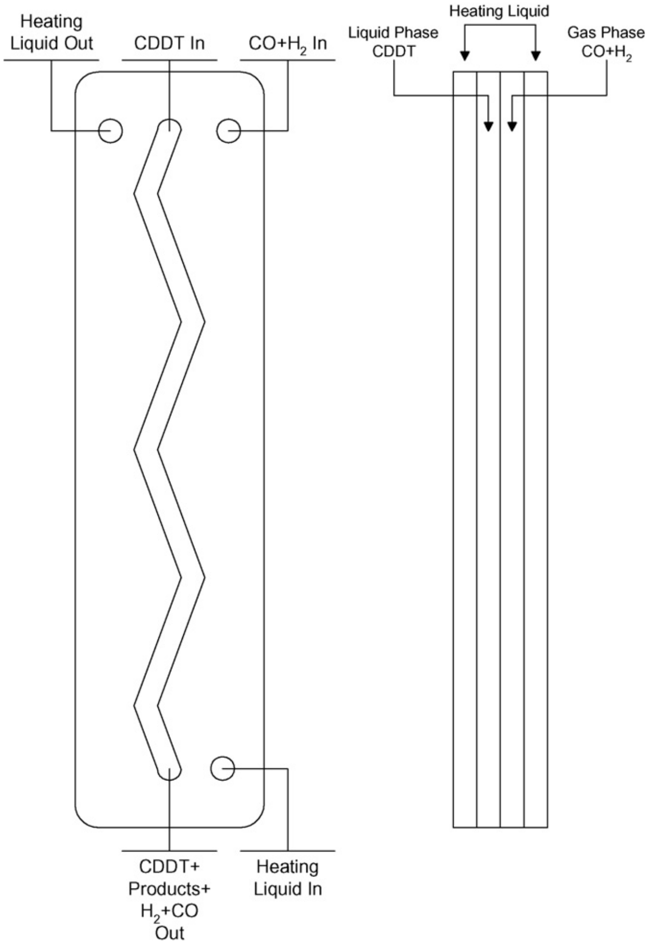

Fig. 2. Schematic diagram of the HEx reactor.

The reaction time was calculated via a procedure described as follows. The total volume of the reactor used was 3 ml. The ratio of gas/liquid used was 1/1. This means that inside the reactor there is 1.5 ml of liquid and 1.5 ml of gas. In these conditions, the reaction time is obtained by multiplying the reaction time by 1.5 (volume of liquid in the reactor) and divided by 100 (which is the total volume of the solution/CDDT + catalyst). This methodology of calculating the reaction time is imposed by the fact that only a volume of 1.5 ml of liquid is present at any time in the reactor. The rest of the liquid is in the circuit at lower temperature, without stirring and either at atmospheric pressure, or in the absence of hydrogen and CO. Consequently, it can be assumed that the reaction does not take place outside the reactor.

The results obtained by GC analysis were represented as a function of reaction time. All the analyses were carried out by gas chromatography using RPA (relative peak area) data to estimate the amount of the products. The hydroformylation was investigated by varying the following parameters: reaction time, temperature, pressure and catalyst concentration.

3. Results and discussion

3.1. Batch autoclave experiments

The catalyst is known to decompose at temperatures above 110–120 °C. Consequently, all reaction data in this study were obtained at temperatures significantly lower than this. Fig. 3 presents the reaction profile for the reaction of hydroformylation of CDDT in a stirred batch reactor at 80 °C, 12 bar and 0.3 mol% catalyst.

After 5 h of reaction 30% of the cyclododecatriene was left, 60% of the monoaldehyde was obtained, along with 10% of the dialdehyde and almost no trialdehyde.

The yield of the monoaldehyde reached a maximum after 5 h of reaction; after which the rate of dialdehyde formation began to dominate. This is a typical example of a reaction profile for consecutive reactions [24]. The concentration of the initial reagent (CDDT) decreases continuously. The concentration of the monoaldehyde increases reaching a maximum value (61% after 330 min), then it decreases, showing that this is an intermediate compound, which can follow subsequent reaction towards the formation of dialdehyde, etc.

