

Catalytic upgrading of refinery cracked products by *trans*-hydrogenation: a review

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Abstract The production of high premium fuel is an issue of priority to every refinery. The *trans*-hydrogenation process is devised to convert two low valued refinery cracked products to premium products; the conversion processes involve the combination of dehydrogenation and hydrogenation reaction as a single step process. The paper reviews the recent literature on the use of catalysts to convert low value refinery products (i.e. alkanes and alkynes or alkadienes) to alkenes (olefins) by *trans*-hydrogenation. Catalysts based on VO_x, CrO_x and Pt all supported on alumina have been used for the process. However, further studies are still required to ascertain the actual reaction mechanism, mitigating carbon deposition and catalyst deactivation, and the role of different catalysts to optimize the reaction desired products.

Keywords *Trans*-hydrogenation · Catalysis · Hydrocarbon · Dehydrogenation · Hydrogenation

Introduction

The production of olefins has been of major industrial importance since World War II using catalysts to yield high-octane aviation fuel [1]. Since then the petroleum industries have been constantly developing new processes for improved olefin production, involving new catalyst formulations and modifications to reactor and plant design. This

effort has also been extended to accommodate different hydrocarbon feeds in order to maximize production. Currently, olefins are produced via a number of processes in oil refining industries to successfully maximize the production. For example in the late 1980s, the CatofinTM process was designed for the on-demand production of propylene and isobutylene using propane and isobutane, respectively [2–4].

Gasoline is a hydrocarbon based fuel obtained from petroleum fraction. However, its exact chemical composition can be varied by blending with other specific hydrocarbons to produce a very high grade fuel depending on the demand, applications and environmental constraints. The major component of fuel used in internal combustion engines comprises of mainly straight chain and isomers of light and medium alkanes with specific concentrations of aromatics to achieve an optimum octane number [5–7]. Environmental problems associated with aromatics, however, have placed a ban on their usage recently due to health concerns [8, 9]; even with the recent ban, gasoline will remain a popular fuel for transportation, combustion engines and industrial applications [10, 11] for many years to come. Therefore, devising the most appropriate method of upgrading the octane number is an important issue from both research and policy perspectives.

Olefins are class of hydrocarbons that are unsaturated with a single double bond and general chemical formula of C_nH_{2n}. Olefins are regarded as the building block of the petrochemical industry due to their relatively high reactivity, making the olefin molecule ideal for the conversions into valuable end products [12].

The global production of olefins is around 400 MT per year generated from one billion tons of various hydrocarbon feedstocks, with about 60% of the global feedstock processed within the fluid catalytic cracking unit of oil refineries, whilst the other 40% are processed within the

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steam cracking of naphtha, steam cracking, ethylene plants, and liquefied petroleum gas [13]. Currently this is an area of globally active R&D targeted at maximizing production due to worldwide high demands.

The primary purpose of the *trans*-hydrogenation process historically has been to convert low-value cracked hydrocarbons into valued distillate products. Although *trans*-hydrogenation is not a new technology for production of olefins there is scant scientific attention toward the invention. The *trans*-hydrogenation of alkanes and alkynes (or alkadienes) into alkenes (olefins) is a method of converting two low value chemicals into two high value chemicals. It is well known that hydrocarbon feed stock streams, such as naphtha, LPG, or gas oil are cracked in a furnace to produce mixtures of hydrocarbons of varying molecular weight [14–19], a typical percentage composition (by weight) is presented in Table 1.

The olefin component is generally the most important, used for the production of high-octane fuel and polymerization [14, 19]. Therefore, there is a need to maximize its production as the most valuable product of the cracked component. However, inevitably compounds such as alkanes and alkynes are also products of cracking and although the alkyne can be hydrogenated to the respective alkene, this uses hydrogen. Similarly the alkane can be dehydrogenated but there is then the need for separation. In contrast when both react via catalytic *trans*-hydrogenation the yield of the olefin is increased without the need of hydrogen or separation technology. The two low value products can be mixed and fed into a simple refinery process (Fig. 1).

Trans-hydrogenation has been disclosed in a numbers of patents over a period of decades [19–24]. However, it has only recently been studied in the academic literature [25–27]. The *trans*-hydrogenation process has significance as a safe environmentally acceptable technique for upgrading feedstock containing C2–C5 alkanes and alkynes/alkadienes.

