Direct conversion of carboxylic acids (C_n) to alkenes ($C2_{n-1}$) over titanium oxide in absence of noble metals

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Abstract

Carbon-carbon bond formations and deoxygenation reactions are important for biomass up-grading. The classical ketonic decarboxylation of carboxylic acids provides symmetrical ketones with 2n+1 carbon atoms and eliminates three oxygen atoms. Herein, this reaction is carried out with titanium oxide at 400 ºC, and an olefin with 2n+1 carbon atoms is obtained instead of the ketone. For olefin formation hydrogen transfer reactions are required from suitable precursors to form aromatics and coke.

Additional aldol condensation reactions increase further molecular weight in the product mixture. Hence, a combination of titanium oxide with a hydrodeoxygenation bed provides double amount of diesel fuel as the combination with zirconium oxide when reacting hexose-derived pentanoic acid.

Keywords

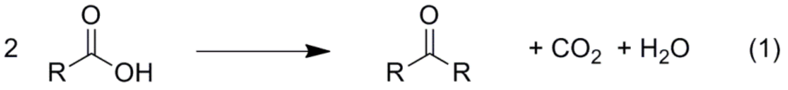
Aldol condensation, Carbon-carbon bond formation, Ketonic decarboxylation, Hydride transfer, Second generation diesel fuel

Introduction

The connection of two carboxylic acids to a ketone, i.e. the ketonic decarboxylation or ketonization of carboxylic acids, has experienced a revival during the last decade.[1, 2] Before World War I this reaction was applied industrially for the synthesis of small ketones, especially acetone. The change to a petroleum based economy has generated competitive routes and for instance acetone is produced from cumene as by-product of the Hock process. For this reason most industrial processes based on the ketonic decarboxylation have been discontinued.

At the beginning of our century sustainability became an important issue in chemistry.[3] New biorefinery concepts were designed based on renewable materials such as lignocellulose since the latter does not compete with food production.[4] However, the composition of these bio-based materials is diametrically opposed to the composition of petroleum-based materials: the former are extremely oxygen-rich whereas the latter are nearly oxygen free. This means that the bio-based raw materials have to be deoxygenated to convert them into classical commercial products derived from petroleum. As a second characteristic difference, lignocellulose is built-up from small molecules from five to nine carbon atoms. When lignocellulose is degraded without cleaving carbon-carbon bonds, mainly sugar molecules of five and six carbon atoms are obtained. As a consequence, two or more of these five to six carbon-atom molecules have to be connected together if molecules with a larger number of carbon atoms are desired for their use as chemicals or fuels.[5-7]

The carbon-carbon bond formation in biomass derived products can be carried out after complete hydrodeoxygenation of the feed or starting with oxygen-containing platform molecules. Both strategies have been employed in proposals for the production of fuels from biomass. Hence, hexose is completely deoxygenated to butene which is then oligomerized.[8-11] Aldol condensation reactions[12, 13] and hydroalkylations/alkylations[14-19] have also been employed to build up fuel precursors from small molecules. Thereby, it can be seen that the latter transformations can proceed with a high degree of selectivity (with respect to the carbon atom number), and it has been proposed to carry out the carbon-carbon bond formations with moderately oxygenated molecules.[20] The ketonic decarboxylation fits very well this requirement since two carboxylic acid molecules with n carbon atoms are converted into one molecule of ketone with 2n–1 carbon atoms, carbon dioxide and water (Eq. 1).[1, 2] By-products are innocuous and solvent is not required. Hence, the reaction also meets the demands of Green Chemistry.[3] The reaction is carried out in the gas phase over a metal oxide catalyst. Different sites intervene in the reaction mechanism: Lewis-acid metal centers and basic surface oxygen atoms. It has been proposed that the carboxylic acid form a beta-keto acid which is then decarboxylated.[21] Interestingly, many different oxides have been reported as suitable materials for this transformation: CeO_2,[21-24] ZrO_2,[21, 25, 26] MgO,[27, 28] MnO_2,[26, 29] Mn_3O_4,[26] Fe_2O_3,[30, 31] Fe_3O_4,[32] Cr_2O_3,[33, 34] Al_2O_3,[21, 26] ThO_2,[35, 36] Bi_2O_3,[26] TiO_2.[37, 38]. In many cases the desired ketone product has been obtained almost quantitatively.



Herein we report on the use of titanium dioxide as catalyst for the ketonic decarboxylation. Although this material has been employed before as catalyst and support for this reaction,[37-41] it will be described here that the reaction outcome at selected reaction conditions, is very different from the performance of other materials such as ZrO_2. In fact, on TiO_2 an olefin was observed as main product instead of the typical ketone obtained when working at 400 ºC. The mechanism of the olefin formation has been studied here and it will be presented that a hydride shift is involved in absence of any noble metal. Furthermore, changes in the hydrogenated product mixture induced by aldol condensations, which occur under the ketonic decarboxylation conditions, will be discussed in comparison with ZrO_2.

Experimental Part

General

Decanoic acid, pentanoic acid, 2-undecanone, 2-pentanone, cyclopentanone, 4-methyl-1-cyclohexene, α-terpinene, limonene and nitrobenzene were supplied from Acros, Aldrich and Takasago, and used as received. Titanium oxide (surface area 151 m^2/g) and *monoclinic* zirconium oxide were received from ChemPur (Germany) as pellets and a titanium oxide sample from Evonik (P25; surface area 55 m^2/g) in powder form. They were pelletized (if necessary), crushed and sieved, and the 0.4 – 0.8 mm fraction employed as catalysts. All reactions were carried out in a tubular fixed-bed continuous flow reactor. The set-up has been described in a previous work.[21] Briefly, the reagents were placed in a syringe at room temperature except for decanoic acid for which the syringe was heated to 45 ºC. The reactor was loaded with 2.50 g of catalyst diluted with silicon carbide. Typically, a feed rate of 0.15 mL min^{-1} was employed and nitrogen or hydrogen gas was used as carrier gas (50 or 100 mL min^{-1}). The reactions were carried out at atmospheric pressure and at temperatures between 300 and 450 ºC. An ice bath or acetone plus dry ice bath were used to condense the products.

Different gas chromatographs were employed for analyzing the products off line. The liquid products were analyzed with an Agilent 7890A with split injection equipped with a HP-5 column (30 m x 0.320 mm x 0.25 µm) and for simulated distillation a Bruker 450-GC gas chromatograph equipped with an Agilent J&W GC Column CP-SimDist (10 m x 0.53 mm x 2.65 µm), both of them with a FI detector. Permanent gases were analyzed off-line on a GC apparatus RGA analyzer equipped with three channels. Hydrogen was analyzed on a 2 m molecular sieve 5 Å column and TCD detector. Permanent gases such as CO and CO_2 were separated on a 2.5 m molecular sieve 13X column and quantified by a TCD detector. Low molecular weight hydrocarbons were analyzed on a 50 m Plot/Al_2O_3 column with a FI detector. The reaction products were identified by GC-MS with an Agilent Technologies 6890N gas chromatograph using a HP-5 column (30 m x 0.320 mm x 0.25 µm) coupled with a mass selective detector Agilent 5973N.

Catalyst characterization

The X-ray diffraction measurements to analyze the phase of TiO_2 were performed on a PANalytical CUBIX-PRO diffractometer equipped with a PW3050 goniometer (Cu Kα radiation) provided with a variable divergence slit. Nitrogen physisorption isotherms were obtained using a Micromeritics ASAP 2420 analyzer. The metal oxide was out-gassed in vacuum at 400 ºC for 12 h prior to the analysis. The Brunauer–Emmett–Teller (BET) method was used to calculate the surface area in the range of relative pressures between 0.01 and 0.20 Pa and the Barrett-Joyner-Halenda model for the determination of the pore volumes. Infrared (IR) measurements were performed with a Nicolet 710 FTIR spectrometer using vacuum cells. For the measurement, the metal oxide was pressed into a self-supporting wafer and was activated overnight at 400 ºC and in vacuum of 10^{-4} to 10^{-5} Torr in the IR chamber. Pyridine was allowed to enter the chamber and excess pyridine was desorbed at room temperature applying vaccum. Then pyridine was desorbed at increasing temperature at 150, 250 and 350 ºC for 60 min at each temperature. After each desorption step the sample was cooled down and an IR spectrum recorded. The thermogravimetric (TG) analysis was obtained on a Mettler Toledo TGA/SDTA 851 instrument. The sample (approximately 5–10 mg) was placed in an alumina crucible on a precision balance with a S type thermocouple. The sample was heated at a rate of 10 K per minute from 30 ºC to the final temperature in a controlled atmosphere.

Synthesis and catalytic reaction of the aldol condensation product of cyclopentanone (2-cyclopentylidenecyclopentanone)

Into a 100 mL round bottom flask equipped with reflux condenser and magnetic stirring bar cyclopentanone (50 mL) was introduced and an aqueous NaOH solution (10 wt.%, 5 mL). The reaction mixture was stirred and heated to reflux temperature. After 20 h the mixture was cooled down to room temperature and the organic phase was separated from aqueous phase by decanting. The crude product was distilled under reduced pressure and 2-cyclopentylidenecyclopentanone was isolated (97% purity, 43% yield).