A first order behaviour with respect to olefin concentration is generally found in hydroformylation reaction [25]. Consequently, as the concentration of CDDT decreases, the rate of

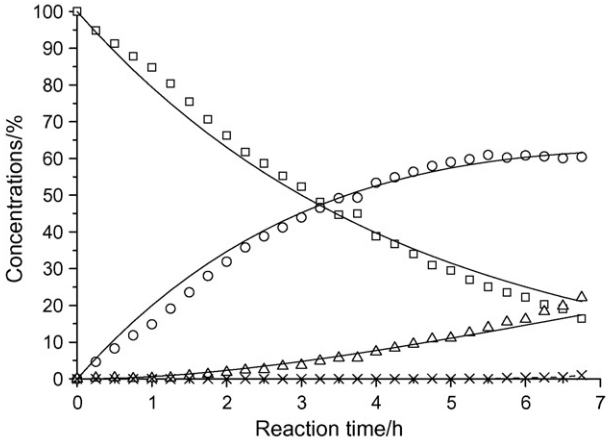

Fig. 3. Reaction profile for the CDDT hydroformylation in a batch reactor at 80 °C and 12 bar; (□) cyclododecatrien; (○) monoaldehyde; (△) dialdehyde; (×) trialdehyde. The lines indicate the result of the fitting functions.

consumption of the substrate d[CDDT]/dt decreases as well. As a result, the rate of formation of monoaldehyde is reduced and also the over-hydroformylation to dialdehyde gains importance, as the concentration in monoladehyde reaches a maximum value before decreasing. At the end of the reaction (6.75 h), about 16% of the cyclododecatriene was left with 60% of the monoaldehyde, 22% of the dialdehyde and 1% of the trialdehyde.

These results confirm the highly selective catalysis in the hydroformylation of the *trans*,*trans*,*cis*-(1,5,9)-cyclododecatriene to (4,8)-cyclododecadiene-1-carboxaldehyde [26]. The ratio between the (E, Z)- and (Z, E)-isomers was 1:13.

Although the rate of CDDT consumption (d[CDDT]/dt) decreases with the reaction time, it is interesting to note that the rate of formation of products expressed by the equation $d[M+2D+3T]/dt$, where M, D and T represent the concentration of the monoaldehyde, dialdehyde and trialdehyde in the reaction mixture respectively, appears to remain substantially constant (Table 1). This result suggests that the reaction is catalyst activity (viz. turn over frequency or TOF) limited.

A second reaction test was carried out under the same conditions of temperature and pressure, but using a catalyst loading of only 0.03 mol%. As a result, the reaction rate increased from 0.059 mol h^{-1} g$_{\mathrm{cat}}{}^{-1}$ to 0.162 mol h^{-1} g$_{\mathrm{cat}}{}^{-1}$, and the TOF value increased from 54 to 149 h^{-1}, suggesting that the reaction is mass transfer limited in these conditions (Table 2). However, the selectivity to monoaldehyde is almost identical at the same conversion for the entire range of conversion studied (Fig. 4).

Table 1
Data analysis for the progress of reaction in batch autoclave reactor at 80 °C, 44 bar and 0.3 mol% catalyst

Time (h)	[CDDT]	[M]	[D]	[T]	dt	[M + 2D + 3T]	d[M + 2D + 3T]/dt
0	100	0	0	0	–	0	–
0.25	90.88	8.63	0.49	0	0.25	9.61	38.44
0.75	79.83	18.68	1.26	0	0.5	21.2	23.18
1.25	63.16	33.89	2.71	0.24	0.5	40.03	37.66
1.75	42.66	49.93	7.12	0.28	0.5	65.01	49.96
2.25	27.5	58.78	13.31	0.41	0.5	86.63	43.24
2.75	15.63	61.15	22.53	0.69	0.5	108.28	43.3
3.25	12.02	59.75	26.86	1.37	0.5	117.58	18.6
3.75	5.87	52.94	37.93	3.26	0.5	138.58	42
Average							37.05

Table 2
Average values of the relative reaction rate, TOF and TOF$_{p0}$ obtained using the batch autoclave and HEx reactors

