Propylene from Renewable Resources: Catalytic Conversion of Glycerol into Propylene

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Propylene, one of the most demanded commodity chemicals, is obtained overwhelmingly from fossil resources. In view of the diminishing fossil resources and the ongoing climate change, the identification of new efficient and alternative routes for the large-scale production of propylene from biorenewable resources has become essential. Herein, a new selective route for the synthesis of propylene from bio-derived glycerol is demonstrated. The route consists of the formation of 1-propanol (a versatile bulk chemical) as intermediate through hydrogenolysis of glycerol at a high selectivity. A subsequent dehydration produces propylene.

With diminishing oil reserves, the production of bulk commodity chemicals will increasingly rely on alternative renewable feedstocks such as biomass.[1] In this regard, new sustainable routes to synthesize propylene are of particular interest, as propylene is one of the most important and widely used commodity chemicals derived from petroleum.[2] The primary use of propylene is for the production of polypropylene, which is one of the most important thermoplastic resins. The global polypropylene demand was 26.6 million tonnes in the year 2000 and it is expected to reach 59.6 million tonnes in the year 2020.[3]

Until recently, most propylene produced was a co-product in ethylene production in steam crackers and a by-product in oil refineries.[4] With traditional sources of propylene increasingly unable to meet growing market demands, considerable research efforts have been directed towards the development of new and greener alternatives for the on-purpose production of propylene.[5] Examples of such processes include dehydrogenation of propane (PDH), olefin metathesis, methanol to propylene (MTP), and oxidative dehydrogenation (ODH) of propane.[6] Of all these processes, PDH has been proven within the last couple of years to be very effective in producing propylene on-purpose, offering an economically attractive alternative to traditional petroleum-based propylene generation.[6g–h] Despite the great success achieved with on-purpose technologies, all

relevant methods still very much depend on fossil fuels as the main raw materials.

Herein, we report the synthesis of on-purpose propylene using bio-derived glycerol as a renewable feedstock.[7] During the past decade, glycerol has emerged as a versatile low-cost bio-feedstock for the production of a variety of value-added products, essentially because of the large surplus of glycerol formed as a by-product during the production of biodiesel.[8] Given its nontoxic and highly functionalized nature, glycerol represents an ideal raw material with a potential to be converted into many useful chemicals.[9] The principle challenge in utilizing this particular molecule lies in the development of new, innovative. and economically feasible catalytic processes that allow a selective transformation of glycerol to bulk commodity chemicals on a large scale.[8b] Despite recent significant progress in developing new processes for converting glycerol into various low-volume oxygenated chemical compounds,[8, 9] a highly selective route to light olefins,[10] in particular highly demanded propylene, has remained largely underdeveloped.

As outlined in Scheme 1, our strategy for implementing the synthesis of propylene from glycerol relies on the formation of 1-propanol (1-PO) as the key intermediate. First, the targeted
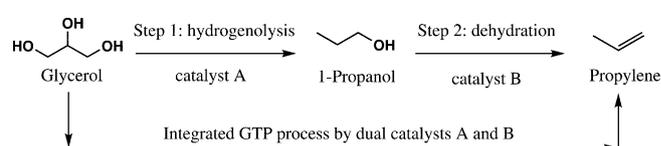

Scheme 1. Catalytic conversion of glycerol to propylene (GTP).

production of bio-1-PO, a previously unappreciated transformation for biomass valorization, can be attained through iridium-catalyzed and highly selective hydrogenolysis of glycerol. By a subsequent dehydration over an acidic H-ZSM-5 zeolite catalyst, 1-PO can be converted into propylene. Significantly, propylene can be directly produced in high yields from glycerol by means of a continuous fixed-dual-bed catalytic system. Details of the development and optimization of this process are described below.