The condensation product (97%) was passed through the fixed-bed continuous-flow reactor (described above) filled with 2.50 g of TiO_2 at 425 ºC, together with nitrogen as carrier gas (100 mL min^{-1}; F = 9.09 g h^{-1}; WHSV = 3.64 h^{-1}).

Isolation of the olefin product and catalytic transformation of the latter

The product fractions obtained when passing 2-undecanone over TiO_2 were jointed and the mixture (38 g) was distilled at reduced pressure (5 mbar). The distillate was collected in different fractions obtaining a 17% yield for the C_{11} olefinic fraction.

This product fraction was used as feed and passed through the fixed-bed reactor filled with 2.50 g of TiO_2, together with nitrogen as carrier gas (100 mL min^{-1}). The flow rate of the organic liquid was 6.66 g h^{-1} and the reaction temperature 425 ºC (WHSV = 2.66 h^{-1}).

Results and Discussion

Catalyst characterization

The crystalline phase and textural properties of the TiO_2 catalyst (ChemPur) were evaluated by X-ray diffraction and nitrogen adsorption. The X-ray diffraction pattern shows that the titanium oxide was crystallized as anatase phase (Figure 1). Broad signals indicate that the particles are very small. This was confirmed by measuring the surface area by nitrogen adsorption. A surface area of 151 m^2/g was determined which is quite high for a metal oxide. Pore diameters of 79 Å (BJH) measured are typical for the interparticle void between the oxide particles.

The material possessed considerable Lewis acidity. This was evidenced by *in-situ* IR spectroscopy with pyridine as a probe molecule (Figure 2). The typical band at 1450 cm^{-1} indicates strong Lewis acidity since it is still detected even after pyridine desorption at 350 ºC in vacuum. The sample did not show any Brönsted acidity (cf. Figure 2, band lacking at 1550 cm^{-1}).

From these analyses it can be concluded that the titanium oxide consisted of small nanoparticles with a high surface area and strong Lewis acid sites.

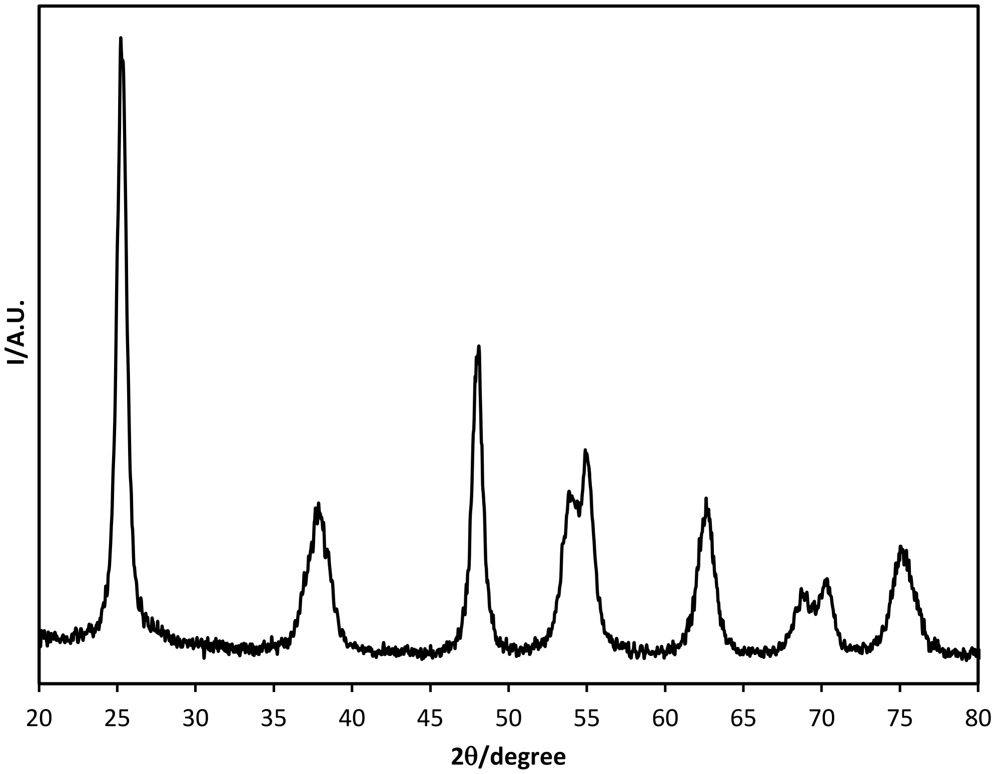


Figure 1. X-ray diffraction pattern of TiO_2.

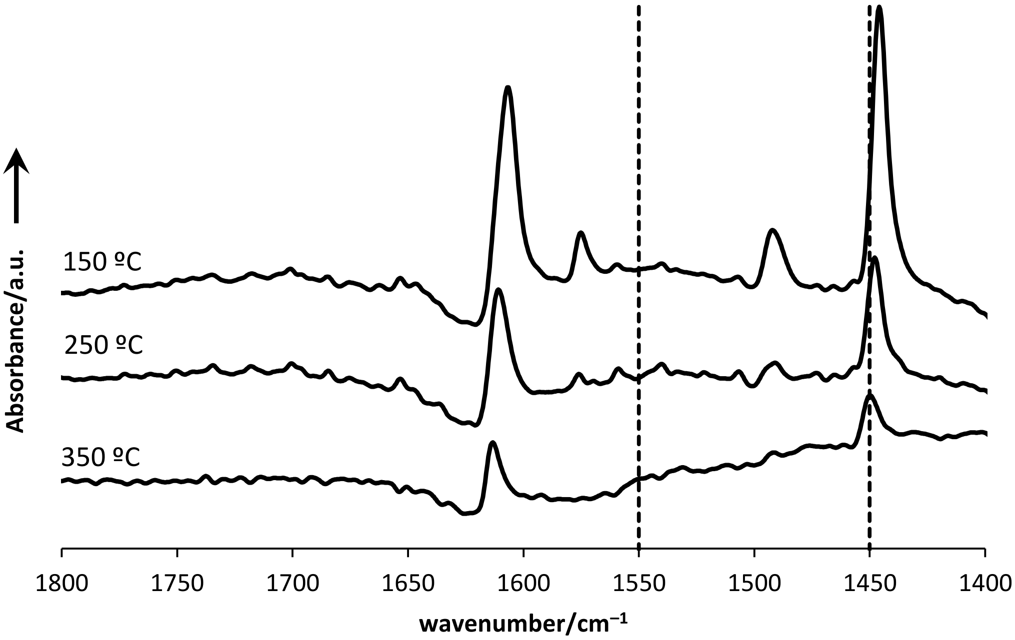
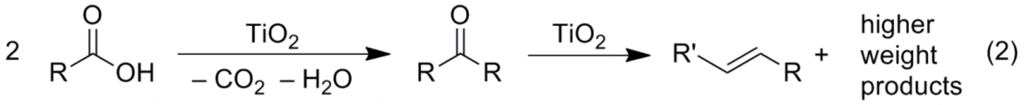


Figure 2. IR spectra of the pyridine adsorption onto TiO_2. Experimental conditions: Pyridine was adsorbed at room temperature and desorbed at increasing temperatures (150, 250 and 350 ºC) for 60 min at each temperature.

Catalytic performance of TiO_2

Titanium oxide was placed in a fixed bed continuous flow reactor to assess its catalytic activity for the ketonic decarboxylation. Hence, decanoic acid was selected as substrate and passed through the catalytic bed in the temperature range of 300 to 450 ºC (Figure 3). It can be seen that the catalytic performance differs significantly from the zirconium oxide. Considerable catalytic activity was already observed at 300 ºC with the TiO_2 catalyst. At 325 ºC conversion was already higher than 50%. At both temperatures the ketone was the only product observed on TiO_2. At a temperature of 350 ºC and higher, the conversion was complete but a second product was obtained: a mixture of nonadecene isomers, i.e. molecules with the same number of carbon atoms but with a double bond instead of the carbonyl functional group. In a working hypothesis it was proposed that the olefin was produced from the ketone by reduction to the corresponding alcohol and subsequent dehydration (Eq. 2). The formation of the olefin increased with temperature from 325 to 400 ºC. At 400 ºC a maximum yield of approximately 35% was observed (Figure 3). At higher temperature the yield decreased slightly. The maximum yield for the ketone was observed at 350 ºC with approximately 70%. At higher temperature the yield decreased and at 400 ºC almost no ketone was observed anymore (Figure 3). Furthermore, it was observed that one condition for this outstanding reactivity of the titanium oxide was the high surface area. When a sample (P25) with a surface area of 55 m^2/g instead of 151 m^2/g was employed, the selectivity towards the ketone below 400 ºC was 90% and the olefin yield reached only 25% at 425 ºC (See Supplementary Information, Figure S1).