No.	T (°C)	p (bar)	ccat. (mol%)	Rate mol h^{-1}g$_{\mathrm{cat}}^{-1}$	TOF (h^{-1})	TOF$_{p0}$ (h^{-1})	$\overline{\mathrm{TOF}_{p0}}$(autoclave)
Autoclave							
1	80	12	0.3	0.059	54	13.8	13.75
2	80	12	0.03	0.162	149	18.6	
3	80	44	0.3	0.120	110	13.7	
No.	T (°C)	p (bar)	ccat. (mol%)	Rate mol h^{-1}g$_{\mathrm{cat}}^{-1}$	TOF (h^{-1})	TOF$_{p0}$ (h^{-1})	$\frac{\mathrm{TOF}_{p0}\,(\mathrm{MSR})}{\overline{\mathrm{TOF}_{p0}}\,(\mathrm{autoclave})}$
HEx reactor							
4	60	29.8	0.3	0.480	441	68.1	5.0
5	75	29.6	0.3	0.877	806	125.0	9.1
6	85	30.2	0.3	1.203	1105	169.5	12.3
7	85	14.78	0.3	0.822	755	171.7	12.5
8	85	30.6	0.15	1.174	1079	164.3	12.0
9	90	26.95	0.3	1.313	1206	197.1	14.3

$\overline{\mathrm{TOF}_{p0}}$(autoclave): average value of the TOF normalised at atmospheric pressure for 0.3 mol% catalyst loading.

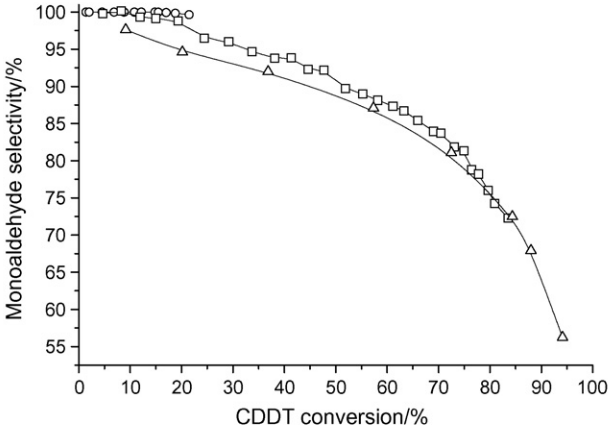

Fig. 4. Effect of the catalyst loading and pressure over the selectivity to monoaldehyde in autoclave: (□) 80 °C, 12 bar, 0.3 mol% catalyst; (○) 80 °C, 12 bar, 0.03 mol% catalyst; (△) 80 °C, 44 bar, 0.3 mol% catalyst.

The increase of the working pressure from 12 to 44 bar, using 0.3 mol% catalyst loading, lead to a significant increase in the gas uptake rate. After 2.75 h of reaction, 60% monoaldehyde was obtained at 85% conversion. Consequently the reaction rate increased from 0.059 mol h^{-1} $g_{cat}{}^{-1}$ to 0.120 mol h^{-1} $g_{cat}{}^{-1}$ and the value of TOF increased from 54 to 110 h^{-1}. It is obvious however that the reaction rate did not increase in the same ratio as the pressure. Consequently the total order of reaction can be determined. For this purpose the kinetic equation of this reaction for a given temperature is denoted as follows:

$$\mathrm{TOF} = k[\mathrm{CDDT}]\,p^n \tag{1}$$

where k represents the rate constant, [CDDT] represents the concentration of CDDT, p represents the total pressure and n represents the total order of reaction.

Using the autoclave data, the total order of reaction has a value of 0.55. By using the same method a value of turn over frequency, TOF_{p^0}, can be calculated which corresponds to the intrinsic turnover frequency normalised to the atmospheric pressure. The resulting values are reported in Table 2 and allow comparing the intrinsic reaction rate independently of the pressure used during the experiment.

Given that for the reaction carried out at 80 °C and 12 bar the amount of trialdehyde produced is very low its formation can be neglected. That will allow simplification of the equations for a kinetic analysis for the transformations $\mathrm{CDDT}\xrightarrow{k_1}$ $\mathrm{Monaldehyde}\xrightarrow{k_2}\mathrm{Dialdehyde}$. For these reactions the following kinetic equations can be written:

$$-r_{\mathrm{CDDT}} = -\frac{\mathrm{d}[\mathrm{CDDT}]}{\mathrm{d}t} = k_1[\mathrm{CDDT}]\,p^n = k_1'[\mathrm{CDDT}] \tag{2}$$

$$r_M = \frac{\mathrm{d}[M]}{\mathrm{d}t} = k_1[\mathrm{CDDT}]\,p^n - k_2[M]\,p^n = k_1'[\mathrm{CDDT}] - k_2'[M] \tag{3}$$