Table 1 Typical percentage composition by weight of naphtha cracking products

Component	Wt% Composition
Hydrogen	1
Benzene	6
Methane	16
Toluene	3
Ethene	32
Aromatics	2
Propene	16
Fuel oil	4
C4 hydrocarbons	8
Others	12

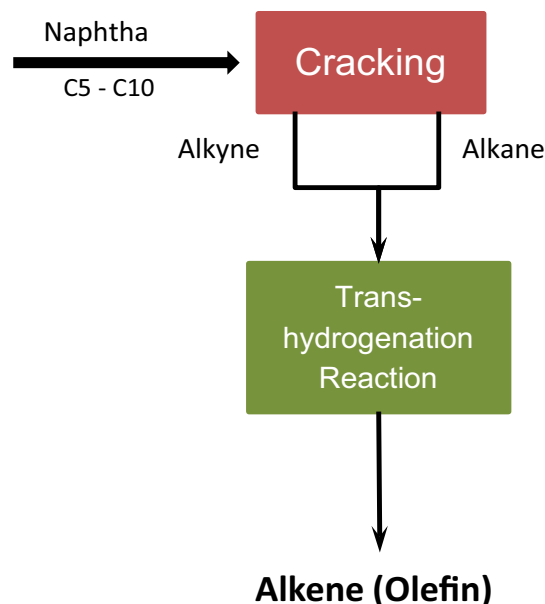
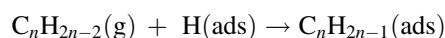
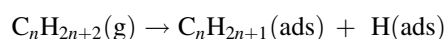


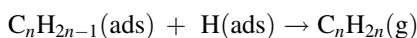
Fig. 1 Proposed operation unit for *trans*-hydrogenation process in a refinery

The aim of this review is to present the role of heterogeneous catalysis in the conversion of low-value refinery products into more valued ones using *trans*-hydrogenation. Taking into account the available patents and academic literatures, emphasis will be placed on the choice of catalyst, reactant ratio and general reaction conditions employed for the conversion of alkane (paraffin) and alkyne and/or alkadiene to the desired olefins. The paper will provide a basis for identifying the progress made on the topic and possible ways forward.

Dehydrogenation and hydrogenation processes in *trans*-hydrogenation

Ideally dehydrogenation and hydrogenation processes should occur simultaneously during the *trans*-hydrogenation reaction with the aim of obtaining two olefinic molecules. Dehydrogenation proceeds by the removal of hydrogen from the alkane in the feed using an appropriate catalyst to form the olefin and hydrogen. The hydrogenation reaction involves the addition of absorbed hydrogen on the catalyst surface to the alkyne or alkadiene hydrocarbon in the feed and producing the corresponding olefin. A generic simplified mechanism is outlined below





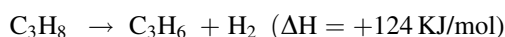
Alkane dehydrogenation is endothermic ($\sim 124 \text{ kJ mol}^{-1}$) and a significant amount of energy is required to break C–H bonds in a molecule. The equilibrium conversion of the process is limited by the reaction temperature and as that increases so does conversion [28]. Hence to accommodate the thermodynamic limitations typical reaction temperatures are $\geq 550 \text{ }^\circ\text{C}$: at these temperatures all C–H bonds in an alkane have equal chance to react [29–32]. However, at such high temperatures secondary reactions such as cracking and carbon deposition are also favoured; therefore, the reaction tends to get less selective as temperature and conversion increase. The equilibrium conversion can also be increased by decreasing the pressure and indeed some on-demand dehydrogenation processes operate at partial pressure less than 1 atm often with the use of a diluent in the alkane feed [33]. Carbon deposition during dehydrogenation is a major process problem and limits the time on-stream for the catalysts. Carbon deposition occurs via a series of progressive dehydrogenation, condensation, polymerisation and cyclisation processes leading eventually to graphitic precursors such as pyrene, perylene and fluoranthene. To cope with such carbon laydown all current processes operate cyclically to regenerate deactivated catalysts and use the heat liberated to offset the reaction endotherm.