When ZrO_2 was employed as catalyst, at the same temperature, i.e. 400 ºC, the maximum yield of ketone (approx. 95%) was observed. At higher temperatures the selectivity decreased slightly and below 400 ºC the conversion was clearly lower with ZrO_2 than with TiO_2. However, with ZrO_2, in contrast to the transformation catalyzed by TiO_2, the C_{19}-olefin was not observed in significant amounts. The formation of the olefin with TiO_2 as catalyst was unexpected since this product has not been reported before in the literature on a metal oxide, as far as we know. Highly selective transformation to the ketone[42, 43] or water and tar producing reactions have been described at above 350 ºC.[39] In any case, the different reaction outcome was interesting and its origin should be elucidated.

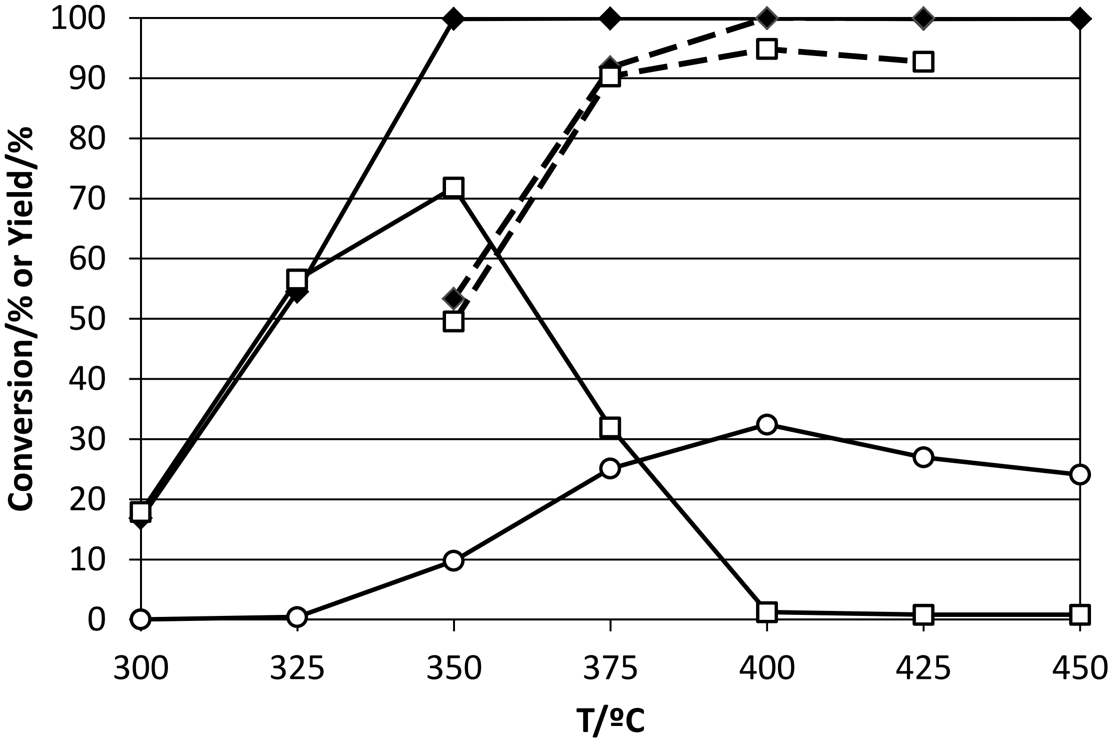


Figure 3. Transformation of decanoic acid over TiO_2 (continuous line) and ZrO_2 (dashed line) in the temperature range from 300 to 450 ºC. ◆ conversion, □ 10-nonadecanone yield, O nonadecene yield (only TiO_2). Reaction conditions: 2.50 g of metal oxide, WHSV = 3.17 h^{-1}, F = 7.92 g h^{-1}, 50 mL min^{-1} of N_2.

When the yield of the two products was depicted versus conversion (Figure S3), it can be concluded from the shape of the graph that the ketone is a primary unstable product and the olefin a secondary product. This result supports the proposed formation of the olefin from the ketone as depicted in Eq 2. For further evidence, a ketone, namely 2-undecanone, was submitted to the reaction conditions. Also in this case the olefin was observed for a time on stream of 2.8 h (Figure 4). During this time the yield was quite constant at approx. 25%. However, conversion of the ketone decreased slightly from full conversion to approximately 90%. When the olefin produced from 2-undecanone, was purified by distillation (90% purity) and submitted to the reaction conditions, almost no change was observed (conversion < 2%). This means that the olefin is relatively stable under reaction conditions and does not undergo neither hydrogenation nor oligomerization reactions. Interestingly, the yield of the olefin from the ketone was not influenced by the carrier gas: an identical yield was observed with either nitrogen or hydrogen as carrier gas (Figure 4). The rest of the products were lower molecular weight olefins (C6 to C10; < 10% yield; for more detail see Figure S4) and higher molecular weight products (40 to 50%).

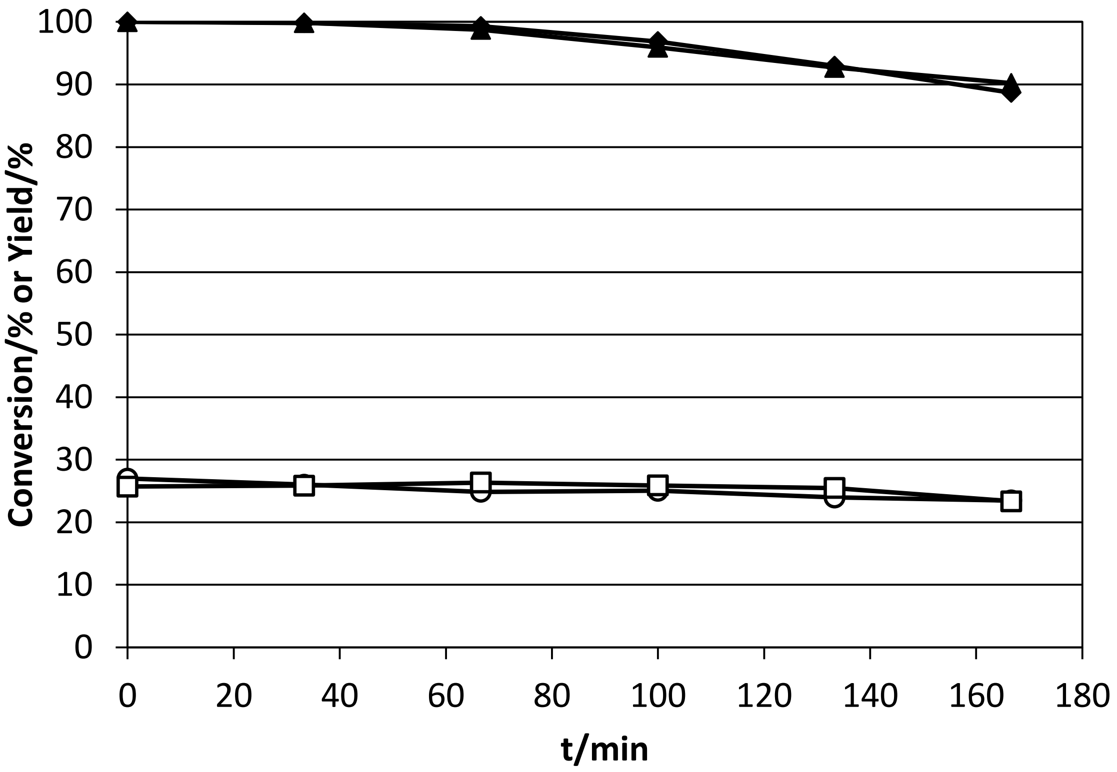


Figure 4. Transformation of 2-undecanone under ketonization conditions in the presence of TiO_2. Reaction conditions: 2.50 g of TiO_2, F = 7.47 g h^{-1}, WHSV = 2.99 h^{-1}, 425 ºC, carrier gas N_2 or H_2 50 mL min^{-1}. ◆ conversion (N_2), ▲ conversion (H_2), □ undecene yield (N_2), O undecene yield (H_2).

In summary, experimental results confirm titanium oxide as a ketonic decarboxylation catalyst. However, under certain reaction conditions (higher reaction temperature) the ketone is transformed into an olefin. This reaction can be depicted as a cascade reaction, i.e. as reduction of the ketone to the corresponding alcohol and subsequent dehydration (Eq. 2). However, for such a process, a reductant or a hydrogen source is missing. This issue will be further studied in the next section.

Hydrogen transfer reactions with titanium oxide

With the aim to reveal the nature of the reductant, the evolution of the reaction was followed for a longer time on stream. Hence, in Figure 5 it can be seen that the formation of the olefin is quite constant for 340 min involving a small decrease. On the other hand, the supposed intermediary ketone is observed in increasing amounts (faster than the olefin disappears) and after 230 min the yield is very similar to the olefin. After 340 min, the catalyst was treated with air at 450 ºC but the tendencies in the product composition continued for both products and a recovery of the initial catalytic activity for the olefin formation was not observed, when the catalyst was used again.