$$r_D = \frac{\mathrm{d}[D]}{\mathrm{d}t} = k_2[M]\,p^n = k_2'[M] \tag{4}$$

where

$$k_1' = k_1 p^n \tag{5}$$

$$k_2' = k_2 p^n \tag{6}$$

The values of k_1' and k_2' can be obtained by solving the system (Eqs. (1)–(3)) and putting the initial limits:

$$[\mathrm{CDDT}]_{(0)} = 100\% \tag{7}$$

and

$$[M]_{(0)} = [D]_{(0)} = 0\% \tag{8}$$

The values obtained for the rate constants k_1 and k_2 are

$$k_1 = \frac{k_1'}{12^{0.55}} = \frac{0.2308}{12^{0.55}} = 0.0588\,\mathrm{h}^{-1}\,\mathrm{bar}^{-0.55}$$

$$k_2 = \frac{k_2'}{12^{0.55}} = \frac{0.06388}{12^{0.55}} = 0.0163\,\mathrm{h}^{-1}\,\mathrm{bar}^{-0.55}$$

These values were used to describe the functions that generated the lines describing the variation of the concentrations of cyclododecatriene, monoaldehyde and dialdehyde in Fig. 3. The mathematical simulation is in good agreement with the experimental data.

The variation of the selectivity to monoaldehyde with the cyclododecatriene conversion shows that the increase of the pressure has a slightly negative effect (Fig. 4). However, it is difficult to state that this difference is real and it is not just caused by the experimental error, especially if is considered that for high conversion, the values of selectivity trend to converge. The conclusion is that for a given temperature of reaction, the selectivity to monoaldehyde is not related with the pressure or catalyst concentration, but only with the concentration of cyclododecatriene and monoaldehyde. For consecutive reactions there is a maximum concentration of the intermediate product (desired product in this case) that can be reached [24]. The value of this concentration and the time at which it occurs is obtained by putting the condition of maximum to the differential equation: $\mathrm{d}[M]/\mathrm{d}t = 0$. The solution of this equation will give the following expressions:

$$t_{\max} = \frac{\ln k_1'/k_2'}{k_1' - k_2'} \tag{9}$$

$$[M]_{\max} = [\mathrm{CDDT}]_{(0)}\left(\frac{k_1'}{k_2'}\right)^{\frac{k_2'}{k_2'-k_1'}} \tag{10}$$

where $t_{\max}$ is the reaction time for which the maximum concentration in monoaldehyde, $[M]_{\max}$, is reached. This implies that the maximum concentration and consequently maximum yield will be a function of only initial concentration of cyclododecatriene and the rate constants k_1' and k_2', which are only functions of temperature, as the effect of the pressure will simplify. Thus, this explains why the pressure and the concentration of catalyst have such a low influence for the selectivity to monoaldehyde. The values of $t_{\max}$ and $[M]_{\max}$ obtained

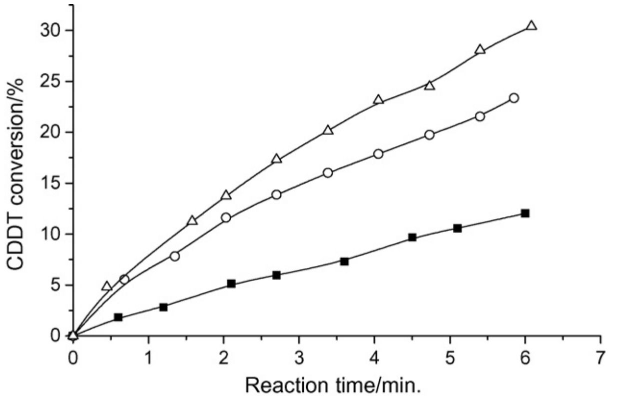

Fig. 5. Variation of CDDT conversion with the reaction time at 60, 75 and 85 °C in the HEx Reactor using 0.3 mol% catalyst and approximately 30 bar average pressure: (■) 60 °C; (○) 75 °C; (△) 85 °C.

using the Eqs. (9) and (10) are 7.7 h (or 462 min) and 61%, respectively.

3.2. Heat-exchange reactor experiments

Fig. 5 presents the reaction profile for the CDDT conversion in the HEx reactor as a function of temperature at 30 bar average pressure.