We began our studies by exploring the hydrogenolysis of glycerol to 1-PO in aqueous solutions. Although many attempts have been made towards the hydrogenolysis of glycerol to 1,2-propanediol (1,2-PDO) and 1,3-propanediol (1,3-PDO),[11] the direct conversion of glycerol to 1-PO, a major commodity chemical currently produced through hydroformylation of ethylene to form propanal followed by hydrogenation,[12] remains essentially unexplored. Our initial investigation focused on the hydrogenolysis of a diluted aqueous glycerol

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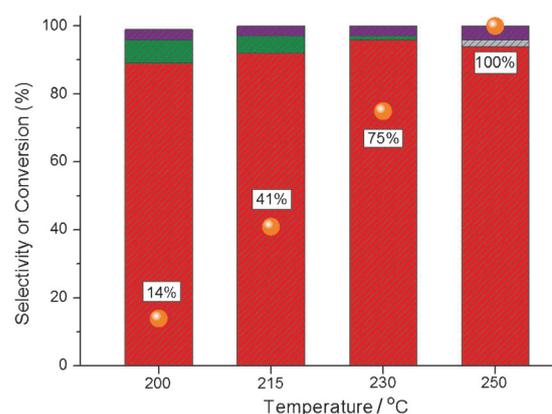E-mail: yongcao@fudan.edu.cn
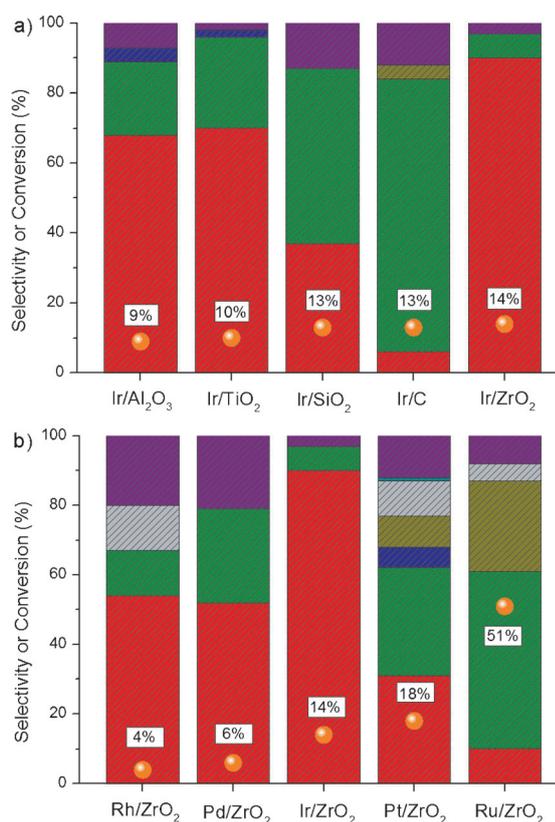
Figure 1. Catalytic hydrogenolysis of aqueous glycerol (10 wt%) over a) 1 wt% Ir supported on different oxides; and b) various noble metals loaded on ZrO_2. Reaction conditions: glycerol 1.0 g, metal 0.12 mol%, 200°C, 4 h, 5 MPa H_2 (RT). Selectivity: ■ gas, ■ MeOH, ▨ EtOH, ■ EG, ■ 1,3-PDO, ■ 1,2-PDO, ■ 1-PO; conversion: ● glycerol.

Figure 2. Catalytic hydrogenolysis of aqueous glycerol (10 wt%) over 1 wt% Ir/ZrO_2 performed at different temperatures. Reaction conditions: glycerol 1.0 g, Ir/ZrO_2 (Ir 0.12 mol%), 4 h, 5 MPa H_2 (RT). Selectivity: ■ gas, ▨ EtOH, ■ 1,2-PDO, ■ 1-PO; conversion: ● glycerol.

(10 wt%) under 5 MPa of H_2 at 200°C with iridium supported on various inorganic oxides as catalysts (Figure 1a). Iridium was selected because iridium nanoparticles (NPs) and/or complexes are known to catalyze a wide range of organic transformations including selective hydrogenation and hydrogenolysis.[13] In all cases, 1-PO and 1,2-PDO were formed as the major products in the liquid phase. All catalysts display an appreciable or pronounced activity for glycerol conversion, but Ir deposited on ZrO_2 (Ir/ZrO_2) appears to be particularly effective for the 1-PO formation, with selectivities of up to 90% at 14% glycerol conversion. The benefit of using Ir as a catalyst becomes clear when comparing the activity of Ir/ZrO_2 with the activity of Rh/ZrO_2, Pd/ZrO_2, Ru/ZrO_2, or Pt/ZrO_2 (Figure 1b). Note that previously reported solid catalysts, such as ZrO_2-supported Ru NPs (Ru/ZrO_2),[14] showed good activity but inferior selectivity in terms of 1-PO formation relative to Ir/ZrO_2 under the present reaction conditions.