Alkyne hydrogenation in contrast is exothermic and produces significant amount heat. Alkynes are thermodynamically less stable than the respective alkene due to the nature of their bonding and strongly adsorb on catalyst surfaces. Therefore, in catalytic hydrogenation there are significant numbers of hydrogenation catalysts effective in promoting the addition of hydrogen; however, few are selective in producing the desired alkene rather than the alkane. Palladium is the metal of choice for selective hydrogenation of alkynes but even using palladium catalysts may be partially deactivated as in Lindlar's catalyst or poisoned as in the addition of carbon monoxide in ethyne hydrogenation, to limit the production of the alkane. Although alkene hydrogenation is inhibited by the presence of alkynes, in the absence of the alkyne research indicates that the alkene will react more rapidly [34]. Research has also shown that in a competitive environment the alkyne can influence the reactivity of other alkynes and alkenes [35, 36]. However, all of these studies have been performed at low temperatures (typically $<100 \text{ }^\circ\text{C}$), whereas in *trans*-hydrogenation the reaction will take place at moderate to high temperatures ($>400 \text{ }^\circ\text{C}$). Although this has little effect on the thermodynamics of hydrogenation, it does have a significant effect on the potential for side reactions due to the high reactivity of alkynes or alkadienes.

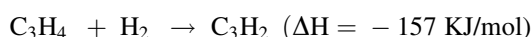
Trans-hydrogenation processes

As outlined above *trans*-hydrogenation involves the dehydrogenation of an alkane to produce an alkene (olefin) and hydrogen and hydrogenation of an alkyne or alkadiene with the hydrogen generated from the dehydrogenation step to produce another alkene (Fig. 2).

By coupling the endothermic dehydrogenation process with the exothermic hydrogenation process it is possible to generate a process where the reaction conditions may be adjusted in order to produce a reaction that is net endothermic, net exothermic, or thermally stable, which can simplify and reduce the cost involved in the process [24]. For example with propane and propyne, the dehydrogenation reaction is significantly endothermic:



However, the hydrogenation reaction is even more significantly exothermic:



Taken together results in an overall exothermic process.



However, in many instances the ration of alkane to alkyne will not be 1:1 but an overall heat balance can be deduced from the enthalpy of reactions and the number of moles of the converted reactant. This can be represented by:

$$\frac{n_{\text{hydrog}} \times \Delta H_{\text{hydrog}}}{n_{\text{dehydrog}} \times \Delta H_{\text{dehydrog}}} \times 100.$$

So for example, if 30 and 15 mol of propane and propyne, respectively are converted in a *trans*-hydrogenation reaction, the hydrogenation reaction step would provide about

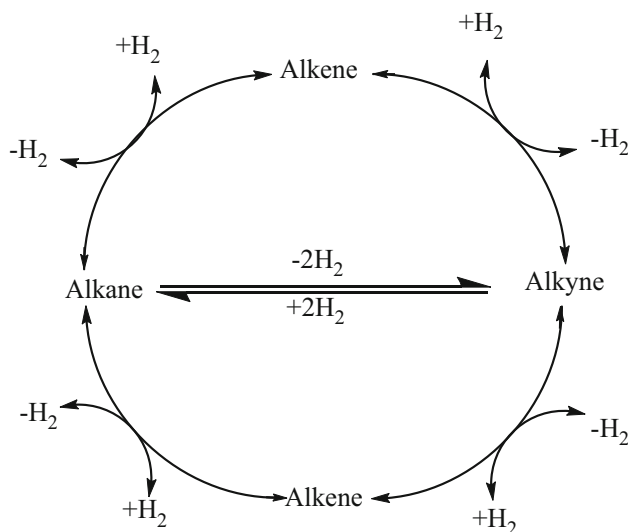


Fig. 2 General concept of a *trans*-hydrogenation process

63% of the heat required for the dehydrogenation reaction step.

Trans-hydrogenation is thermodynamically favoured at most temperatures for the reaction of alkanes with alkynes; however, this is not always the case when alkadienes are the hydrogen acceptors. If we calculate the free energy for the *trans*-hydrogenation of pentane with 1-hexyne, 1,5-hexadiene and 2,4-hexadiene then we find that the ΔG of the process moves from negative to positive (Table 2). Therefore, there can be thermodynamic constraints on the process.

Catalytic processes for *trans*-hydrogenation

Trans-hydrogenation catalysts

Catalysts used in *trans*-hydrogenation reactions are typically based on dehydrogenation catalysts [20]. The logic that underlies this is the evidence that dehydrogenation is the more difficult reaction. Although alkanes can exchange hydrogen at low temperatures on a catalyst surface [30, 31, 37] indicating that breaking the first C–H bond in an alkane is not necessarily difficult, removal of the second hydrogen is rate determining and thermodynamic limits ensure that high temperatures are needed [38, 39]. In contrast the addition of hydrogen to an alkyne or alkadiene is thermodynamically favoured at most temperatures.