The decrease of the catalyst concentration from 0.3 to 0.15 mol% in the HEx reactor (entries 6 and 8 in Table 2), show that by halving the concentration of the catalyst, the relative reaction rate, as well as TOF and TOF_{p0} values are constant. On the other hand, if the effect of the catalyst concentration in the case of the stirred batch reactor is compared (entries 1 and 2 in Table 2), the relative reaction rate increases by decreasing the catalyst concentration. These results indicate that the reaction is mass transfer limited in the autoclave and not mass transfer limited in the HEx reactor. As in the case of the stirred batch reactor, the decrease of the catalyst concentration seems to have no effect over the selectivity to monoaldehyde (Fig. 6). Again, the difference observed in the selectivity to monoaldehyde at the same conversion for the HEx reactor seems to be within the experimental error. However, for high conversion values, it appears that the selectivity to monoaldehyde obtained in the HEx reactor is superior to the selectivity obtained in the autoclave for similar catalyst loading.

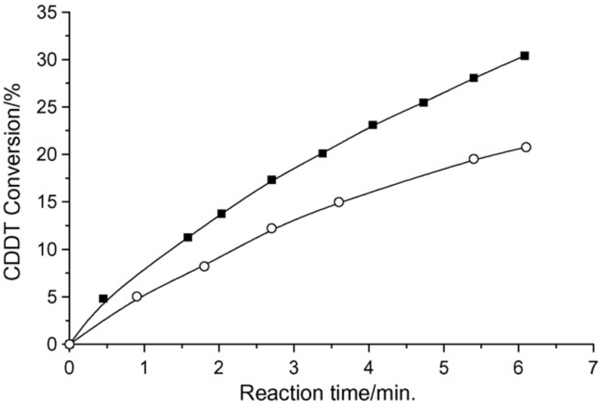

Fig. 7. Variation of the CDDT conversion as a function of the reaction time at 85 °C and 0.3 mol% catalyst at two different pressures in the micro-structured reactor: (■) 30.2 bar average pressure; (○) 14.8 bar average pressure.

Fig. 7 presents the variation of CDDT conversion as a function of the reaction time for the reaction carried out at 85 °C and 0.3 mol% catalyst concentration in the HEx reactor at two pressures: 15 and 30 bar. As expected, the reaction rate increases with the increase of the pressure. However, similarly to the reaction carried out in the autoclave, the increase in the reaction rate is not in the same proportion as the increase in pressure. The same method is used to calculate the total order of reaction as in the case of the autoclave, using Eq. (4). The result of the analysis of these data shows that the reaction order is identical in the two types of reactor, having a value of 0.55. Fig. 8 presents the variation of the selectivity to monoaldehyde as a function of the CDDT conversion for both reactors studied. At *iso*-conversion values, in the range of conditions of this study, it appears that the HEx reactor presents slightly higher selectivity to the desired product (monoaldehyde). The same figure also suggests that in

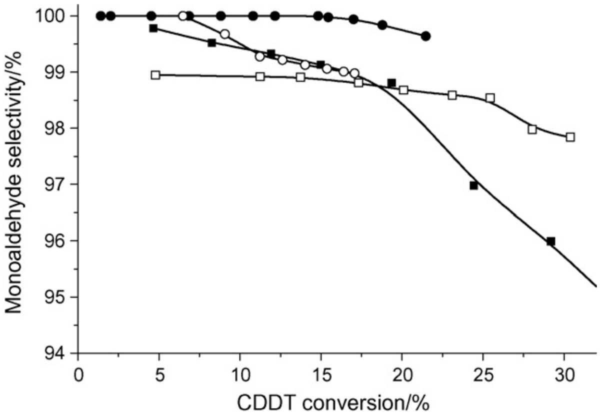

Fig. 6. Comparison of the effect of the catalyst concentration over the selectivity to monoaldehyde for the stirred batch reactor and micro-structured reactor: (■) autoclave, 80 °C, 12 bar, 0.3 mol% catalyst; (●) autoclave, 80 °C, 12 bar, 0.03 mol% catalyst; (□) HEx reactor, 85 °C, 30 bar, 0.3 mol% catalyst; (○) 85 °C, 30 bar, 0.15 mol% catalyst.

