n-Butane Carbonylation to *n*-Pentanal Using a Cascade Reaction of Dehydrogenation and SILP-Catalyzed Hydroformylation

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A novel gas-phase process has been developed that allows direct two-step conversion of butane into pentanals with high activity and selectivity. The process consists of alkane dehydrogenation over a heterogeneous Cr/Al_2O_3 catalyst followed by direct gas-phase hydroformylation using advanced supported ionic liquid phase (SILP) catalysis. The latter step uses rhodium complexes modified with the diphosphite ligands biphephos (BP) and benzopinacol to convert the butane/butene mixture from the dehydrogenation step efficiently into aldehydes. The use of the BP ligand results in improved yields of linear pentanal because SILP systems with this ligand are active for both isomerization and hydroformylation. © 2014 American Institute of Chemical Engineers *AIChE J*, 61: 893–897, 2015

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Introduction

Modern homogeneous catalysts are highly efficient in converting C—C double bonds into value added products as exemplified in, for example, hydroformylation, hydrogenation, hydrocyanation, carbonylation, and coupling reactions.[1,2] With a changing feedstock scenario, especially in the United States, the direct use of alkanes rather than alkenes should be highly attractive for future petrochemical processes.[3,4] A typical C—H activation route for light alkanes (C_2—C_5) includes alkane dehydrogenation in the presence of a heterogeneous catalyst.[5] This reaction is strongly endothermic and high reaction temperatures and/or hydrogen removal are necessary for thermodynamic reasons to achieve a high rate of alkane conversion. In practice, the product stream from the dehydrogenation units always contains a significant amount of unreacted alkanes, resulting in low alkene concentrations. For subsequent reaction steps, this mixture is typically distilled in a highly energy-intensive process with great energetic effort to provide a pure alkene stream for the subsequent alkene functionalization unit. Concentrated feedstock streams are necessary in current state-of-the-art technologies to allow sufficiently high reaction rates for reasonably sized reactor equipment. Many of the aforementioned alkene functionalization reactions involve transition metal complexes with expensive ligand systems so that catalyst recycling and catalyst immobilization strategies are crucial in process economics.[6]

In recent years, we and other research groups have established the concept of SILP catalysis as an efficient tool for continuous gas-phase processing of immobilized transition metal catalysts.[7–10] In SILP systems, a thin film of ionic liquid containing the dissolved catalyst complex is dispersed over the large inner surface of a porous support. The ionic liquid can be fixed to the surface by either physisorption or chemisorption. Ionic liquids have extremely low vapor pressures under industrial operating conditions, and SILP systems have been demonstrated to provide high operational stability in gas contact without the need for structural modification of the ligand by ionic anchor groups.[11–15] In the last 5 years, our joint academic-industrial research team has developed dedicated SILP hydroformylation catalysts that allow conversion of mixed and dilute industrial feeds using diphosphite-based rhodium complexes; SILP systems with the ligands 6,6′-((3,3′-di-*tert*-butyl-5,5′-dimethoxy-[1,1′-biphenyl]-2,2′-diyl)*bis*(oxy))didibenzo[d,f][1,3,2]-dioxaphosphepine (BP)

Additional Supporting Information may be found in the online version of this article.

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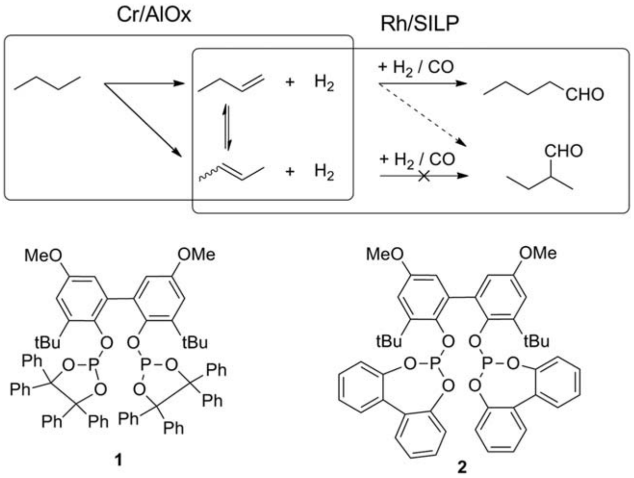

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Scheme 1. Hydroformylation of mixed C_4 feed using Rh-SILP catalysts with diphosphite ligands BzP 1 and BP 2.