As the combination of Ir with zirconia appeared to be essential for achieving a high catalytic activity for selective 1-PO formation, the next step was to further improve the glycerol conversion while keeping the undesired formation of 1,2-PDO or gaseous by-product at its minimum. Using the Ir/ZrO_2 catalyst, we first studied the effect of hydrogen pressure on the hydrogenolysis of glycerol at 200°C (Figure S1 in the Supporting Information). By increasing the hydrogen pressure from 2 to

5 MPa at 200°C, only a marginal increase of glycerol conversion from 8 to 14% was achieved. Further investigation into the effect of the reaction temperature at 5 MPa, however, revealed that an increase of temperature from 200 to 250°C dramatically boosted glycerol conversion from 14 to 100% (Figure 2). Note that an even higher selectivity of up to 96% toward 1-PO formation can be achieved at 230°C. Thus, the maximum yield of 1-PO can reach up to 94% at 250°C and 5 MPa of H_2. This result is remarkable and becomes more relevant for recycling: the catalyst can be reused at least five times with minimal decrease in both glycerol conversion and selectivity to 1-PO (Figure S2). Of yet further interest is that the specific activity based on 1-PO formation using the Ir/ZrO_2 catalyst is up to 2.90 mol h^{-1} g$_{Ir}^{-1}$, that is, this catalyst is over 150 times more active than the previously reported $Pt-H_2SiW_{12}O_{40}/ZrO_2$ catalyst (80% selectivity to 1-PO at full glycerol conversion).[12] To the best of our knowledge, our result represents the first example of a heterogeneously catalyzed synthesis of renewable 1-PO by means of an efficient and near quantitative conversion of bio-derived glycerol.

The outstanding catalytic activity for hydrogenolysis of glycerol over Ir/ZrO_2 at the conditions mentioned above clearly reflects the fast surface kinetics caused by the intimate interaction of the Ir species with the underlying ZrO_2 support. Preliminary mechanistic analysis of this hydrogenolysis reaction by monitoring the kinetics of glycerol conversion revealed that during the whole reaction process 1-PO was always the primary product (Figure S3), without detecting 1,2-PDO and 1,3-PDO. Moreover, it was confirmed in two separate experiments that the formation of 1-PO directly from 1,2-PDO occurred at a considerably higher rate than that from 1,3-PDO (Table S2), thus verifying that 1-PO was mainly produced by the formation of 1,2-PDO as an intermediate during the reaction (Scheme S1). To better understand the superior performance of Ir/ZrO_2, we characterized the various supports by using NH_3-temperature-programmed desorption (NH_3-TPD). ZrO_2 shows a greater abundance of surface acidic sites in comparison to the other supports (Figure S4). These data, together with the catalytic results in Figure 1, strongly suggest that the unique bifunctional

character of the Ir/ZrO$_2$ catalyst is essential to facilitate glycerol conversion to 1-PO in a highly selective manner.

A full characterization of the Ir/ZrO$_2$ sample was thus performed, and the following features of this Ir-based catalyst have been discovered. According to the X-ray absorption near edge structure (XANES) data (Figure S5), Ir exists only in its metallic state in the Ir/ZrO$_2$ catalyst. The X-ray diffraction (XRD) patterns of the Ir/ZrO$_2$ catalyst after reuse revealed that the crystal phase was similar to that of the fresh Ir/ZrO$_2$ (Figure S6), and no distinct metallic Ir reflections were visible for both fresh and used Ir/ZrO$_2$ samples, owing to the fact that the Ir particle sizes were very small. This scenario can be further corroborated by transmission electron microscopy (TEM) images of the Ir/ZrO$_2$ catalyst after the reuse, which revealed that the average diameter (ca. 1.7 nm) and size distribution of the Ir NPs were similar to those of the fresh Ir/ZrO$_2$ and that no aggregation of the used Ir NPs occurred (Figure S7). By using inductively coupled plasma atomic emission spectroscopy (ICP–AES) analysis, it was confirmed that there was no leaching of Ir during the reaction, verifying the inherent stability of the Ir/ZrO$_2$ catalyst. These results are consistent with the retention of the catalytic activities of the Ir/ZrO$_2$ catalyst during recycling experiments.

