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Isobutane dehydrogenation in a membrane reactor Influence of the operating conditions on the performance

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Abstract

Isobutane dehydrogenation has been investigated in a membrane reactor combining a bimetallic PtIn/zeolite fixed-bed catalyst and a microporous MFI-alumina tubular membrane. The membrane reactor performance has been studied as a function of the feed and sweep flow rates and of the sweep (co- or counter-current sweep modes). Isobutene yields up to four times higher than that observed in a conventional reactor have been obtained. Depending on the conditions, it is shown that the performance of the membrane reactor is controlled either by the membrane or by the catalyst. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Isobutane; Dehydrogenation; Zeolite membrane; Membrane reactor

1. Introduction

Isobutane dehydrogenation can be performed on an industrial level using different processes (Oleflex, Star, Catofin, FDB4, etc.). The reaction being endothermic, the thermodynamic limitation requires the use of high temperatures, which necessitates expensive reactor materials and high operation costs and leads to catalyst deactivation. Therefore, all industrial processes include a catalyst regeneration step, with either a circulating bed or an alternate reactor system [1].

It is well known that membrane reactors, combining a dehydrogenation catalyst and a hydrogen permselective membrane, can give higher yields than conventional reactors, owing to the equilibrium shift produced by the selective extraction of a reaction product (H_2) through the membrane. Here, the membrane plays the role of a selective extractor, which corresponds to the most common combination of a membrane and a catalyst in membrane reactors [2]. When compared to conventional processes, the same isobutene yield can be obtained at lower temperatures, which may lead to a better situation for the economy of the process and the stability of the catalyst.

As the demand for MTBE will follow the regulation concerning oxygenates as octane boosters for gasoline, the need for new sources of isobutene does not currently seem to be a priority [3]. However, the dehydrogenation of isobutane can be considered a good model reaction for membrane reactors (extractor type), and several authors have considered this reaction [4–8]. In this contribution, we report on the influence of the operating conditions on the performance of a reactor combining a tubular microporous zeolite membrane and a fixed-bed catalyst placed in the core volume of the tube.

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2. Experimental

The *catalyst* was a bimetallic PtIn supported on a MFI zeolite [9]. Indium was introduced within the zeolite precursors before hydrothermal synthesis. After calcination the final material contained 0.8 wt.% Indium. Platinum (0.5 wt.%) was then introduced in the zeolite via an exchange/impregnation technique with $Pt(NH_3)_4(OH)_2$. Before catalytic use, the solid was activated in situ under flowing H_2 at 823 K during 10 h. For experiments in the membrane reactor, in order to avoid an excessive pressure drop in the catalyst bed, the powder was transformed into pellets of ca. 2 mm size, using a lab extrusion machine.

The *MFI membrane* was obtained by synthesis of zeolite crystals inside the pores of a macroporous host material (pore-plugging method) [10]. The composite membrane obtained presented several advantages when compared to conventional supported zeolite films (less long-range stresses during thermal cycling, maximum defect of the size of the pore of the host). The chosen support was a commercial SCT-US Filter T1-70 tube, made of three layers of macroporous α-alumina (from outer to inner side, respective thickness: 1500, 40 and 20 μm and pore size: 10, 0.9 and 0.2 μm). The precursor solution of the MFI zeolite was obtained by mixing silica (Aerosil 380) and a template (tetrapropylammonium hydroxide, TPAOH). After a 3-day ageing period, that solution was poured in a Teflon-lined autoclave containing the SCT porous ceramic tube. Hydrothermal synthesis was then performed at 443 K for 3 days, and the membrane was calcined at 773 K under a flow of 5% O_2 diluted in N_2. Characterisation of the membrane showed it could be considered defect-free (i.e. the transport through the membrane is controlled by the micropores of the MFI structure) [10].

The *reactor module* was made of a stainless steel shell containing the composite membrane tube, which was packed with the catalyst (Fig. 1, shown in co-current mode). The endings of the membrane tube (15 cm length) were enamelled on a 2.5 cm length and equipped with compression fitting graphite seals (Fargraf-Coltec) in order to ensure tightness between the inner compartment and the outer compartment, where the permeating gases are swept by nitrogen. The reactor temperature was measured by a thermocouple moving along the axis of the membrane, in a gas-tight stainless steel tube (1/16 in. diameter). An electric tape wound around the stainless tube heated the membrane module. The density of whorls was adjusted along the reactor length, in order to obtain a temperature profile within ±5 K.