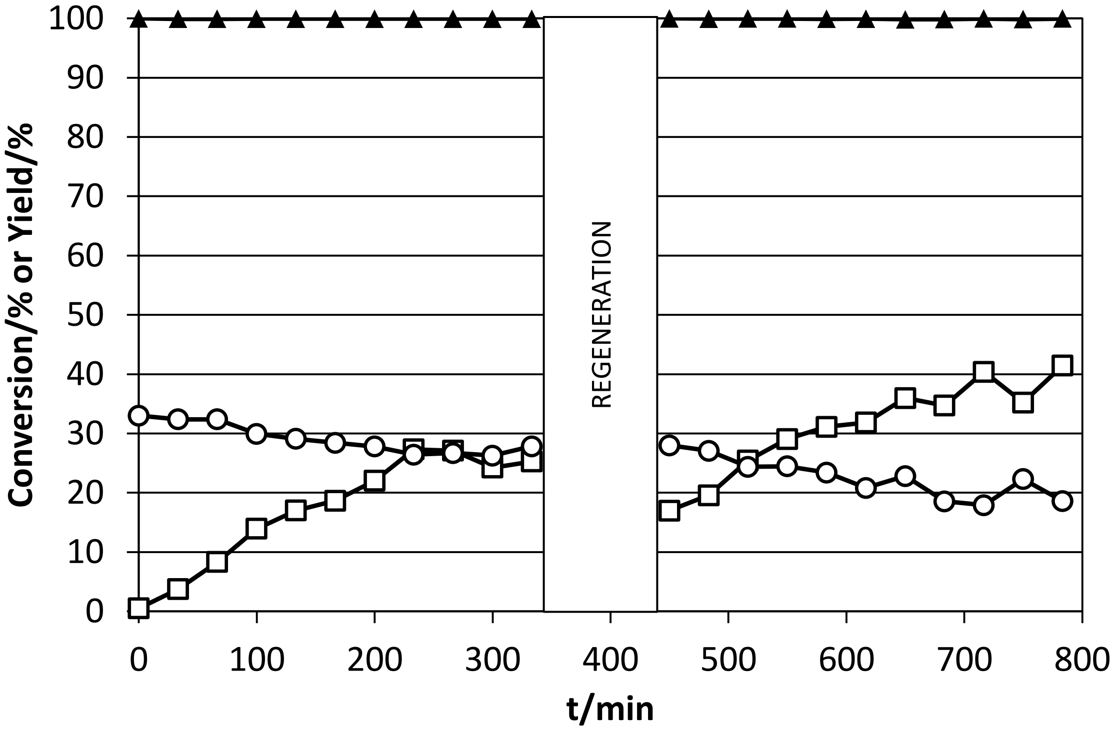


Figure 5. Transformation of decanoic acid over TiO_2 with time on stream at 400 °C. Reaction conditions: 2.50 g of TiO_2, F = 7.92 g h^{-1}, WHSV = 3.17 h^{-1}, N_2 50 mL min^{-1}. After 340 min, the catalyst was re-activated by *in-situ* calcination (air 50 mL min^{-1}, 450 °C, 2 h) and the reaction continued. ▲ conversion, O nonadecene yield, □ 10-nonadecanone yield.

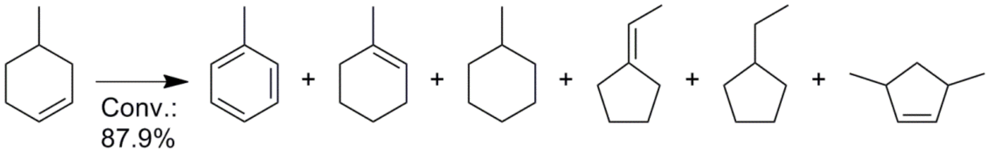
In the long term experiment more than 35 g of carboxylic acid was processed per g of catalyst and 2 equivalents (in mol) of olefin were obtained per mol of TiO_2. This indicated that a surface modification of the catalyst or changes in the catalyst bulk composition were not the origin for ketone reduction. After the reaction, the amount of coke was measured by TG to be 7.6 wt% of the catalyst. It cannot be excluded that there was some contribution of the coke to the reduction of the intermediate ketone but, again, the amount of coke is too low to count for the ketone reduced to provide the olefin. Therefore, it was concluded that a hydrogen source has to be formed as a side product. As a starting hypothesis it was speculated that hydrogen transfer reactions occur and that cyclohexane rings, saturated or partly unsaturated, act as hydrogen source. In order to check this hypothesis, first dehydrogenations were studied under reaction conditions. Hence, potential hydrogen-donor model compounds such as methyl-cyclohexene, α-terpinene and limonene were selected. In literature, it has been shown recently that the latter can be dehydrogenated with TiO_2 to the corresponding product, i.e. *para*-cymene, which was observed in 90% yield.[44] However, it has been further reported that the catalytic activity depended not only on the chemical composition of the catalyst, but also on the properties and the amount of the catalytic sites. Therefore, the activity of the TiO_2 used in the present study had to be confirmed for this dehydrogenation reaction. Indeed, under the present reaction conditions, the conversion of limonene and α-terpinene was complete and *para*-cymene was obtained in 65 and 68% yield, respectively (Table 1, entries 1 and 2). Furthermore, dehydrogenation was slightly higher since approximately 5% of side products were probably formed from *para*-cymene by Lewis-acid catalyst isomerization reactions.

Table 1. Dehydrogenations of limonene and α-terpinene in the presence of titanium oxide at 425 ºC. Reaction conditions: 2.50 g of titanium oxide, F = 7.6 g h^{-1}, WHSV = 3.04 h^{-1}, N_2 100 mL min^{-1}.

		product yield		
		para-cymene	para-cymene isomers[a]	other[b]
Entry	Substrate	[%]	[%]	[%]
1	limonene	65	3	24
2	α-terpinene	68	6	19

[a] Isomers of *para*-cymene such as for instance tetramethylbenzene, ethyldimethylbenzene, etc. [b] Amount missing to 100 caused by losses due to the small scale operation.

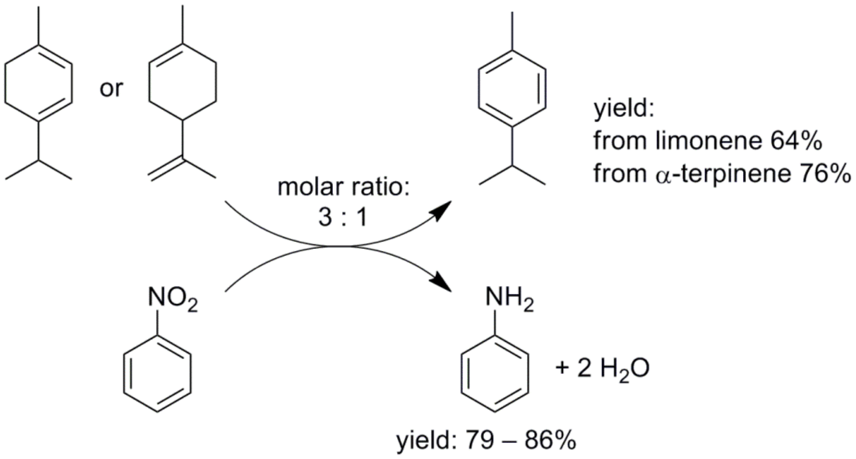
If the substrate is less prone to aromatization, for instance in the case of cyclohexene derivatives with only one double bond, isomerization of the carbon skeleton competes even more efficiently. Hence, with 4-methyl-1-cyclohexene (**1**) the corresponding dehydrogenation product, i.e. toluene (**2**), was observed with a yield of 15% (Eq. 3). With the same skeleton, double bond isomerization (compound **3**) and hydrogenation (compound **4**) was observed. Other products involved carbon skeleton isomerization, for instance compounds **5**, **6** and **7**.



(3)

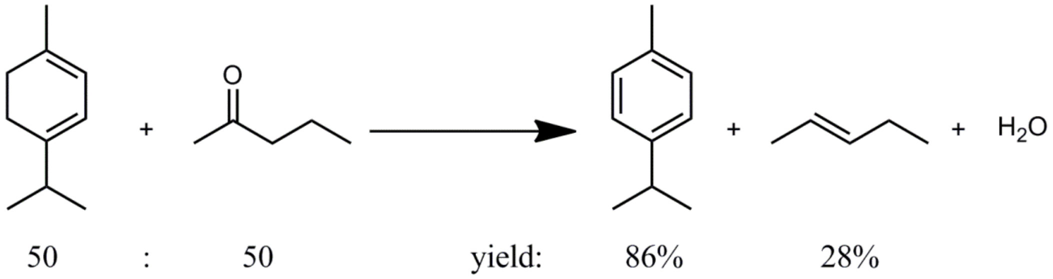
	1		2	3	4	5	6	7	Other
		Yield/%:	15.4	20.2	12.1	2.3	2.6	9.7	25.6

Although the yield of the dehydrogenation product was low in the case of cyclohexene **1**, all three test reactions demonstrate unambiguously that dehydrogenation reactions are possible under the employed reaction conditions, even in absence of metal catalysts based on precious metals, Cu or Ni. As next step the hydrogen transfer should be confirmed. As the reduction product of the ketone, i.e. the corresponding alcohol, was supposed to be unstable under reaction conditions and dehydrated to the olefin, a different substrate was selected, namely nitrobenzene. The latter can be hydrogenated easily with formation of two molecules of water. Hence, mixtures of limonene with nitrobenzene and α-terpinene with nitrobenzene in a 3 to 1 molar ratio were contacted with titanium oxide at 425 ºC. The dehydrogenation of the monoterpene worked as before and *para*-cymene was obtained in a yield of 64 to 76% (Scheme 1). However, additionally the hydrogen evolved from the molecule was utilized to reduce nitrobenzene to aniline. This means that the hydrogen transfer reaction worked well and hydrogen loss, if any, was minimal.