Bearing in mind that the water content in crude glycerol can vary quite significantly depending on different biodiesel processes, we have investigated the effect of feedstock concentration on the Ir-catalyzed hydrogenolysis of glycerol. As shown in entries 1–4 of Table 1, glycerol with concentrations ranging from 5–50 wt% can be efficiently converted to 1-PO. It is also well known that crude glycerol, which is obtained directly from the bio-diesel industry by transesterification, contains several impurities such as methanol (from an incomplete removal by distillation) and salts (sodium chloride or sodium sulfate from neutralization of the basic catalysts with HCl or H$_2$SO$_4$).[8a] As a cost-effective option, it is highly desirable that a less refined glycerol can be directly utilized for downstream applications. We have thus checked the tolerance of Ir/ZrO$_2$ towards the possible impurities during the hydrogenolysis of a simulated crude glycerol. As can be seen from Table 1, the catalytic performance of the Ir/ZrO$_2$ sample in terms of activity and selectivity did not change with the addition of NaCl (4 wt%) and methanol (1 wt%) (entry 5). In the more challenging reactions uisng simulated crude glycerol with a higher amount of NaCl (15 wt%) and methanol (1 wt%) as the reactant, more Ir catalyst was required to obtain the desired yield (entry 6).[15] These results are extremely welcome in view of the fact that crude glycerol with varying amounts of water and impurities can be directly used as a viable

carbon source for selective biomass conversion, which may open the possibility to develop cost-effective and ecofriendly technologies for the large-scale production of industrial chemicals based on biogenic crude glycerol.

Based on the above results, we next focused on the second step for the proposed GTP process, that is, the consecutive conversion of 1-PO to propylene. We initially examined the dehydration of neat 1-PO vapors in a vertical fixed-bed reactor under atmospheric pressure at 250 °C with various solid acid catalysts, including HZSM-5, SAPO-34, MCM-41, and Al$_2$O$_3$ (Table 2). When using the HZSM-5 zeolite, a highly active and selective catalyst for the dehydration of ethanol,[16] high conversions and selectivities were obtained. However, other solid acid catalysts, such as SAPO-34, MCM-41, or Al$_2$O$_3$, were not effective for the dehydration of neat 1-PO, producing large amounts of n-propyl ether as undesired by-product under identical reaction conditions. Among the various solid acid catalysts examined herein, HZSM5 material with a SiO$_2$/Al$_2$O$_3$ molar ratio of 30 achieves, by far, the best catalytic performance. Notably, by using the HZSM-5-30 sample as catalyst,

Table 1. Catalytic performances for hydrogenolysis of aqueous glycerol with different composition.[a]

Entry	Feed composition	Concentration [wt%]	Conversion [%]	Selectivity [%] 1-PO	others[b]
1	glycerol	5	100	92	8
2	glycerol	10	100	94	6
3	glycerol	30	100	93	7
4	glycerol	50	100	93	7
5	crude glycerol[c]	10	100	94	6
6	crude glycerol[d]	10	100	93	7

[a] Reaction conditions: glycerol 1.0 g, catalyst Ir/ZrO$_2$ (Ir 0.12 mol%), 250 °C, 4 h, 5 MPa H$_2$ (RT). [b] Others including propane, methane, and ethanol. [c] Simulated crude glycerol 1.0 g (glycerol/NaCl/methanol at a mass ratio of 95:4:1). [d] Simulated crude glycerol 1.0 g (glycerol/NaCl/methanol at a mass ratio of 84:15:1), Ir 0.20 mol%.

Table 2. Dehydration of 1-PO to produce propylene over various solid acid catalysts.[a]

Entry	Catalyst	Conversion [%]	Selectivity [%] propylene	propyl ether	higher hydrocarbon	Yield [%]
1	HZSM-5-30[b]	>99	>99	trace	trace	>99
2	HZSM-5-60	96	99	trace	1	95
3	HZSM-5-100	91	96	trace	4	87
4	HZSM-5-200	78	91	trace	9	71
5	SAPO-34	35	82	18	–	29
6	MCM-41	27	78	22	–	21
7	Al$_2$O$_3$	42	66	34	–	28
8	HZSM-5-30[c]	>99	>99	trace	trace	>99
9	HZSM-5-30[d]	>99	>99	trace	trace	>99