The reactor could be fed with isobutane, hydrogen and nitrogen with different ratios. All streams were mass flow (Brooks 5850E) controlled. ΔP, the pressure difference across the membrane, was regulated by an automatic valve (Kämmer 800377) connected to a differential manometer (Keller DP232), whereas the pressure at the retentate outlet was measured by a manometer (Keller PAA23). Permeate and retentate outlet flow rates were measured with film flowmeters. Reaction products were analysed on-line using a gas chromatograph (Shimadzu, GC14A) equipped with FID (hydrocarbons) and TCD (hydrogen) detectors.

For pure separation experiments, the catalyst was replaced by inert glassy beads of similar size. The separation factor S was defined as the enrichment factor in the permeate as compared to the feed composition

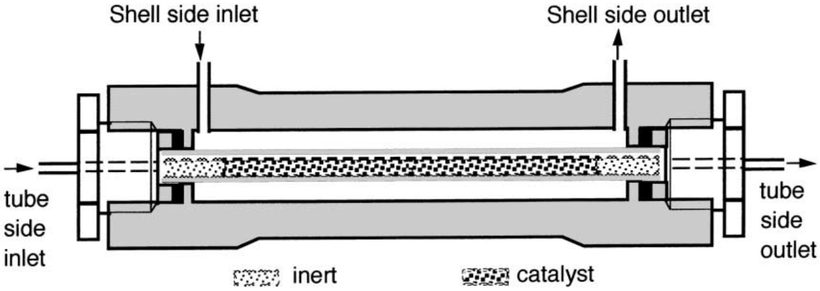

Fig. 1. Schematic of the membrane reactor.

ratio (where x denotes the molar fraction):

$$S_{A/B} = \frac{x_A^{\text{permeate}}/x_A^{\text{feed}}}{x_A^{\text{permeate}}/x_B^{\text{feed}}}$$

Most of the catalytic experiments in the membrane reactor were performed under the following conditions: $T = 730\,\text{K}$; ΔP (differential pressure across the membrane) $= 0$; pressure: 100–170 kPa (depending on the sweep flow rate); feed composition: 0.2 i-C_4H_{10}, 0.2 H_2, 0.6 N_2; sweep: N_2; catalyst weight: $\approx$2.4 g. Like in industrial processes, some hydrogen was added to the feed in order to limit catalyst deactivation. Conversion of isobutane (C) was calculated taking into account both permeate and retentate compositions.

3. Results

3.1. Catalyst stability measurements

The stability of the catalyst was first tested for the dehydrogenation of n-butane using a conventional microreactor, under conditions, where equilibrium is not achieved. Fig. 2 shows the performance of the PtIn/MFI solid compared to that of a standard PtSn/Al_2O_3. The selected catalyst presents a much better stability. The slight maximum observed for times on stream near 5 h could be due to in situ activation of the PtIn/MFI catalyst under reaction conditions.

3.2. Hydrogen/isobutane separation experiments

They were performed under conditions (temperature, feed flow rates, sweep) similar to those used for the catalytic tests. Fig. 3 shows the separation factor S H_2/i-C_4 as a function of the sweep (flow rate, co- or counter-current mode).

The counter-current mode shows an only slightly better performance. However, as shown by Fig. 4, when the fraction of the feed of isobutane permeating through the membrane is not affected by the type of sweeping, that of hydrogen is high and close to 100% with the counter-current sweep mode. For these conditions, less than 1% of the hydrogen fed into the module is present at the outlet of the tube side.

3.3. Membrane reactor experiments

Several modes were compared. To illustrate the effect of the membrane reactor, experimental conditions were chosen in order to obtain limited conversions at equilibrium in conventional reactors. Selectivity toward isobutene is rather high (ca. 90%), n-butane being the main by-product.