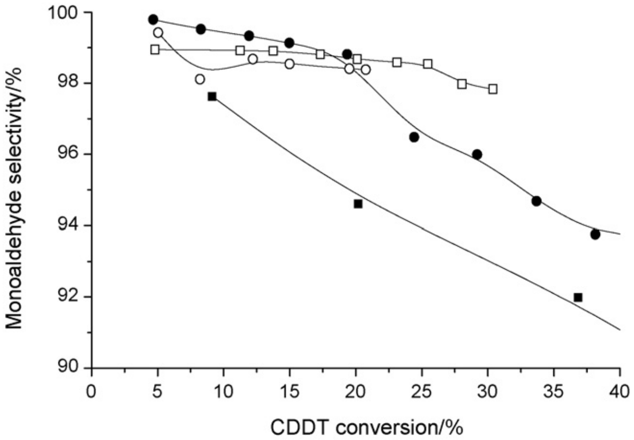

Fig. 8. Monoaldehyde selectivity as a function of CDDT conversion in autoclave and HEx reactor (HExR) using 0.3 mol% catalyst concentration: (■) autoclave, 80 °C, 44 bar; (●) autoclave, 80 °C, 12 bar; (□) MSR, 85 °C, 30 bar; (○) MSR, 85 °C, 15 bar.

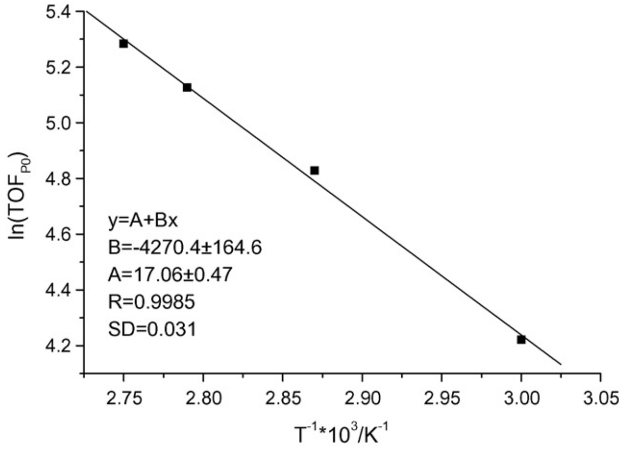

Fig. 9. Arrhenius plot for the kinetic data obtained in the HEx reactor.

the case of the HEx reactor, the pressure has no influence over the selectivity to monoaldehyde, at least for the range of conversions studied, for the same reasons as discussed above.

The values obtained for the intrinsic reaction rate normalised to atmospheric pressure, TOF$_{p0}$, can be used to calculate the activation energy. This was achieved using an Arrhenius-type plot (Fig. 9). The value of the activation energy calculated in this way was 35.5 ± 1.4 kJ mol^{-1}. This value for the activation energy is in good agreement with the results obtained by Disser et al. for the hydroformylation of a wide range of alkenes [27]. For instance, in the earlier study, the reported value of the activation energy for 1-hexene is in the range 31–40 kJ mol^{-1}, depending on the reaction system adopted. Their results also claim that no significant influence of the chain length is observed over the value of Ea. However this value of the activation energy is about half of what is reported in literature for other hydroformylation reactions by other teams [28–33]. In these cases, values of Ea ranging from 55 kJ mol^{-1} for 1-butene and 1-dodecene to 84 kJ mol^{-1} for 1-hexene were reported. Despite a lower value of the activation energy than most of the studies cited, the reaction is clearly not mass transfer limited according to results obtained using different concentrations of catalyst.

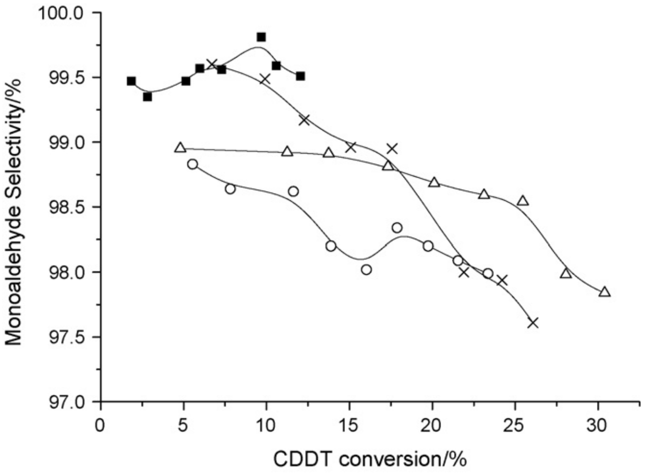

Fig. 10. Variation of the selectivity to monoaldehyde as a function of CDDT conversion: (■) 60 °C, 0.3 mol% catalyst, 29.8 bar average pressure; (○) 75 °C, 0.3 mol% catalyst, 29.6 bar average pressure; (△) 85 °C, 0.3 mol% catalyst, 30.2 bar average pressure; (×) 90 °C, 0.3 mol% catalyst, 27.0 bar average pressure.