and 2,2′-((3,3′-di-*tert*-butyl-5,5′-dimethoxy-[1,1′-biphenyl]-2,2′-diyl)-*bis*(oxy))*bis*(4,4,5,5-tetraphenyl-1,3,2-dioxaphospholane) (BzP) (Scheme 1) have been studied in detail.[16,17]

With the BP ligand, consecutive isomerization and hydroformylation of a highly dilute C_4 feed (reactive alkene content 30%) proceeded with a reasonable TOF of 200 h^{-1} and a STY of 100 $kg_{n\text{-pentanal}}\ m_{SILP}^{-3}\ h^{-1}$. A more complex industrial mixture of butenes consisting of *iso*-butene (43.1%), 1-butene (25.6%), *trans*-2-butene (9.1%), *cis*-2-butene (7.0%), butanes (14.9%), and 1,3-butadiene (0.3%) could be converted into the desired *n*-pentanal product with high activity (TOF > 400 h^{-1}) and selectivity of more than 98% over 900 h of time on stream. For the latter example, a STY of 850 $kg_{n\text{-pentanal}}\ m_{SILP}^{-3}\ h^{-1}$ was demonstrated, a productivity that falls well within the range observed in typical industrial gas-phase processes. More importantly, the catalyst selectively converted the 1-butene fraction while leaving the *iso*-butenes untouched. In this way, separation between these two types of alkene, which is usually problematic due to their very close boiling points, is avoided.

Having two highly active catalysts at hand, we were interested in evaluating their potential in the direct conversion of alkanes into valuable aldehydes by a cascade of consecutive dehydrogenation and hydroformylation reactors. The very attractive new features of SILP catalysis as compared with traditional liquid phase hydroformylation—namely, the applicability of gas-phase reactors and the highly active conversion of alkenes from dilute feeds—triggered these research efforts. Here, we present our initial results from such a reaction sequence, demonstrating impressively that SILP catalysts may open up a very attractive route to direct alkane functionalization in suitable gas-phase process sequences.

The experiments were performed in a continuous cascade reactor setup. A simplified flow scheme of the rig used is depicted in Figure 1. The plant can be divided into three main sections: the dehydrogenation part, the condensation/collection part, and the isomerization/hydroformylation part. The catalyst used in the dehydrogenation of *n*-butane is an alumina-supported chromium catalyst (10 wt % of Cr compounds) provided by Evonik Industries AG. The SILP catalyst used for the hydroformylation has already been reported by our group.[16] Its Rh loading is 0.2 wt %.

The dehydrogenation reactor is an Alloy 600 fixed-bed reactor, which can be operated at temperatures up to 1173.15 K at atmospheric pressure. Ten grams of the dehydrogenation catalyst were placed in the reactor.

The dehydrogenated C_4 stream is condensed in the storage tank and dosed by the high-performance liquid chromatography (HPLC) pump into the hydroformylation reactor to overcome the pressure gap. The tank is filled with cylindrical packing and cooled to 253.15 K. Hydrogen and the lighter aliphatic compounds exit the tank at the top. One level sensor was mounted on the bottom and at the top of each tank and thus confirmed accumulation of liquefied feed stock or prevented a fill up of the tank. The fixed bed hydroformylation reactor contains 2–3 g of the SILP catalyst and is operated at 1 MPa and 373.15–393.15 K. The ratios of carbon monoxide to hydrogen to C_4 mixture can be varied by changing the volume flows of the mass flow controllers or the volume flow of the HPLC pump. The product streams of both reactions, dehydrogenation and isomerization/hydroformylation, can be analyzed alternatingly by online gas chromatography (GC). Our system, thus, allows continuous, direct, two-step carbonylation of *n*-butane to pentanals under technically relevant conditions.

The dehydrogenation of *n*-butane was performed initially at 723.15 K and atmospheric pressure. Figure 2 shows the conversion of *n*-butane and the selectivity for the various butenes for the Cr on alumina catalyst as a function of