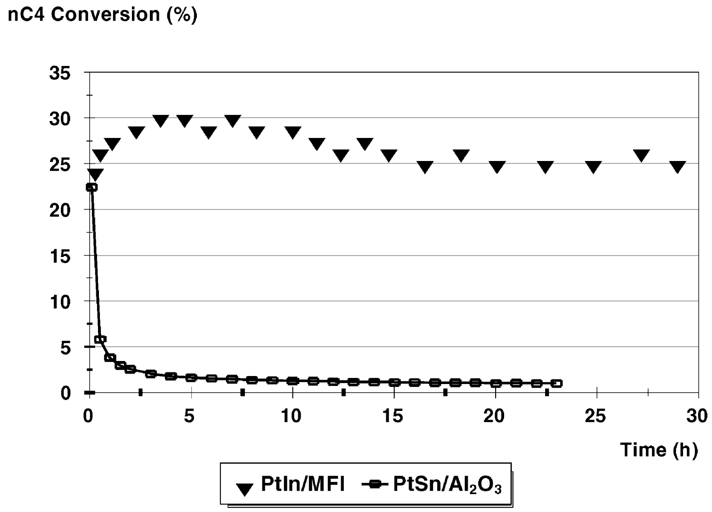

Fig. 2. Conversion of n-butane as a function of time on stream. $T = 820\,\text{K}$; feed 0.2 n-C_4, 0.8 N_2; catalyst weight over flux ratio $= 48\,\text{g}\,\text{min}\,\text{mol}^{-1}$.

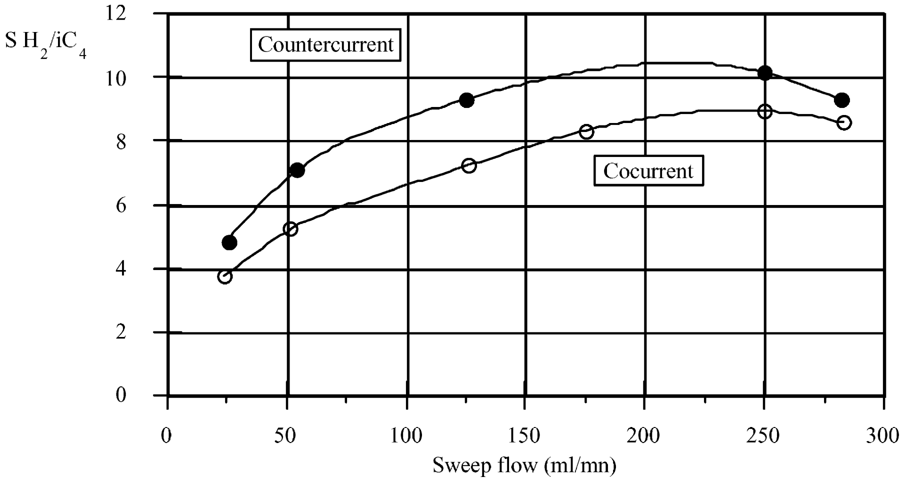

Fig. 3. H_2/*i*-C_4 separation factor (*S*) as a function of sweep flow rate and mode. $T = 730\,K$, feed $50\,ml\,min^{-1}$ (0.2 iC_4H_{10}, 0.2 H_2, 0.6 N_2), sweep: N_2.

Table 1 presents some data on the retentate composition according to different experimental conditions. As can be seen, there is an increase in nitrogen composition on the retentate side. However, the permeate analysis confirmed that this increase was mainly due to the decrease in the concentration of the other components, especially hydrogen. In all cases, H and C balances were controlled and there was almost no back-permeation from the sweep to the reaction zone.

Permeate composition data show that the separative performance of the membrane is similar to that indicated in Fig. 3. Therefore, the presence of the catalyst did not affect the membrane properties.

Fig. 5 gives the conversion C for different reactor configurations, as a function of the feed and sweep flow rates. In absence of sweep (conventional reactor mode) the conversion is independent of feed flow rate and is close to that predicted by thermodynamics for equilibrium. The membrane mode induces a positive effect on the conversion, especially for high contact times. Only small changes are observed when changing the sweep mode from co- to counter-current, however.