[a] Reaction conditions: catalyst 2.0 g, 250 °C, neat 1-PO feedstock, weight hourly space velocity WHSV = 1.0 h^{-1}, at atmosphere pressure, N$_2$ flow rate 20 mL min^{-1}, time on stream 2 h. [b] HZSM-5-X denotes a HZSM-5 zeolite with a SiO$_2$/Al$_2$O$_3$ molar ratio of X. [c] 10 wt% aqueous 1-PO solution. [d] 50 wt% aqueous 1-PO solution.

neat 1-PO can be quantitatively converted into propylene. To investigate the intrinsic reason for different catalytic performances, we characterized the various solid acid catalysts by using NH_3-temperatue-programmed desorption (NH_3-TPD). According to Figure S9, all catalysts showed two peaks, clearly indicating the presence of both weak and medium strong acidic sites. Importantly, it is revealed that the HZSM-5-30 sample has more weak acidic sites than medium strong acidic sites in comparison to other materials. Combining the results from the activity tests and NH_3-TPD, it is likely that the dehydration of 1-PO proceeds effectively in the presence of solid acid catalysts because of the presence of a higher population of weak acidic sites.

Given the observed high dehydration activity, more relevant studies have been performed to simulate the H_2O-containing feed produced from the aqueous glycerol hydrogenolysis process described above (Table 2). The diluted aqueous 1-PO vapors were readily dehydrated to propylene with high yield in aqueous solution at different 1-PO concentrations (10 and 50 wt%, respectively). Rapid deactivation represents a serious problem for HZSM-5 zeolite-catalyzed alcohol dehydrations because of its low anticoking ability.[17] To examine the likely stability of HZSM-5-30 for the dehydration of aqueous 1-PO to propylene, we investigated the long-term performance. In our catalytic system, no deactivation was observed for up to 50 h on stream. However, the conversion of 1-PO decayed rapidly after 50 h and regeneration, therefore, seems crucial for practical applications. Note that such deactivation could be largely ascribed to the blocking of the active acid sites by carbon deposition as revealed by thermogravimetric analysis (Figure S10). For regeneration of the deactivated HZSM-5-30 after 60 h on steam, the reaction was interrupted under an N_2 steam, and then air was introduced at 500 °C to burn off carbon species deposited on the catalyst. After the first and second regeneration, a high yield of propylene (over 99%) could be achieved again (Figure 3). To the best of our knowledge, such superior catalytic performance has to date never been achieved in the selective conversion of bio-derived 1-PO to propylene.
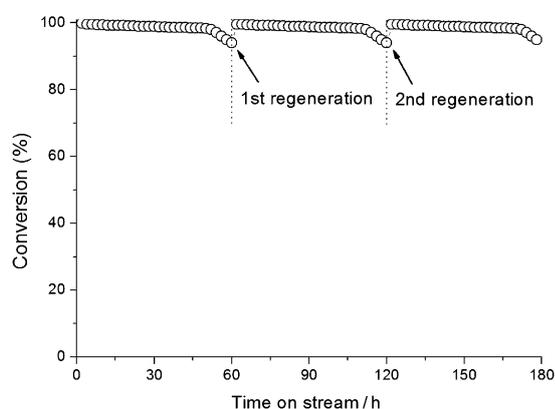
Figure 3. Long-term performance of dehydration of aqueous 1-PO (50 wt%) over HZSM-5-30. Reaction conditions: 2.0 g HZSM-5-30, 250 °C, 50 wt% aqueous 1-PO feedstock, WHSV = 1.0 h⁻¹, at atmosphere pressure, N_2 flow rate 20 mL min⁻¹, selectivity to propylene always > 99%.

Thus far, a stepwise approach to synthesize propylene using glycerol as a renewable feedstock has been outlined. From a process integration point of view, the efficiency and utility of this sequence could be improved if a direct continuous process that combines the conversion of glycerol to 1-PO coupled with a consecutive dehydration step could be implemented. In a related study, Sousa Fadigas et al.[18] described in a recent patent that the direct conversion of glycerol to propylene can be achieved by using a complex multi-metallic catalyst composed of Fe–Mo mixed oxides supported on activated carbon. However, issues such as poor long-term performance of the catalyst and unsolved reaction pathway remain of concern. We have performed a similar direct conversion of glycerol into propylene under relatively mild conditions (250 °C, 5 MPa) by combining Ir/ZrO$_2$ with a 1-PO dehydration catalyst in a fixed-dual-bed reactor (Scheme S2). Nevertheless, preliminary experiments with the fixed-dual-bed reactor showed that the yield of propylene from glycerol conversion was significantly lower than expected: only 67% of propylene was detected (Table 3,