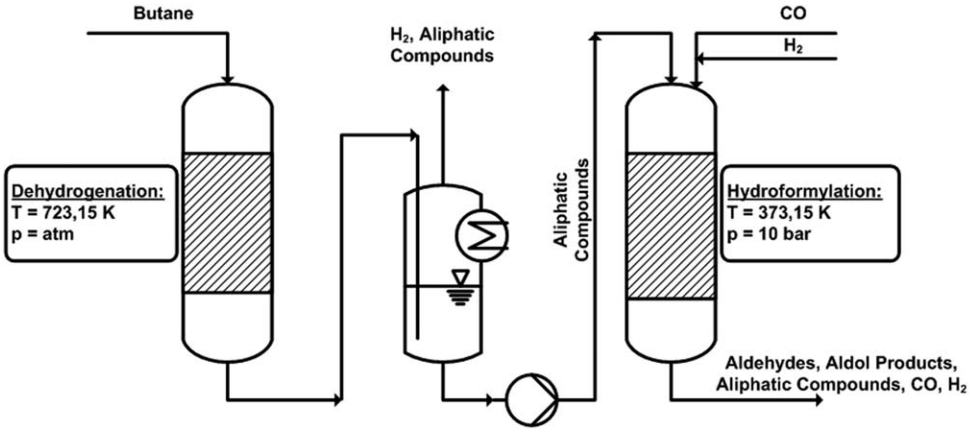

Figure 1. Flow scheme of the dehydrogenation/hydroformylation cascade rig.

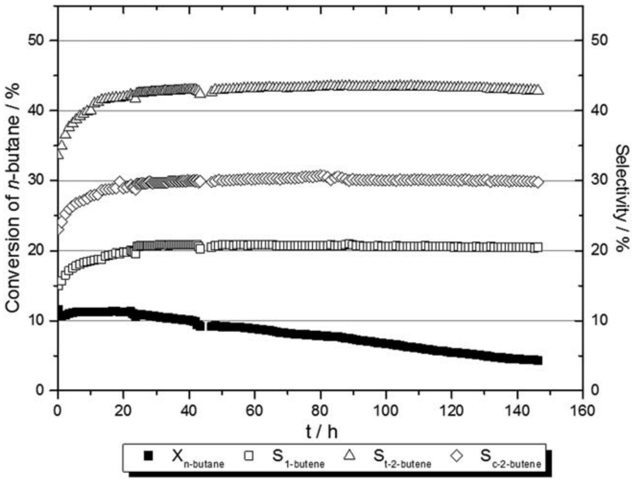

Figure 2. Conversion and selectivity as a function of reaction time for the catalytic dehydrogenation of *n*-butane with an alumina supported chromium catalyst.

$T = 723.15$ K, $p_{n\text{-butane}} = 0.1$ MPa, total volume flow = 43.4 $\text{mL}_N\ \text{min}^{-1}$, $m_{\text{Cr/AlOx}} = 10$ g, $w_{\text{Cr}} = 10$ wt %.

reaction time. The conversion of *n*-butane in the starting phase was approximately 11%. This is in good accord with thermodynamic equilibrium conversion under these reaction conditions, indicating that no major side reactions (cracking or coking) occurred. After 20 h of time on stream, the catalyst began to deactivate slowly but still converted 4% of the butane to butenes after 140 h of time on stream. The deactivation can be attributed mainly to coke formation and consequent blocking of the active centers.[18] Note that the selectivity for the individual butenes increased during the first 20 h of time on stream. Obviously, the fresh catalyst showed a higher degree of cracked product formation. With the onset of deactivation the selectivity for the butenes remained constant and corresponded well to the thermodynamic composition of the butenes at the operating temperature.[19] The overall selectivity for the butenes was higher than 94%. Butadiene could be detected only in traces at the reaction temperature used. The remaining 6% selectivity could be assigned to ethylene and propylene, being formed through cracking reactions.

The C_4 stream from the dehydrogenation reactor was condensed in the storage tank at 253.15 K, 14 K below the boiling point of the most volatile C_4 product, 1-butene, at atmospheric pressure. The liquid level was controlled by a sensor in the tank. Hydrogen and cracking products left the tank from the top. After 44 h of butane dehydrogenation, the hydroformylation reaction was started at 373.15 K and a total pressure of 1 MPa. The volume flow of the C_4 stream was kept constant while the flows of hydrogen and carbon monoxide were varied during the continuous experiment. The molar ratio of synthesis gas to C_4 feedstock was varied from 2:1, through 1:1, to 1:2. Figure 3 illustrates the conversion of 1-butene and the selectivity for the desired *n*-pentanal as well as the regioselectivity and the selectivity for the undesired next higher aldol product. As expected from our previous results, the Rh-BzP-SILP catalyst converted almost exclusively the 1-butene fraction while 2-butene left the reactor unreacted. Side reactions in the form of 1-butene hydrogenation and pentanal aldolization were observed only to a small extent. Interestingly, the conversion of 1-butene could be increased dramatically by decreasing the syngas:C_4 molar ratio. At a ratio of 2:1, the conversion of 1-butene was about 60%, and increased to as much as 93% at a 1:2 ratio. We ascribe this behavior to two effects: the increase of residence time with reduced synthesis gas flow and the specific dependence of the reaction rate on the partial pressures in the reactor.