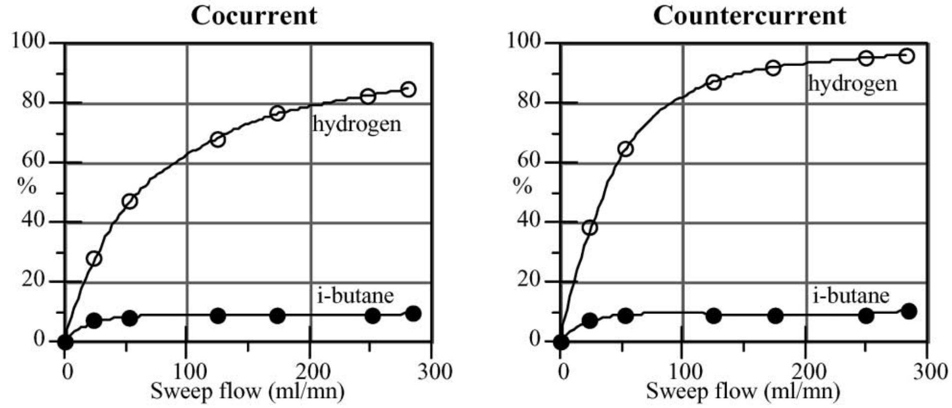

Fig. 4. Fraction of fed H_2 an iC_4 permeating through the membrane as a function of sweep flow rate and mode. $T = 730\,K$, feed $50\,ml\,min^{-1}$ (0.2 *i*-C_4H_{10}, 0.2 H_2, 0.6 N_2), sweep: N_2.

Table 1
Retentate outlet composition and R values as a function of sweep mode and flow rate[a]

Reactor configuration	Sweep (ml/min)	Pressure (atm)	Retentate outlet composition (%)				R	K_{eq}
			N_2	i-C_4H_{10}	i-C_4H_8	H_2		
Co-current	25	1.06	70.3	12.4	2.60	14.7	0.033	0.033
	50	1.07	73.85	11.9	2.95	11.3	0.030	
	125	1.21	78.95	10.7	3.55	6.80	0.027	
	235	1.40	81.1	9.95	3.85	5.10	0.028	
	300	1.65	83.5	9.15	3.80	3.55	0.024	
	400	1.90	84.4	8.60	3.85	3.15	0.027	
Counter-current	25	1.06	72.05	12.6	2.55	12.8	0.027	0.033
	50	1.07	77.3	11.8	3.30	7.60	0.022	
	125	1.21	82.69	10.25	4.16	2.90	0.014	
	235	1.40	84.45	9.10	4.55	1.90	0.013	
	300	1.65	86	8.55	4.25	1.20	0.010	
	400	1.90	86.85	8.20	4.05	0.90	0.008	

[a] $T = 730$ K, feed: 50 ml min^{-1} (0.2 i-C_4H_{10}, 0.2 H_2, 0.6 N_2), sweep: N_2.