Fig. 10 presents the variation of the selectivity to monoaldehyde as a function of CDDT conversion at the four temperatures studied using the HEx reactor. At all times, the selectivity to monoaldehyde is higher than 97%, irrespective of the temperature used. In this case, even for 30% conversion of CDDT, the selectivity does not decrease below 97.5%. The observed differences can most probably be ascribed to the experimental error. Indeed, considering only the 10% error generally accepted for the GC analysis method, at a CDDT conversion of 12% the following concentration ranges of monoaldehyde may be derived:

- 60 °C – 11.98 ± 1.20% = 10.8–13.2%
- 75 °C – 11.46 ± 1.15% = 10.3–12.6%
- 85 °C – 12.36 ± 1.24% = 11.1–13.6%
- 90 °C – 12.17 ± 1.22% = 11.0–13.4%

It is evident that these values are not significantly different. That is, temperature has ostensibly no influence over the monoaldehyde selectivity. The probable explanation for this is that the activation energies for the hydroformylation of monoaldehyde to dialdehyde and the hydroformylation of CDDT to monoaldehyde are similar. And hence the values of the reaction rate constants k_1 and k_2 are influenced to the same extent by the increase in temperature. As a result, the concentration profile of the reaction products could follow the same trend at different temperatures and consequently similar selectivity to monoaldehyde and dialdehyde will be achieved.

An alternative explanation is linked to the low value of activation energy. The smaller the value of Ea, the less influence temperature will have over the kinetic rate of the reaction. As the kinetics of the reaction govern the selectivity and distribution of products, low Ea values will also translate into low influence of temperature on selectivity.

Table 2 presents the average values of the relative reaction rates, TOF and TOF$_{p0}$ obtained in the HEx reactor under different operating conditions, as well as the values obtained using the autoclave. These values were obtained from the values of the initial reaction rate of CDDT. The comparison of the normalised reaction rate obtained in the MSR with the value of the reaction rate observed in the autoclave is given by the ratio $\mathrm{TOF}_{p0}(\mathrm{MSR})/\overline{\mathrm{TOF}_{p0}}(\mathrm{autoclave})$. This parameter shows a 9 times to 12.5 times increase in the reaction rate when the micro-structured reactor is used for similar conditions of temperature. It is also worth noticing that the value of TOF$_{p0}$ obtained at 60 °C in the micro-structured reactor is 5 times higher than the value of TOF$_{p0}$ obtained at 80 °C in the autoclave.

4. Conclusions

The potential to intensify homogeneously catalysed gas liquid reactions by use of a structured reactor has been investigated using the hydroformylation of cyclododecatriene as an example reaction, where the monoaldehyde was the desired product. Specifically, the reaction has been carried out at varying process conditions in a heat-exchange (HEx) reactor with mm-scale channels. Experiments have also been carried out in a laboratory scale autoclave as a reference.

The use of such a reactor offers many potential advantages and opportunities for process intensification including enhancement of the mass transfer by virtue of the flow structuration and high heat transfer rates courtesy of the high specific heat transfer surface available which in turn offers an opportunity for solvent free operation. Other advantages of structured reactors such a simple scale out and continuous operation are well known.

Experiments in the HEx reactor showed an apparent activation energy of 35.5 kJ mol^{-1}. The order of reaction for hydrogen and carbon monoxide of 0.55 was observed in both the HEx and autoclave reactors. Classic series selectivity type concentration profiles were observed in both reactors. These were used to develop simple pseudo-first order kinetic models, which allowed analysis of observed reaction rates based on a turnover frequency analysis.

The apparent turnover frequency in the HEx reactor was 10–15 times that observed in the autoclave. Improved selectivity was also observed in the HEx reactor relative to the autoclave. These changes are a result of the improved mass transfer obtained in the structured flow in the HEx reactor.

The reaction in the autoclave was mass transfer limited, and the apparent turnover frequency was a function of the catalyst concentration. By contrast, the measured turnover frequency in the HEx reactor was independent of the catalyst loading, indicating operation in the absence mass transfer limitations.

This study thus demonstrates the potential of mm-scale structured HEx reactors for solvent free operation of exothermic homogeneously catalysed gas–liquid reactions such as hydroformylation.

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