Although many metals and oxides are claimed in the patent examples cited above only two catalytically active materials are used with any regularity, these are Pt and chromia. However, it is interesting to note that the catalyst rarely is mentioned in the claims of the patents as usually they are standard commercial catalysts used in dehydrogenation processes. Hence the platinum catalyst is typically modified with tin, while the chromia is modified with potassium. The role of both these modifiers is to reduce carbon deposition and more general by-product formation from the dehydrogenation process. Vanadia has also been used in the academic literature [27].

Chromia catalysts have been subject to extensive characterisation using a variety of techniques such as electron spin resonance (ESR) [40, 41], infrared spectroscopy (IR)

[42, 43], diffuse reflectance spectroscopy (DRS) [44, 45], photon electron spectroscopy (XPS) [46, 47], X-ray diffraction (XRD) [48–50], thermo-gravimetric analysis (TGA) [49, 50] and Raman spectroscopy [51, 52]. Although in the as-prepared catalyst chromia is often in a 6+ oxidation state, the active phase for dehydrogenation and hydrogenation is thought to be Cr^{3+} in the form of a polychromate following reduction either by hydrogen or the reactants.

Catalyst systems based on chromia catalysts

One of the earliest patents relating to transhydrogenation was published in 1985 [23]. In this patent the reaction between ethylene and isobutane was exemplified as a way of increasing isobutene yield at lower temperatures as part of an MTBE process. Typical dehydrogenation catalysts such as chromia/alumina were used. Here the transhydrogenation reaction was used to produce a more valuable olefin at the expense of a cheaper one. Reaction conditions were typically $\sim 500\text{ }^\circ\text{C}$ and atmospheric pressure although temperatures between 400 and 500 $^\circ\text{C}$ and pressures between 1 and 10 bar were claimed. In one example with an inlet ratio of 1:2 ethylene:isobutene at 500 $^\circ\text{C}$ and 1 bar, an outlet of 25% ethane and 21% isobutene was obtained.

In another patent relating to *trans*-hydrogenation, granted in 1994 [53], the reaction of propane 80% v/v and 1,3-butadiene 20% v/v was exemplified to demonstrate the effectiveness of *trans*-hydrogenation for promoting the production of propene. A basic dehydrogenation catalyst $\text{CrO}_x/\text{alumina}$ was used in the process. The reaction conditions were typically 550 $^\circ\text{C}$ temperature, 1 atm pressure and a WHSV of 5.4 h^{-1} . About 15% by volume of propene was produced after $\sim 2\text{ h}$ into the reaction together with other valuable hydrocarbons. The amount of carbon deposit formed during the reaction, which resulted in catalyst deactivation, was also determined. Therefore, catalyst regeneration was performed online using an air stream to remove the deposited carbon. The catalyst was then reduced in flow of hydrogen at same reaction temperature (550 $^\circ\text{C}$) and the reaction repeated again.

Table 2 Free energy for the reaction of pentane with 1-hexyne, 1,5-hexadiene and 2,4-hexadiene

	Free energy (ΔG) of reaction of pentane with hydrogen acceptors at			
	200 $^\circ\text{C}$	300 $^\circ\text{C}$	400 $^\circ\text{C}$	500 $^\circ\text{C}$
1-hexyne	−45.83	−47.10	−48.38	−49.65
1,5-hexadiene	−2.35	−2.80	−3.25	−3.70
2,4-hexadiene	+30.34	+28.87	+27.50	+26.13

There is only a very limited academic literature on *trans*-hydrogenation reactions. However, in a couple of papers Jackson et al. studied the *trans*-hydrogenation of propane and propyne over a chromia/alumina catalyst in a 1:1 ratio to generate propene [25, 26]. The catalyst was activated by reducing in hydrogen before use and the reaction temperature varied between 500 and 600 °C. The reactants were first passed over the catalyst individually to determine their reactivity in the absence of the other reactant. When propyne was passed over the catalyst all the propyne reacted and further reduced the catalyst. There was also a decrease in carbon deposition with increasing reaction temperature. This was a surprising result, which was due to the way that propyne fragmented at high temperature forming a methyl fragment which was hydrogenated to methane faster as the temperature increased leaving less carbon deposit on the catalyst surface [26]. When propane was passed over the catalyst, almost no dehydrogenation took place at the lowest temperature (500 °C) in keeping with the thermodynamic limitations. The dehydrogenation of propane increased with increasing temperature but so did by-product reactions. Isotopic studies revealed that each propane fragmented to produce a species (CH or CH₂) that had an equal chance of hydrogenation to methane. However, in contrast, with propyne the extent of carbon deposition on the catalyst surface increased with increasing temperature [25].