Table 3. Direct conversion of glycerol into propylene over Ir/ZrO$_2$ coupled with HZSM-5-30.[a]

Entry	Catalyst	P_{H_2} [MPa]	Conversion [%]	Selectivity [%]
1[b]	Ir/ZrO$_2$&HZSM-5-30	5	100	67
2[b]	Ir/ZrO$_2$&HZSM-5-30	3	100	79
3[b]	Ir/ZrO$_2$&HZSM-5-30	1	100	85
4[b]	Ir/ZrO$_2$&HZSM-5-30	0.5	73	88
5[c]	Ir/ZrO$_2$	1	100	5
6[d]	HZSM-5-30	1	21	–

[a] Reaction conditions: Ir/ZrO$_2$ 2.0 g, HZSM-5-30 2.0 g, 250 °C, 30 wt% aqueous glycerol, WHSV = 1.0 h⁻¹, H_2/glycerol = 100 (molar ratio), time on stream 2 h. [b] The main by-product was propane. [c] The main by-product was 1-PO. [d] The main by-product was acrolein.

entry 1). To suppress the undesirable formation of propane during the reaction, we thus decided to decrease the hydrogen pressure used for the continuous flow reaction. Thus, it is possible to achieve a high propylene yield of up to 85% by decreasing the hydrogen pressure from 5 to 1 MPa (entries 2–4). Importantly, under the conditions in entry 3 of Table 3, no significant decreases in glycerol conversion and propylene selectivity occurred within 40 h, and the propylene yield could be maintained at about 85% (Figure S11). The results, while preliminary, are encouraging. From a practical perspective, future research should focus on a full optimization of the reaction parameters as well as a further screening of dual catalyst systems for the selective production of propylene by means of a direct conversion of glycerol.

In summary, we have demonstrated a selective route for the synthesis of propylene using biorenewable glycerol as reliable and cost-effective feedstock. The route features the formation of 1-PO as intermediate through hydrogenolysis of glycerol, which was achieved with an unprecedented high selectivity.

A subsequent dehydration of the resultant 1-PO produces propylene. Such a glycerol-to-propylene process provides a path to tackle the problem of the glycerol surplus associated with the bio-diesel industry. It may also open new possibilities to produce propylene from renewable resources on a large scale, thus offering a promising opportunity to meet the growing worldwide propylene demand and supply shortage.

Experimental Section

General procedure for the hydrogenolysis of glycerol to 1-PO: A mixture of glycerol (1.0 g), catalysts (metal 0.12 mol%), 2-methoxyethyl ether (2 mmol, internal standard), and water (9 mL) were charged into a 100 mL Hastelloy-C high pressure Parr reactor and stirred at a rate of 800 rpm under 5 MPa H_2 for a given reaction time. The products were analyzed by using a gas chromatograph. The identification of the products was performed by using a GC–MS spectrometer. The conversion and the selectivity were defined on the carbon basis. See the Supporting Information for the experimental details

General procedure for the dehydration of 1-PO to propylene: The dehydration of 1-PO was performed in a vertical fixed-bed reactor (inner diameter 10 mm, length 500 mm) under atmospheric pressure at 250 °C. The catalyst (2.0 g) was placed in the middle of a stainless reactor. The 1-PO feedstock was continuously introduced into the reactor by means of an HPLC pump at a WHSV of 1.0 h^{-1}. The products were obtained when the reaction reached steady state. Then, the liquid and gas products were cooled, collected in a gas–liquid separator and analyzed by using a gas chromatograph.

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[7] Bio-crude glycerol was assessed by ICIS at $154–220 per tonne FOB (free on board) in 2012 in the US. However, US polymer grade propylene prices for 2012 were at ca. $1280 per tonne (based on data and information from ICIS Chemical Business. Available electronically at http://www.icis.com).

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[15] It is important to note that in a continuous flow process, the NaCl accumulation may deactivate the catalyst rapidly. Discussion of this issue is, however, beyond the scope of this study.

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