To provide support for the latter argument, kinetic studies were carried out to determine effective reaction orders in the hydroformylation reactor. These experiments revealed positive orders of 0.7 for the alkene and 0.4 for hydrogen. For carbon monoxide a slightly negative order of 0.1 was found. These data correspond well with the Wilkinson mechanism and recently published results for SILP catalyzed hydroformylation.[17,20,21] The overall selectivity for the linear aldehyde was greater than 96% throughout the experiment and the regioselectivity for *n*-pentanal, at >99.5%, was exceptionally high. 2-propyl-2-heptenal was formed by aldol condensation of two molecules of *n*-pentanal. Butanal and propanal, produced by dissolved propylene and ethylene in the condensed C_4-mixture, could be detected in traces. The amount of these byproducts was lower than the amount of the branched C_5-aldehyde. Selectivity for the aldol product as determined by GC was between 2 and 4%. Our recent results suggest an accumulation of liquid aldehyde and aldol products in the pore system of our SILP catalyst. The products build up an additional solvent for the catalyst complex in the pore system. The amount of liquefied product in the pore system is mainly influenced by the equilibrium of the vapor pressure of the product to the saturation vapor pressure. Under stationary conditions product formation and product evaporation from the pore system are in equilibrium.[22]

To increase the *n*-pentanal yield and to optimize the utilization of the 2-butene fraction formed in the

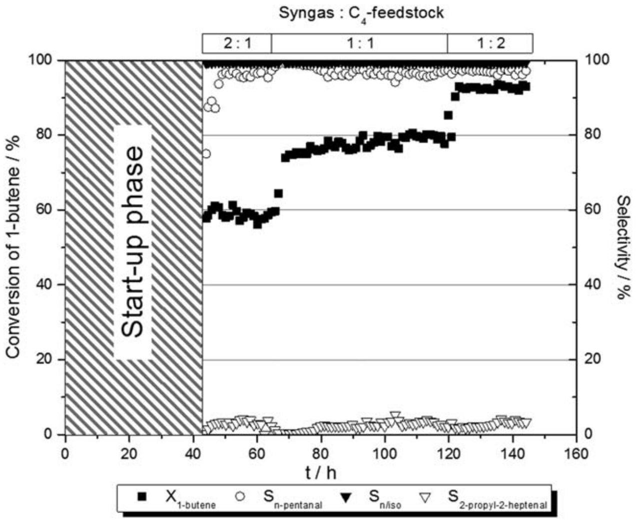

Figure 3. Conversion and selectivity plotted as a function of reaction time for a dilute dehydrogenated C_4 stream in the presence of Rh-BzP-SILP catalyst.

$p_{\text{total}} = 1$ MPa, $T = 373.15$ K, total volume flow = 64.9–129.9 $\text{mL}_N\ \text{min}^{-1}$, $p_{C_4\text{-stream}} = 0.333$–$0.666$ MPa, $p_{H_2} = p_{CO} = 0.333$–0.666 MPa, $m_{\text{SILP}} = 3$ g, $w_{\text{Rh}} = 0.2$ wt %, ligand (BzP)/rhodium = 10:1, ionic liquid = 1-ethyl-3-methylimidazolium bis(trifluoromethylsulfonyl)imide, [EMIM][NTf_2], ionic liquid loading = 10 vol % relative to the pore volume.

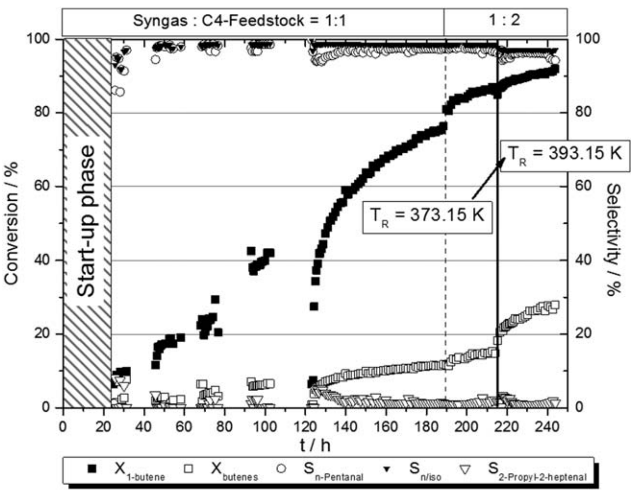

Figure 4. Conversion and selectivity plotted as a function of reaction time for a C_4 feedstock obtained by catalytic butane dehydrogenation at 723.15 K in the presence of a Rh-BP SILP catalyst.