Almost no *trans*-hydrogenation occurred when both the reactants were passed over the catalyst at lowest temperature of 500 °C; however, by 550 °C *trans*-hydrogenation was clearly observed. Using isotopic labels to elucidate the mechanism, the *trans*-hydrogenation reaction was shown to produce propene above the equilibrium value expected from propane dehydrogenation at 550 °C. By 600 °C the conversion of propane was about 80%; however, the yield of propene was low, which was suggested to be due to secondary reaction of the propene forming methane and carbon deposits. These results suggested that at high temperatures a short residence time was required.

Catalyst systems based platinum catalysts

In patent by Gough et al. [21], *trans*-hydrogenation was disclosed for the processing of hydrocarbons from naphtha cracking feedstock over a platinum catalyst. Processed cracked products from the cracking unit were subjected to a *trans*-hydrogenation process using streams of polyunsaturated hydrocarbons as the hydrogen acceptor and that of paraffins as the hydrogen donors. Reaction between a stream containing butadiene and propane was exemplified in the patent. A Pt–Sn/alumina catalyst was used for the process and the reaction conditions were typically in the range 500–600 °C and 1 atm pressure. There was no clear

information to the amount of the reactant fed during the process but a ratio around 10:1 paraffin to polyunsaturated hydrocarbon was emphasised with the paraffin concentration always higher than the concentration of the hydrogen acceptor.

Another patent showing *trans*-hydrogenation was published in 1995 [19]. A non-acidic intermediate pore size zeolite (ZSM-5) with a Pt active phase and a Sn modifier was used. In one example from the patent, a Sn free Pt-high silica ZSM-5 catalyst was used to dehydrogenate isobutane at 550 °C. The reaction was initially conducted with equimolar helium as a make-up gas, which was subsequently replaced with ethene. When the ethene was added, the isobutene yield fell as the ethene inhibited the alkane adsorption. To mitigate against this inhibition tin was added to the catalyst and a subsequent example reports *trans*-hydrogenation of propene with isobutane. The patent also reports a split bed system where the top bed has a single feed of alkane and is used for dehydrogenation, while just above the bottom bed the alkene is introduced so that the bottom bed has a feed of alkenes and hydrogen.

In another patent by Turner [24], *trans*-hydrogenation was disclosed for the production of isobutene to be subsequently used in the production of methyl tertiary butyl ether (MTBE). The catalyst employed was 1% Pt–Sn/alumina with a weight ratio of 1:1 Pt:Sn. The *trans*-hydrogenation conditions employed were typically 500 °C, 1 atm pressure and a WHSV of 5.5 h⁻¹. The catalyst was first pre-treated in a flow of hydrogen to be fully reduced before commencement of the reaction. An increase yield in the olefinic C4 stream was achieved with about 2.7 and 98.8% conversion of propane and butadiene, respectively.

In *trans*-hydrogenation, because hydrogen is not co-fed in the process, there is a high tendency for the formation of bulk coke deposit. This happens especially with amorphous catalyst supports such as alumina, which have acid sites that promote cracking and alkylation. The use of metal doping and non-acidic catalyst supports are reportedly used to suppressed the effects. A diluent such as steam may also be added, which leads to coke suppression and can serve to activate the catalyst. Methane can also be used as a diluent [25]. Coke deposition is detrimental to the catalyst and leads to catalyst deactivation; however, regeneration processes are often used to remove the deposit and regenerate the catalyst. In patent no WO 1994010264 [21] the regeneration of a Pt/Sn-ZSM-5 catalyst used for *trans*-hydrogenation was performed in a flow of hydrogen at 60 psi pressure and 550 °C temperature for 4–24 h. In another patent [24] regeneration of the catalyst was reported to have been conducted in a stream of pre-heated oxygen-containing gas like air. Regeneration of the catalyst burned off the deposited carbon on the catalyst surface reactivating the catalysts and generating heat.

The reaction stream may comprise of a mixture of reactants instead of same carbon number reactant. For instance, the hydrogen acceptor could be admixture of alkadienes and alkynes of different carbon number, equally the hydrogen donor stream could also be admixture of different carbon number atom alkanes.

Catalyst systems based vanadia catalyst

In a recent study by Wigzell et al. [27] a *trans*-hydrogenation reaction was performed between propyne and butane over a 1% vanadia/ θ -alumina catalyst at 600 °C. Propyne and butane were co-fed, which resulted in an increase conversion of propyne to propene compared to when it was fed singly over the catalyst. The *trans*-hydrogenation reaction was observed to deliver a 72% increase in propene yield, while all the butane reacted was converted to butene isomers. This is the sole example of a vanadia system being used for *trans*-hydrogenation.