Scheme 1. Hydrogen transfer from limonene or α-terpinene to nitrobenzene catalyzed by TiO_2 at 425 ºC. Reaction conditions: 2.50 g of TiO_2, F = 8.19 g h^{-1}, WHSV = 3.28 h^{-1}, N_2 100 mL min^{-1}.

Once having demonstrated that hydrogen transfer reactions are possible with titanium oxide at elevated temperatures, it should be shown that these reactions include the reduction of a ketone to the corresponding alcohol. Hence, 2-pentanone as model compound of a ketone and in a second experiment pentanoic acid were contacted to titanium oxide in presence of alpha-terpinene. From equations 4 and 5 it can be seen that the yield of *para*-cymene increased significantly from 68% (Table 1, entry 2) when the monoterpene is reacted alone, to over 80%. On the other hand, the corresponding olefin was observed in 28 and 37%, respectively. In the case of the olefin, the improvement for the yield was not as clear as it was for the aromatization. However, the beneficial effect might be masked here by the low selectivity and the formation of side products from the alcohol.



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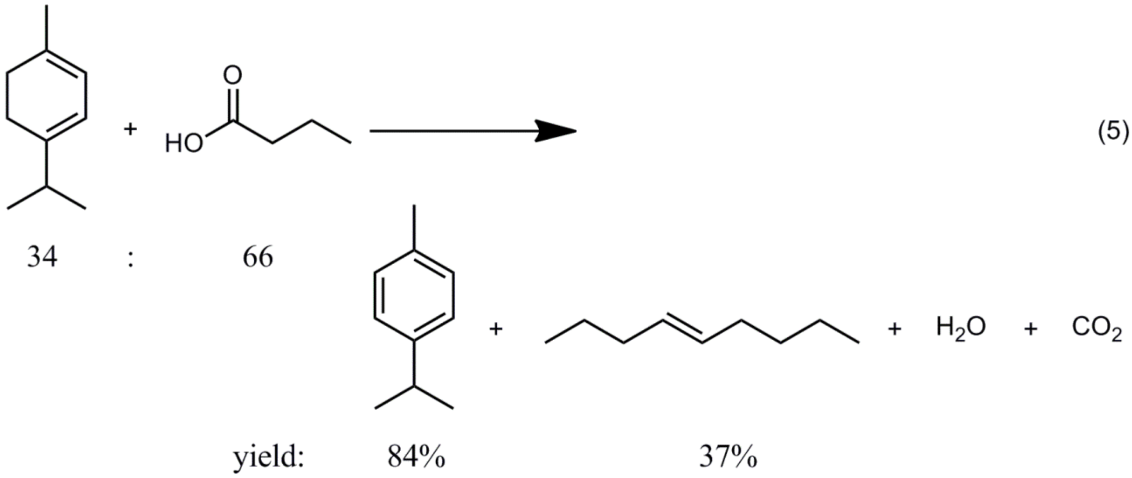
Reaction conditions: 2.50 g of TiO_2, F = 7.35 g h^{-1}, WHSV = 2.94 h^{-1}, 425 ºC, 100 mL min^{-1} of N_2.



(5)

Reaction condtions: 2.50 g of TiO_2, F = 8.06 g h^{-1}, WHSV = 3.22 h^{-1}, 425 ºC, 100 mL min^{-1} of N_2.

In summary, the experimental results demonstrated that hydrogen transfer reactions can occur under reaction conditions and that it is very likely that the ketone is hydrogenated to the alcohol which is then dehydrated to the olefin. The missing piece in the puzzle, however, is still the hydrogen donor molecule. This issue should be strongly related to the observation that significant amounts of higher molecular weight molecules (cf. Figure S4), i.e. molecules with higher molecular weight than the primary ketone product, are formed during the reaction. It is supposed that both issues are related to aldol condensation products of the ketonic decarboxylation product, i.e. the ketone.

The impact of aldol condensation reactions

Titanium oxide is known to catalyze aldol condensations, for instance of acetaldehyde or acetone, at 250 ºC and below.[45-47] As a consequence, it has to be assumed that the primary reaction product of the ketonic decarboxylation, i.e. the ketone which is prone to aldol condensation, can further react under our reaction conditions. Hence, aldol condensations and several other side-reactions (carbon skeleton isomerizations as for instance observed in the transformation of 4-methyl-1-cyclohexene, **1**, reported before) generate a complex product mixture at higher reaction temperature (> 400 ºC). With the aim to identify different reaction pathways, a ketone with lower molecular weight, i.e. 2-pentanone, was selected and submitted to reaction conditions at different W/F contact times. With this substrate it was possible to identify and characterize products built from two or three substrate molecules (Figure 6).

At lower conversion (approx. 30%), the aldol condensation product (unsaturated C_{10}-ketone; Scheme 2) was obtained with higher selectivity and yield (almost 10% yield). At higher conversion the yield decreased to below 3% indicating that this ketone was a primary, unstable product. Therefore, the unsaturated C_{10}-ketone can undergo a second aldol condensation with subsequent cyclization and dehydration to yield a $C_{15}H_{24}$ aromatic isomer, and can also be hydrogenated to the saturated C_{10}-ketone. This again supports clearly that hydrogen transfer reactions occur under the reaction conditions, being in this case the double bond of an α,β-unsaturated ketone the hydrogen receptor. Additionally, the hydrogenated condensation product might loose two or three carbon atoms by the McLafferty rearrangement and give C_7- and C_8-ketones. Furthermore, as observed for the original ketonic decarboxylation reaction, all saturated ketones were converted partly into the corresponding olefins.

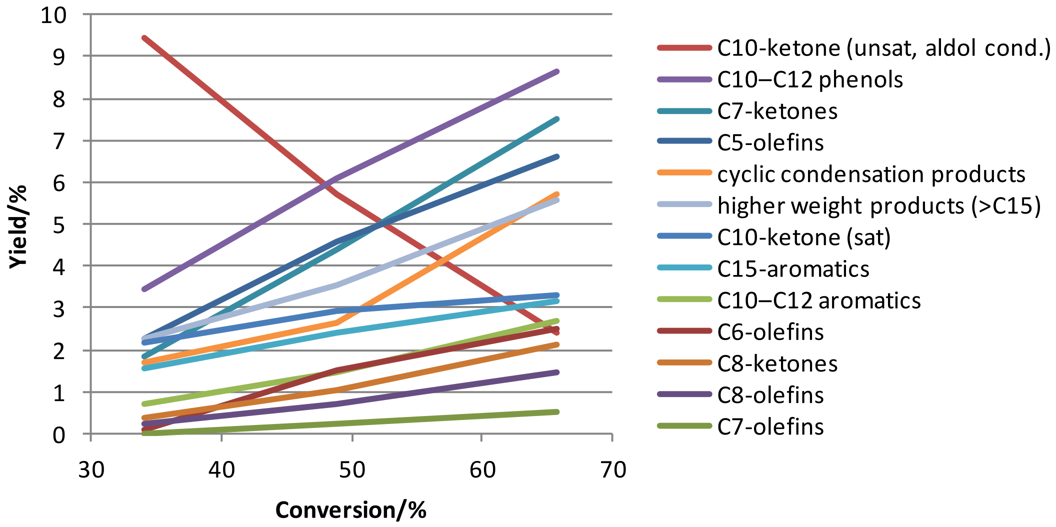
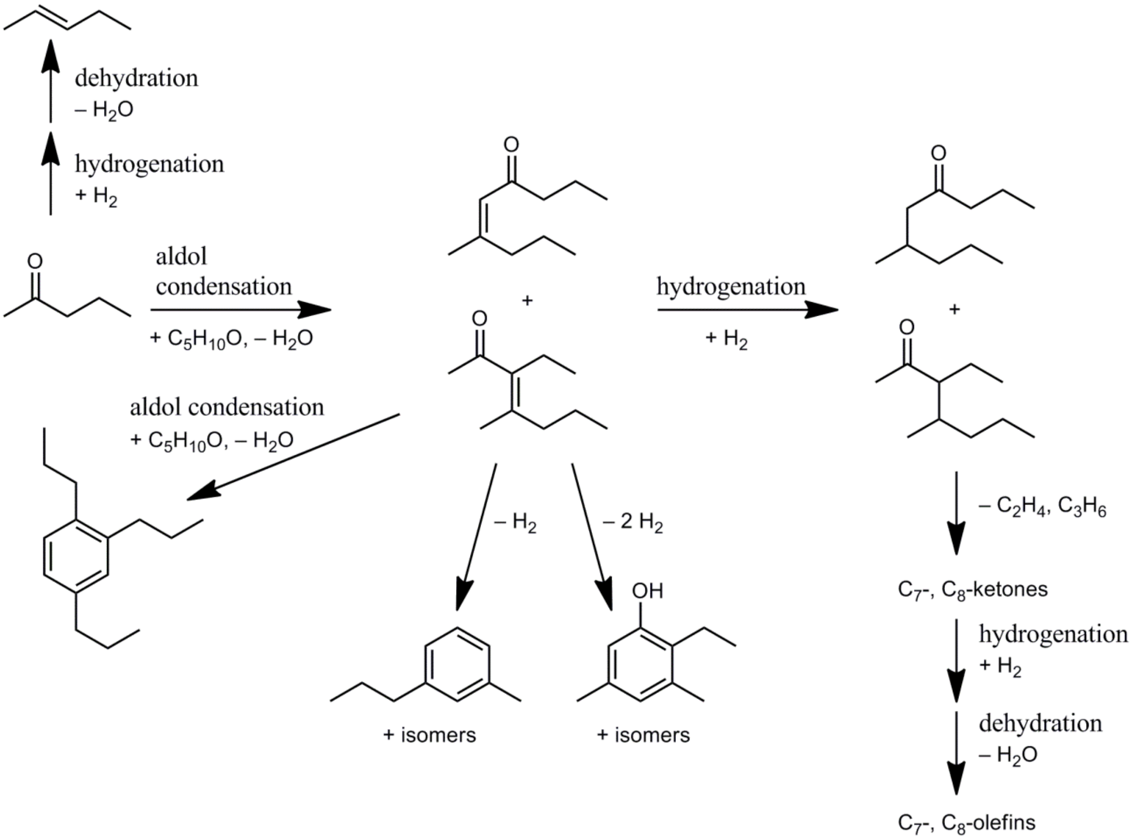