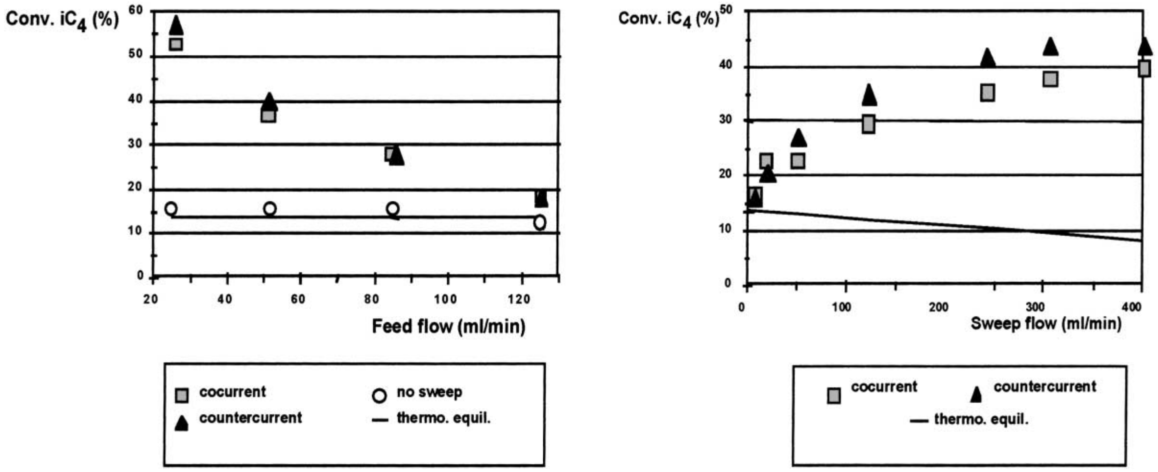

Fig. 5. Performance of the reactor (isobutane conversion). Left, effect of the feed flow rate for different configurations (sweep 250 ml min^{-1}). Right, effect of the sweep flow rate for different configurations (feed 50 ml min^{-1}). Continuous lines represent the thermodynamic equilibrium in a conventional reactor (there is a decrease when sweep flow rate increases, owing to the increase of pressure, see Table 1, necessary to keep $\Delta P = 0$). $T = 730$ K, feed: 0.2 i-C_4H_{10}, 0.2 H_2, 0.6 N_2, sweep: N_2.

4. Discussion

4.1. Stability of the catalyst

The specific properties of the PtIn/MFI catalyst has been attributed to the presence of small bimetallic PtIn clusters inside the channels of the MFI zeolite [9]. Steric effects likely bring about the good stability of this catalyst in the reaction, by limiting the formation of the precursors of carbonaceous deposits leading to deactivation. By comparison, the PtSn/Al_2O_3 solid is much less stable, probably due to the presence of acid sites on the alumina that favours cracking reactions.

4.2. Separation experiments

At high temperature hydrogen permeates preferentially. Let us emphasise that this is not the case at room temperature, at which the adsorption of isobutane favours its own permeation, leading to almost no separation [11].

As expected, the separation factor S increases with the sweep flow up to a maximum. For high sweeps, i.e. high driving forces, isobutane also permeates, leading to a decrease of the separation factor. The optimum value of S is slightly higher in the case of counter-current sweep (10 versus 8.5 for the co-current, Fig. 3). When co-current sweep is used, the permeation of a component is limited by the equilibrium of its partial pressures in the permeate and retentate sides and high sweep flows are necessary to obtain high extraction (total extraction of a component would require an infinite sweep flow rate). This is not the case for counter-current sweep, for which the driving force is maximal at the outlet of the feed side (retentate). In practice, total extraction of a component is possible. Fig. 4 indeed shows that the extraction of hydrogen in the counter-current mode is almost total, and that the efficiency of the sweep is higher when compared to the co-current mode.

4.3. Membrane reactor performance

Fig. 5 shows that in the absence of sweep, the butane conversion corresponds to that predicted by the thermodynamic equilibrium, which means that the catalyst is active enough to reach this value, even for high feed flows, and that it does not suffer from deactivation during the test. These data correspond to what can be observed in a conventional, non-membrane reactor, and will serve as a reference.

When sweep is used, at high feed flow, the efficiency of the membrane is not high enough to change the conversion, as only a small fraction of the total feed can permeate. For lower feed flows, the selective extraction of hydrogen starts to be significant. This modifies the equilibrium and favours the conversion. When the sweep/feed flow ratio is about 10, the conversion is increased by a factor of 4 with respect to that of the conventional reactor. The very same effects are observed when changing the sweep flow for a given feed flow (conversion increases with the sweep flow rate).

The increase of the separation factor when changing the sweep from co- to counter-current mode does not notably improve the performance. However, the almost total extraction of hydrogen for high sweep/feed flow rates in the counter-current mode (Fig. 4, upper right), should, in principle, lead to a higher performance. In this case the equilibrium should be strongly shifted towards isobutene for these conditions (if the catalyst is active enough, it should allow equilibrium in all points of the fixed-bed).

This absence of performance improvement can be explained by considering the situation at the outlet of the catalyst bed. The local composition of the gas mixture can be characterised by the following ratio R:

$$R = \frac{P_{\mathrm{H_2}}^{\mathrm{retenate}} \cdot P_{i\text{-}\mathrm{C_4H_8}}^{\mathrm{retentate}}}{P_{i\text{-}\mathrm{C_4H_{10}}}^{\mathrm{retentate}} \cdot P_{\mathrm{ref}}}$$

Table 1 compares experimental values of R with that of the equilibrium constant K_{eq} at 730 K. When co-current sweep is used, R reaches a value close to K_{eq}. The small gap between the two values in this case is likely due to the difference between theoretical and actual temperatures (the maximum discrepancy K_{eq}/R corresponds to a temperature difference lower than 10 K). This means that the catalyst works well and follows the extraction of hydrogen by the membrane. This situation was predictable, since at the outlet of the catalyst bed the driving force for H_2 permeation is minimal (close to zero from experimental data). In the absence of hydrogen removal, the catalyst reaches equilibrium at the outlet of the reactor and the global performance is limited by the loss of isobutane, i.e. by the selectivity of the membrane. In a way, when co-current sweep is used, the global performance of the present membrane reactor is controlled by permeation parameters, i.e. by the membrane.