$p_{\text{total}} = 1$ MPa, $T = 373.15$–393.15 K, total volume flow $= 64.9$–86.7 mL_N min^{-1}, $p_{C_4\text{-stream}} = 0.5$–$0.666$ MPa, $p_{H_2} = p_{CO} = 0.333$–0.5 MPa, $m_{\text{SILP}} = 3$ g, $w_{\text{Rh}} = 0.2$ wt %, ligand (BP)/rhodium = 10:1, ionic liquid = 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide, [EMIM][NTf_2], ionic liquid loading = 10 vol % relative to the pore volume; gaps are caused by pump failure.

dehydrogenation reactor, we tested in a subsequent set of experiments a Rh-BP-SILP catalyst system, which is known to convert internal alkenes to linear aldehydes in a combined isomerization/hydroformylation mechanism. The dehydrogenation of the *n*-butane was performed under the same conditions and identical results were obtained (see Supporting Information). As before, hydroformylation with the Rh-BP-SILP catalyst was started after 23 h of dehydrogenation when the level sensor in the storage tank confirmed the availability of liquefied C_4 feedstock for the subsequent hydroformylation. The results for the isomerization/hydroformylation reactor operated with the feed from butane dehydrogenation are shown in Figure 4. The conversion based on all butenes illustrates the ratio of converted internal to terminal alkenes produced during dehydrogenation.

At 373.15 K, the initial conversion of butenes was quite low but increased continuously with reaction time. The activity of the SILP catalyst appeared to level off to a steady state at around 180 h time on stream, after which the syngas ratio was changed. This prolonged activation period is probably caused by the slow formation of the active species due to the big gap in the concentrations of carbon monoxide and the alkene. The resulting overall reaction rate also causes slow formation of aldol condensation products, which have been identified as being beneficial for high activity. After 190 h, the conversion was 78% referred to 1-butene and 12% referred to all butenes. The ratio of the remaining *trans*-2-butene to *cis*-2-butene was in the same range as that obtained after the initial dehydrogenation step (see Figures S1 and S2 in Supporting Information) and remained constant under these conditions (*trans*:*cis* = 1.5). It can be assumed that the rate of isomerization at the bulky Rh-BP center would be higher for *cis*-2-butene than for *trans*-2-butene and would, therefore, result in a change in their amount ratio. Along with the degree of conversion of the butenes, the constant ratio thus further supports the conclusion that only 1-butene was converted to *n*-pentanal under the applied conditions. The regioselectivity of this reaction was higher than 98%, while the selectivity for the aldol product, at 1–3%, was low. When the syngas to C_4 ratio was lowered after 180 h, the conversion of 1-butene increased to 88%, following the trend already observed in Figure 3. At the same time, a minor change was observed in the *trans*:*cis* ratio from 1.5 to 1.7. Under the conditions of a lower syngas to C_4 ratio, 2-butene isomerization to 1-butene evidently contributed to a larger extent to the overall reactivity of the system. This also resulted in the conversion of butenes increasing slightly over time. When the hydroformylation reaction temperature was further increased from 373.15 to 393.15 K, this effect was clearly enhanced. While only 20% of 1-butene was present in the feedstock, the total butene conversion observed was almost 30%, indicating significant isomerization activity of the Rh-BP-SILP catalyst. Under these conditions, the regioselectivity for *n*-pentanal decreased slightly from 98 to 96%. As expected for an isomerizing catalyst system, the *trans*:*cis* ratio of unreacted 2-butenes leaving the reactor changed from 1.7 to 2.2 due to the preferential isomerization and subsequent hydroformylation of *cis*-2-butene.