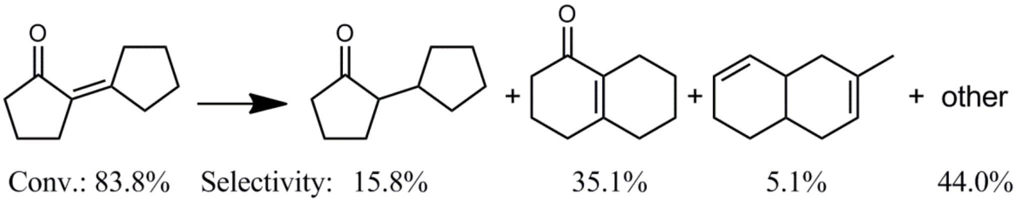
Figure 6. Yield over conversion for the transformation of 2-pentanone over TiO_2. Reaction conditions: 0.50 g of TiO_2, F = 7.28 to 72.8 g h^{-1}, WHSV from 14.6 to 145 h^{-1}, 425 ºC, N_2 100 mL min^{-1}.



Scheme 2. Proposed reaction pathways for the formation of the products observed when 2-pentanone was contacted with TiO_2. Yields are displayed in Figure 6.

The products of interest for the hydrogen production are precursors of the C_{10} aromatics and phenols (Figure 6 and Scheme 2). These can be formed from the unsaturated ketone under liberation of one or two equivalents of molecular hydrogen, respectively. These products clearly identified a reaction pathway to produce hydrogen (equivalents) during their formations.

Another interesting observation was made when employing the aldol condensation product of cyclopentanone as substrate. In this case, skeleton rearrangement and ring expansion occurred (Eq. 6), transforming a five-membered ring into a six-membered ring molecule. Similar skeleton rearrangements were mentioned before. Hence, after this ring expansion, smaller aliphatic rings may also serve as hydrogen source.



(6)

From this study on the reactivity of ketones and aldol condensation products it can be concluded unambiguously that hydrogen transfer reactions occur with titanium oxide without any precious metal. In the case of the α,β-unsaturated ketone (aldol condensation product) the direct hydrogenation product, i.e. the saturated ketone, was detected. As hydrogen donor, aldol condensation products, after cyclization, are proposed. Products such as C_{10} aromatics and phenols were identified which can be obtained from the aldol condensation product, together with one and two equivalents of hydrogen, respectively. Then, it becomes clear that the olefins, observed in the ketonic decarboxylation of carboxylic acids, are formed in a cascade reaction from the primary ketone product by hydrogenation and dehydration. On the other hand, it has been demonstrated that titanium oxide possesses is a high active catalyst for aldol condensations, under the present reaction conditions. This property is clearly responsible for further carbon–carbon bond formations.

Advantages of TiO_2 versus ZrO_2 for the production of fuels by ketonization

The additional carbon-carbon bond formation activity should be interesting for the formation of fuels from biomass platform molecules since an increase in the molecular weight of the products is desired. Hexose-derived pentanoic acid was transformed before into nonane as kerosene component.[48] We achieved that with a double catalytic bed involving ZrO_2 as ketonic decarboxylation catalyst and Pt/Al_2O_3 for subsequent hydrodeoxygenation. Now, the ketonic decarboxylation should be combined with subsequent aldol condensation activity before hydrodeoxygenation, i.e. ZrO_2 substituted by TiO_2 in the first catalytic bed. When the reaction was carried out with the two catalytic beds, simulated distillation of the product (Figure 7) after the two step process, shows nicely that the diesel yield is approximately doubled compared with ZrO_2. Nevertheless, the gasoline fraction increases, probably due to an increased activity of the metal oxide for fragmentation reactions but also to the introduction of branching in the molecules which also facilitates fragmentations. In Figure 8, it can be clearly seen that the substitution of ZrO_2 by TiO_2 in the two step process is favorable when diesel fuel is targeted.

The substitution has an additional effect on the product composition. Hence, when ZrO_2 was employed the main product was nonane with a selectivity of approx. 75%. In contrast, with TiO_2 not only alkanes were obtained but also 5 to 10% of aromatic compounds (Figure 9). Furthermore, under the same reaction conditions, the hydrodeoxygenation was not complete and up to 5% of oxygenated compounds were detected.

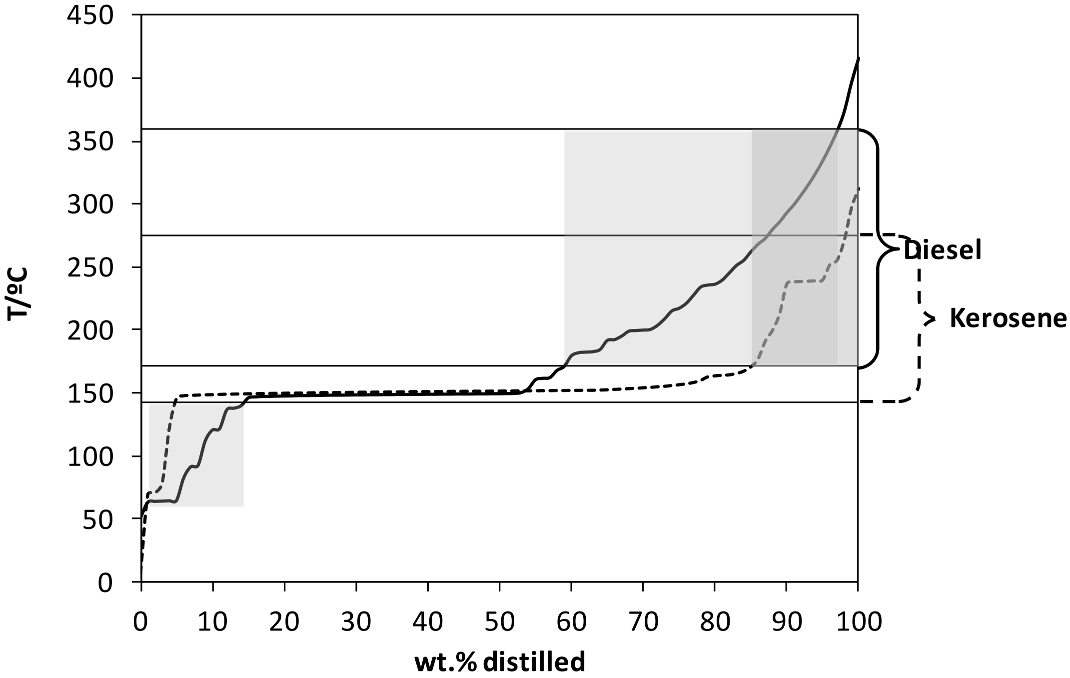


Figure 7. Simulated distillation of the product mixtures of the reactions of pentanoic acid over TiO_2 (continuous line) and ZrO_2 (dashed line) after subsequent hydrodeoxygenation. Horizontal lines indicate temperature limits for the boiling point ranges of kerosene (150 to 275 ºC) and diesel fuel (171 to 359 ºC). Reaction conditions: 2.50 g of metal oxide and 1.5 g of 2% Pt/Al_2O_3 were employed as catalysts, F = 8.37 g h^{-1}, WHSV = 3.35 h^{-1} (with respect to TiO_2 or ZrO_2), 400 ºC, H_2 100 mL min^{-1} (TiO_2) and 470 mL min^{-1} (ZrO_2).