Role of dopants

Trans-hydrogenation reactions over potassium doped chromia catalyst [26] have been reported. However, the dopant has little direct effect on the *trans*-hydrogenation process rather it is used to remove and/or neutralize acid sites on a support such as alumina reducing catalyst deactivation [54]. It does not generally change the reaction mechanism [54, 55]. Use of dopants to enhance *trans*-hydrogenation reactions has also been disclosed in patents. Gough et al. [53] reported that a chromia admixture with a platinum group metal and doped with alkali on alumina effected good *trans*-hydrogenation activity. The doped alkali metal was either potassium or caesium (Cr/Pt–K–Al₂O₃ or Cr/Pt–Cs–Al₂O₃). Catalyst modification using

dopants has also been disclosed in other patents [19, 24, 55].

The effect of tin on a platinum dehydrogenation catalyst is much more significant as it forms an alloy changing the electronic properties of the platinum in such a way as to enhance dehydrogenation activity [56]. The Sn not only modifies the electronic properties of Pt but also reduces the carbon deposition on the platinum. However, the alloy is not stable during regeneration with the Sn segregating from the Pt/Sn alloy during coke burning. The alloy reforms during hydrogen reduction but with multiple reaction/regeneration/reduction cycles there is a slow Sn enrichment of the alloy, resulting in a permanent decrease in the activity.

Table 3 brings together all the studies and relates activity to catalyst formulation and reaction conditions.

Conclusion

Trans-hydrogenation is potentially a feasible system by which the value of cracker streams could be enhanced. The patent literature shows convincing examples where the yield of alkenes has been increased in conjunction with a thermal balance with respect to the endothermic/exothermic nature of the reactions. Indeed taking the patent literature on its own it is difficult to see why *trans*-hydrogenation has not been more widely implemented. In contrast a limited academic literature has shown possibly why such systems are not in widespread use. Although not generally reported in the patents, it is clear that the current catalytic systems would need regular regeneration to sustain activity. If the system needs to be regenerated on a regular basis, then the gains made by *trans*-hydrogenation are limited to the yields of the alkenes over and above the loss of alkene to carbon deposition and the extra capital

Table 3 The activities of some catalyst during *trans*-hydrogenation process

Catalyst system	Reaction conditions	Feeds	Olefin yield	Conversion	Reference
CrO _x /Al ₂ O ₃	500 °C; 1 bar	1:2 ethylene:isobutane	21%	NA	[23]
CrO _x /Al ₂ O ₃	550 °C; 1 atm; 5.4 h ⁻¹ WHSV	80:20 Propane:1,3-butadiene	15%	NA	[53]
CrO _x -K/Al ₂ O ₃	500–600 °C; 1 atm	1:1 propane:propyne	50%	80% based on propane	[24]
Pt–Sn/Al ₂ O ₃	500–600 °C; 1 atm	10:1 paraffin: polyunsaturated hydrocarbons	*	NA	[53]
Pt–Sn/ZSM-5	500 °C	Isobutane, ethene and He	*	NA	[19]
1% Pt–Sn/Al ₂ O ₃ (1:1 Pt:Sn)	500 °C; 1 atm; 5.5 h ⁻¹ WHSV	Propane and butadiene	2.7% increasing	98.8% on propane	[24]
1% VO _x /Al ₂ O ₃	600 °C, 1 atm;	Butane and propyne	72% increase in yield	81% on propyne	[27]

NA not available

cost required for continuous processing with catalysts needing regular regeneration. This means that the catalysts have to be much more efficient and selective for *trans*-hydrogenation than the current systems before they make a compelling case to be included in a refinery processing train.

The limited amount of academic research is a further limitation. Our understanding of the processes suggests that *trans*-hydrogenation systems do not behave as simply two reactions occurring on the same catalyst but only in contact indirectly via Le Chatelier. However, neither do they fully couple as a fully integrated reaction. Selectivity is a major issue as the catalysts can, and do, catalyse a range of reactions. There has been much work on the dehydrogenation side of the reaction but no work has been done on the hydrogenation side. Hence our understanding of this complex process is woefully incomplete. Further research is required to build up our knowledge base and to determine whether it is a realistic expectation to achieve control over selectivity and yield in *trans*-hydrogenation.

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