Experimental

All syntheses were carried out under inert atmosphere in a glovebox. $Rh(acac)(CO)_2$ and the stabilizer *bis*(2,2,6,6-tetramethyl-4-piperidyl)sebacate were purchased from Aldrich. The BzP ligands were synthesized according to the literature.[23] The BP ligand was obtained from Sigma Aldrich. Silica gel 100 (0.063–0.200 mm) and dichloromethane (max. 0.004 vol % H_2O) and the ionic liquid 1-ethyl-3-methylimidazolium *bis*(trifluoromethylsulfonyl)imide, [EMIM] [NTf_2], were purchased from Merck KGaA. The silica gel used was thermally treated at 450°C for 24 h. CO (99.97%), H_2 (99.999%), and *n*-butane (99.5%) were purchased from Linde AG.

The dehydrogenation catalyst was developed in-house and provided by Evonik Industries AG, it was used without further modification. For the preparation of the two SILP catalysts, $Rh(acac)(CO)_2$ was dissolved in water-free CH_2Cl_2 and stirred for 2 min. The BzP ligand was added in tenfold excess (BzP/Rh = 10:1), and the BP ligand in fivefold excess (BP/Rh = 5:1). Both of the catalyst complex solutions were stirred for 5 min and the ionic liquid was then added to the solution. In the case of the BzP modified Rh-SILP, the stabilizer was added in fourfold excess (BzP/stabilizer = 1:4). After 5 min of stirring, the calculated amount of calcinated silica 100 (surface area: 361 m^2 g^{-1}, pore volume 1.02 cm^3 $g^{-1)}$ was added to the solution. After a further 15 min of stirring, CH_2Cl_2 was removed from the suspension by evaporation. The yellow powder obtained was stored under argon until further use.

All organic products were monitored by online GC using a Bruker 450-GC equipped with a HayeSep Q 80/100 mesh (0.5 m × 1/16″ × 1.0 mm), a ShinCarbon micropacked CP Wax 52 CB column (25 m × 0.53 mm × 0.7 mm), an HP-AL/S column (50 m × 0.535 mm × 0.015 mm), a deactivated fused silica column (10 m × 0.32 mm), one thermal conductivity detector, and two flame ionization detectors. The injector temperature was 503.15 K. The split ratio was adjusted to 20:1. Argon was used as carrier gas. The temperatures of the TCD were 503.15 K for the filament and 473.15 K for the housing. The two FIDs were heated to 523.15 K. To detect the high-boiling products and achieve separation of the isomers, the following temperature program was used: initial temperature 328.15 K, initial time 4 min, heating ramp 4.5°C min^{-1}, final temperature 373.15 K for 12 min, heating ramp 10°C min^{-1}, and final temperature 403.15 K for 6 min.

Conclusions

In conclusion, we have demonstrated an efficient route for using cheap and abundant *n*-butane to produce the valuable and industrially important product *n*-pentanal via a combined gas-phase dehydrogenation/isomerization/hydroformylation sequence. The Cr-AlO_x dehydrogenation catalyst used was found to deactivate over 150 h time on stream but yielded high amounts of butenes. Regeneration of this catalyst by coke oxidation has not been performed in this work but may well be practicable. The alkene fraction from the dehydrogenation reactor was converted into aldehydes using Rh-ligand-SILP catalysts in a consecutive gas-phase hydroformylation reactor. The Rh-BzP-SILP catalyst selectively converted 1-butene from the C_4 mixture (ca. 20% 1-butene, ca. 30% *cis*-2-butene, and ca. 43% *trans*-2-butene) produced by butane dehydrogenation at 723.15 K and *n*-pentanal was obtained with an exceptionally high *n*/*iso* selectivity of >99.5%. The yield of *n*-pentanal could be increased by reducing syngas pressures and by reducing the syngas to C_4 ratio in the reactor. Under these conditions, a STY of 140–250 $\text{kg}_{n\text{-pentanal}}\ \text{m}_{\text{SILP}}^{-3}\ \text{h}^{-1}$ could be realized. An additional part of the internal butenes from butane dehydrogenation could be converted when using a Rh-BP-SILP catalyst at elevated temperatures, resulting in STYs of 10–170 $\text{kg}_{n\text{-pentanal}}\ \text{m}_{\text{SILP}}^{-3}\ \text{h}^{-1}$ depending on the reaction conditions. The productivities of the two SILP catalysts in the direct two-step butane carbonylation highlight the potential of this concept for future industrial applications requiring straightforward chemical valorization of alkane feeds from, for example, fracking processes, or the conversion of mixed feeds. The fact that gas-phase SILP catalysis can be applied directly in combination with heterogeneously catalyzed alkane dehydrogenation opens up many pathways for simple alkane functionalization sequences avoiding the use of additional organic solvents and the distillation/purification of alkene substrates prior to catalytic conversion.

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