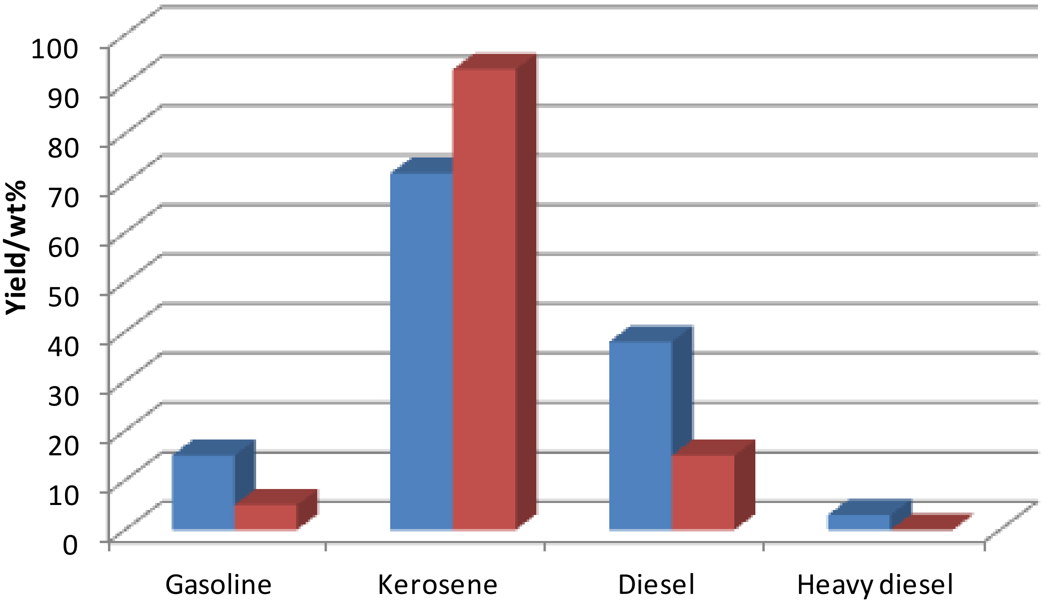


Figure 8. Yields of different fractions of fuels when combining either TiO_2 (blue) or ZrO_2 (red) with a hydrodeoxygenation treatment (Pt/Al_2O_3). Maximum values are stated for kerosene and diesel fuel although both yield can not be achieved at the same time.

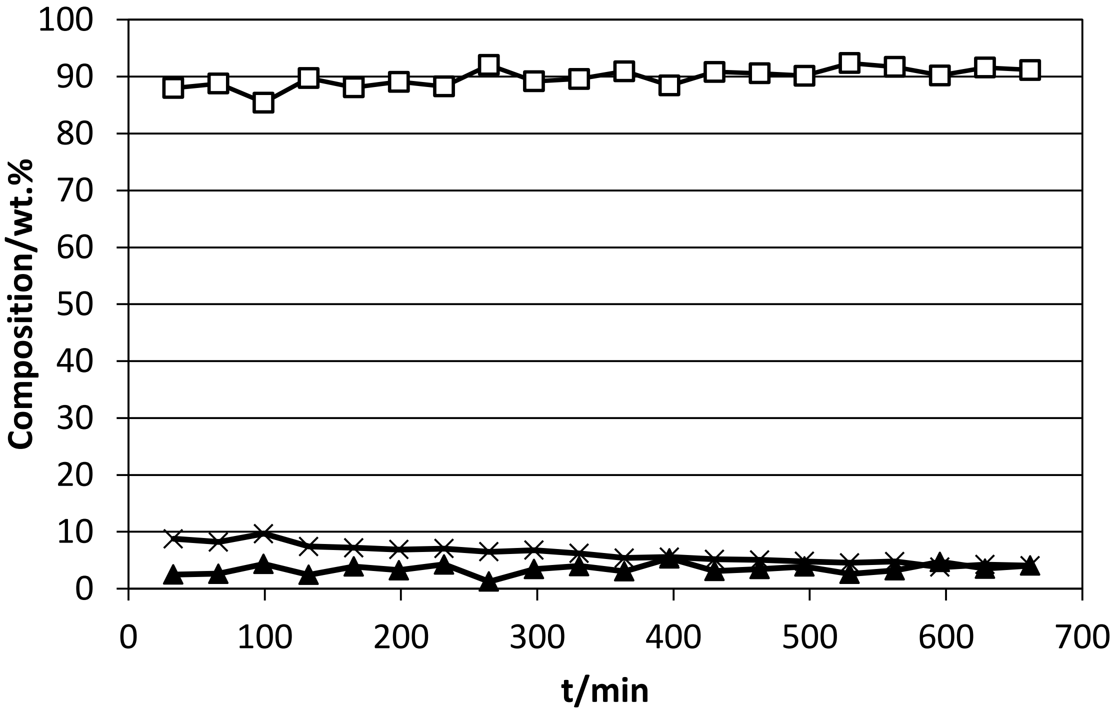


Figure 9. Composition of the liquid product when pentanoic acid was treated in a two-bed process with TiO_2 and Pt/Al_2O_3 under hydrogen atmosphere. □ Alkanes and cycloalkanes , X aromatics, ▲ oxygenated. Reaction conditions: 2.50 g of TiO_2 and 1.5 g of 2% Pt/Al_2O_3, F = 8.37 g h^{-1}, WHSV = 3.35 h^{-1} (with respect to TiO_2), 400 °C, H_2 100 mL min^{-1}.

Conclusions

The catalytic activity of TiO_2 has been compared with ZrO_2 for the ketonic decarboxylation. It has been found that the catalytic activity of TiO_2 starts at lower temperature than with ZrO_2. With TiO_2, several reactions, i.e. ketonic decarboxylation, reduction and dehydration, occur in a cascade mode. Thereby, at 400 ºC the main product observed was an olefin instead of the ketone obtained with ZrO_2. The origin of the reductant could not be clearly identified, but dehydrogenations–hydrogen transfer from hydrogen donating molecules are very likely since aromatics (approx. 11%) and 0.22 wt% coke were formed. Precursors for the hydrogen production can be formed by aldol condensation reactions. The latter reactions also contribute to carbon-carbon bond formations which has a positive effect on the average molecular weight of the product mixture after hydrodeoxygenation.

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Direct conversion of carboxylic acids (C_n) to alkenes ($C2_{n–1}$) over titanium oxide in absence of noble metals

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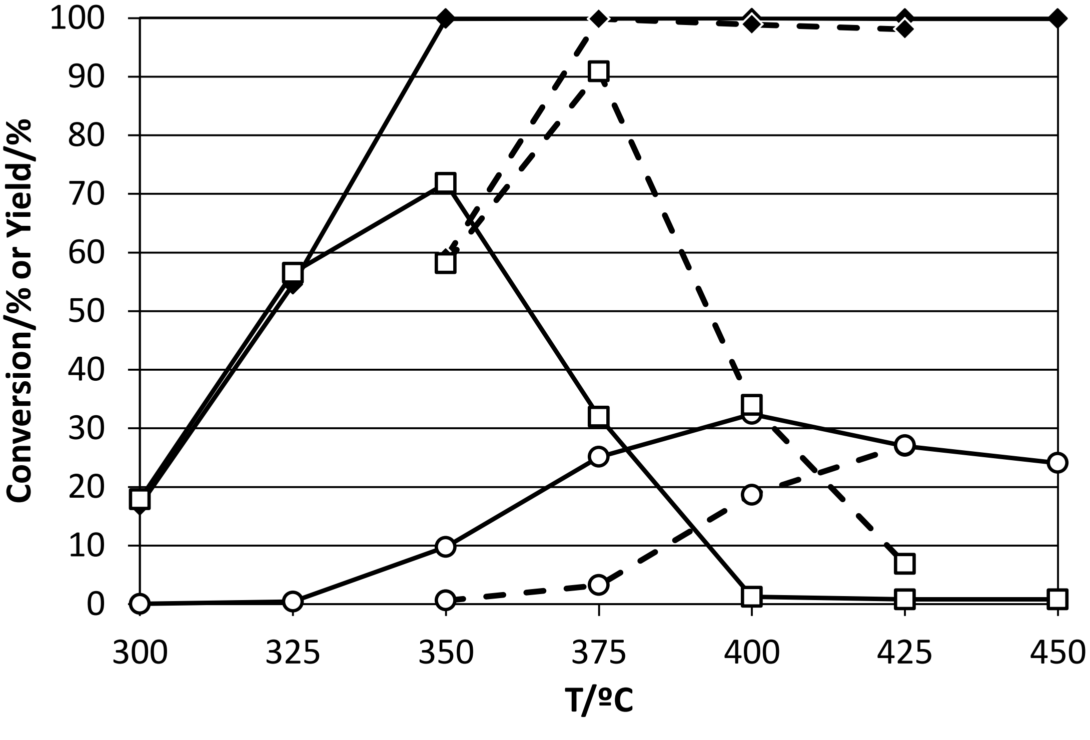

Figure S1. Transformation of decanoic acid over TiO_2 from Chempur (continuous line) and TiO_2 from Evonik (P25, dashed line) in the temperature range from 300 to 450 ºC. ◆ conversion, □ 10-nonadecanone yield, O nonadecene yield. Reaction conditions: 2.50 g of metal oxide, WHSV = 3.17 $h^{–1}$, F = 7.92 g $h^{–1}$, 50 mL $min^{–1}$ of N_2. For DRX pattern of TiO_2 P25 see Figure S2.