The situation is quite different when counter-current sweep is used. Table 1 indeed shows that the gap between K_{eq} and R depends on, and increases with, the sweep flow rate. For high sweep flows, the driving force for hydrogen permeation is very high at the outlet of the catalyst bed and the catalyst is not active enough to restore equilibrium. The performance is a bit better than in the co-current sweep mode (less isobutane, more isobutene). Nevertheless, it is significantly lower than that calculated from the partial pressure of H_2 at the outlet of the bed with a theoretical catalyst able to restore equilibrium. Indeed, this calculated isobutane conversion is close to 70%, whereas only 45% is observed (Fig. 5). In a way, when (high) counter-current sweep is used, the global performance of the present membrane reactor is controlled by activity parameters, i.e. by the catalyst.

Based on separate models of both $H_2/i\text{-}C_4$ separation [12] and dehydrogenation kinetics [13], obtained in pure separative and catalytic studies, a general model for the membrane reactor has been proposed [12]. If the experiment-model agreement is good for co-current sweep, it is not for counter-current. This could be due to the kinetic law, which is not adapted to the local situation of the catalyst at the outlet of the reactor (high hydrogen extraction). The model indeed predicts a performance close to that calculated in the previous section.

4.4. General discussion

As mentioned in the Section 1, isobutane dehydrogenation has been used as a model reaction here. It is clear that the high sweep flow rates we used to obtain significant improvement in isobutene yield could cause economic problems in industrial applications. The targeted product (isobutene) stays mainly in the retentate, however, and its concentration is therefore not directly affected by the sweep. Nevertheless, as can be seen from Table 1, at high counter-current sweep flow rates, isobutene starts to permeate (as does isobutane).

Another point is catalyst stability in the membrane reactor. Even if the PtIn/MFI catalyst was observed to be stable in a conventional micro-reactor, moreover in the absence of H_2 in the feed (see Fig. 1), long duration testing of the membrane reactor during which hydrogen is extracted may result in stability problems for the catalyst. Taking this aspect into account, most of the experiments, as those reported here, were performed by co-feeding hydrogen with isobutane, which does not change the main conclusions of the study (industrial processes generally use hydrogen or steam in the feed).

For the whole study, the same catalyst sample was used without any apparent drop in performance. There might be local deactivations, however, especially at the end of the catalyst bed, where high counter-current sweep results in a low hydrogen concentration. Owing to the lack of long duration tests under these specific conditions, it was not possible to definitely assess this point during the present study.

As far as, the membrane itself is concerned, no change in separation properties ($H_2/i\text{-}C_4$) was observed after all the experiments. Long duration testing would be a worthwhile means of checking membrane stability, however.

5. Conclusion

In this study, it has been shown that the combination of a fixed-bed PtIn-based catalyst and a microporous MFI-alumina tubular membrane may result in an isobutane dehydrogenation performance up to four times higher than that of a conventional reactor operating under similar conditions (temperature, feed composition).

Both feed and sweep flow rates affect the isobutene yield. The lower the feed and the higher the sweep flows, the higher the conversion.

For given feed and sweep flows, the global performance of the present membrane reactor appears to be controlled:

- in the case of co-current sweep, by the selectivity of the separation (loss of isobutane), i.e. by the membrane;
- in the case of counter-current sweep, by the catalyst activity.

This observation shows that just by changing the way of sweeping, the limiting parameter can be either the membrane or the catalyst. It suggests that, in the present example, the two materials present compatible performances [14], but both need to be improved to allow the membrane reactor a better advantage over the conventional one.

Another general issue of the present study is that, with regard to membrane reactors, and owing to their specific reactive environment, the problem of the catalyst may be a non-trivial one, which perhaps has been underestimated until now [2]. In some cases a suitable catalyst has to be designed [2,15].

Acknowledgements

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