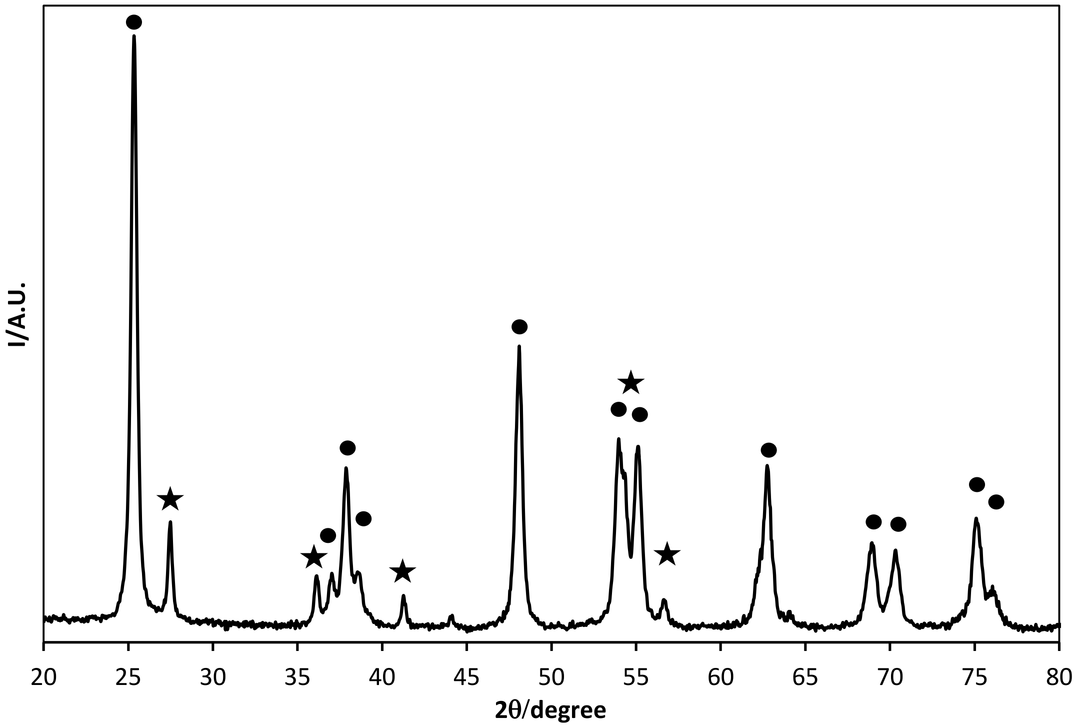

Figure S2. X-ray diffraction pattern of TiO_2 (P25, Evonik; ● Anatase phase, ★ Rutile phase). Surface area 55 m^2/g.

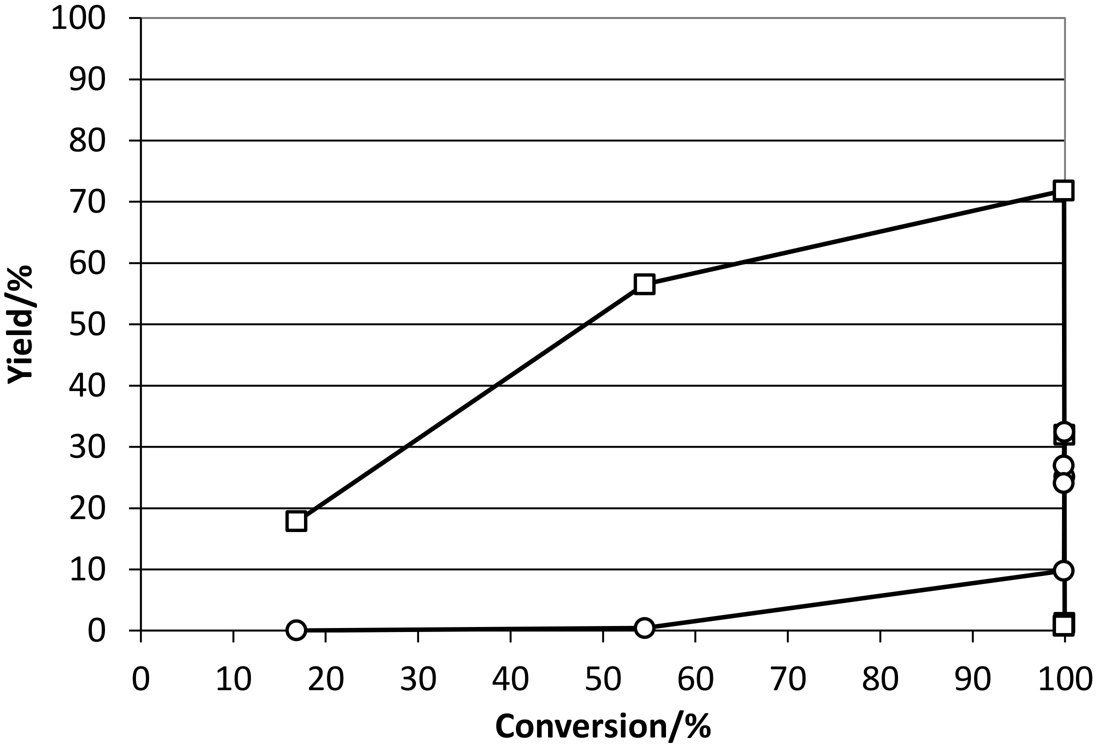

Figure S3. Yield of 10-nonadecanone and nonadecene versus conversion of decanoic acid for the transformation of the acid over TiO_2 in the temperature range from 300 to 450 ºC (cf. Figure 3). □ 10-nonadecanone, O nonadecene. Reaction conditions: 2.50 g of metal oxide, WHSV = 3.17 h^{-1}, F = 7.92 g h^{-1}, 50 mL min^{-1} of N_2.

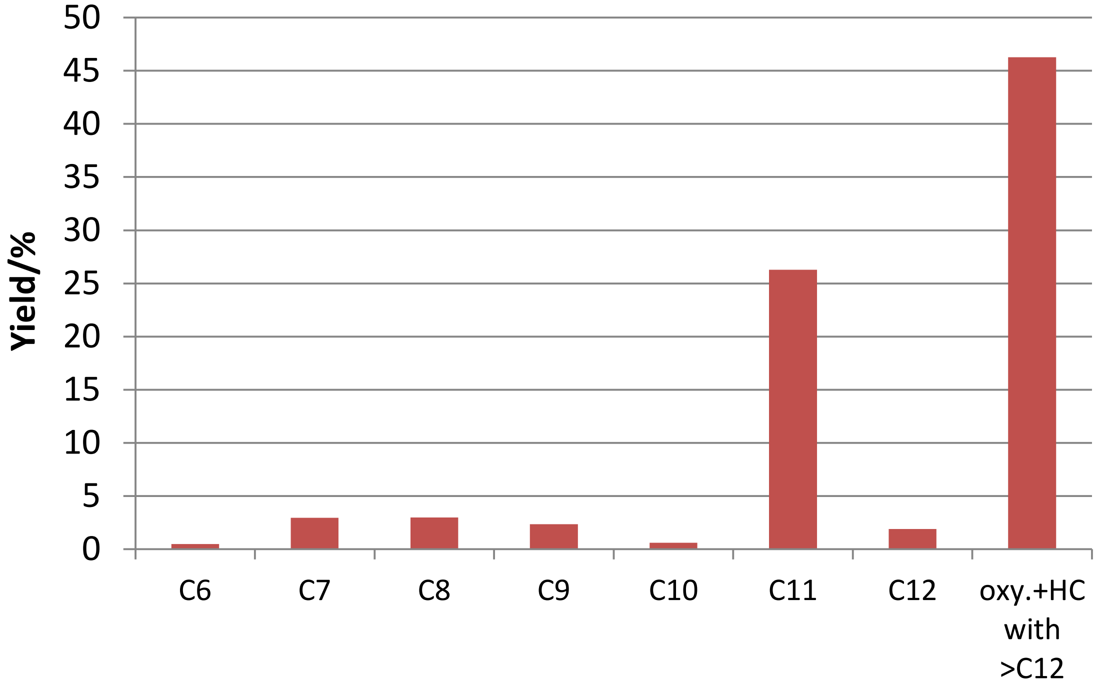

Figure S4. Product composition for the transformation of 2-undecanone under ketonization conditions. Columns from C6 to C12 represent the yield to olefins with 6 to 12 carbon atoms, the last column shows the yield to hydrocarbons and oxygenated hydrocarbons with more than 12 carbon atoms.