Sorption and Reaction of Biomass Derived HC Blends and Their Constituents on a Commercial Pt–Pd/Al₂O₃ Oxidation Catalyst

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Received: 28 March 2021 / Accepted: 10 August 2021 / Published online: 25 August 2021
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Abstract

Within the Research Cluster of Excellence “The Fuel Science Center” at RWTH Aachen University, the production and application of new fuels from bio-based carbon feedstocks and CO₂ with hydrogen from renewable electricity generation is being investigated. In this study, the storage and oxidation of ethanol, 1-butanol, 2-butanone, cyclopentanone, and cyclopentane as well as two blends thereof on a series production Pt–Pd/Al₂O₃ oxidation catalyst were investigated. Hydrocarbon (HC) storage and temperature-programmed surface reaction (TPSR) experiments were carried out to analyze their adsorption and desorption behavior. In addition, the individual HCs and both blends were investigated using Diffuse Reflectance Infrared Fourier Transform Spectroscopy (TP-DRIFTS). In general, all oxygenated HCs are adsorbed more strongly than cyclopentane due to their higher polarity. Interestingly, it could be observed that the two different blends [blend 1: ethanol (50 mol %), 2-butanone (21 mol %), cyclopentanone (14 mol %) and cyclopentane (15 mol %); blend 2: 1-butanol (45 mol %), ethanol (29 mol %) and cyclopentane (27 mol %)] exhibit a different storage behavior compared to the single hydrocarbons. It was shown that the presence of 1-butanol and cyclopentane in blend 2 strongly inhibits the oxidation of ethanol. As a result, the ethanol light-off temperature was increased by at least 100 K. A difference was also found in the storage behavior of cyclopentane. While no significant storage could be detected in the pure compound experiment, the experiments with both mixtures showed a larger amount stored. The presence of adsorbed species of the hydrocarbons and their corresponding reaction products has been demonstrated and gives an insight into the storage mechanism of blends.

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Graphic Abstract

Keywords Oxygenated hydrocarbons · Bio-hybrid Fuels · Pt-Pd/Al₂O₃ · Adsorption · Oxidation · DRIFTS

Abbreviations

OC	Oxidation catalyst
HC	Hydrocarbon
TPSR	Temperature-programmed surface reaction
TP-DRIFTS	Temperature-programmed diffuse reflectance infrared Fourier transform spectroscopy
LGB	Laboratory gas test bench
GHSV	Gas hourly space velocity
OEM	Original equipment manufacturer

LO	Light-Off
FID	Flame ionization detector
FTIR	Fourier-transform infrared spectroscopy
ICP-OES	Inductively coupled plasma atomic emission spectroscopy
BET	Brunauer–Emmett–Teller
GHG	Greenhouse gas

1 Introduction

In order to limiting the increase in the global average temperature to well below 2 °C above the pre- industrial levels, special efforts are needed to reduce greenhouse gas (GHG) emissions [1]. The Research Cluster of Excellence “*The Fuel Science Center*” at RWTH Aachen University investigates the production and application of new bio-hybrid fuels from bio-based carbon feedstocks, CO₂, and hydrogen from renewable electricity generation. The cluster research involves the production pathways from biomass, CO₂, and H₂ to fuels as well as the usage of these fuels in internal combustion engines and the corresponding exhaust gas aftertreatment [2–4]. A variety of different promising fuels for compression and spark ignition engines were identified and investigated for their suitability [5–12].

Lean combustion, i.e. combustion with excess air (relative air-to-fuel ratio $\lambda > 1$), was shown to significantly increase the efficiency of spark ignition engines and thus offers the potential to reduce fuel consumption [13]. Ottenwälder et al. compared a fuel blend of 50 mol % ethanol, 21 mol % 2-butanone, 15 mol % cyclopentane and 14 mol % cyclopentanone with the currently best available fossil fuel RON 102 [14]. They showed that the conventional fuel resulted in more unstable combustion with enleanment and exceeding the 5% IMEP standard deviation limit at $\lambda = 1.6$, while the blend provided stable combustion even at $\lambda = 1.7$ [5]. It was also shown that the HC and CO emissions increase with higher air-to-fuel ratios, while the NO_x emissions reach their maximum value at $\lambda = 1.2$ respectively 1.1 for RON 102 and then steadily decrease as λ increases [14].

For lean-burn-engines the oxidation catalyst (OC) performs an important task during the cold start period when the exhaust gas temperature is below the light-off temperature of the catalyst: The OC operates as a hydrocarbon trap which is able to store hydrocarbons [15–21]. This HC storage is crucial as nearly 60–70% of all HC emissions are emitted during the cold start phase [22]. When the light-off temperature is reached, the stored hydrocarbons can be released and be oxidized on the catalytic surface of the OC. On the other hand, it must be taken into account that stored hydrocarbons may lead to local “hotspots” during oxidation, which in turn may lead to sintering of active sites and thus to accelerated aging of the catalyst [23]. This study allows an insight into the storage and oxidation behavior of different HCs and their blends. The knowledge obtained can be used to optimize the storage behavior of OCs for the future use of alternative fuels and thus improve the cold start performance.

2 Experimental Section

2.1 Catalyst Properties

The investigated catalyst is a series production oxidation catalyst (OC) from a passenger car with a 1995 cm³ Diesel engine. It was purchased from the original equipment manufacturer (OEM) retailer. A detailed examination of the catalyst properties including ICP-OES and BET measurements were carried out by Wolkenar et al. [24].

2.2 Laboratory Gas Test Bench Setup

The measurement of the catalyst performance was carried out on a laboratory gas test bench (LGB). All piping on this test rig is made of grade 2 titanium. The N₂ balanced gas flow was mixed from compressed gas cylinders and evaporated hydrocarbons using different mass flow controllers keeping a constant gas hourly space velocity (GHSV) of 60,000 h^{−1}, which is often used for exhaust gas aftertreatment of internal combustion engines and is close to reality [24–26]. A detailed description of the experimental setup was given by Wolkenar et al. in [24].

2.3 HC Storage

For the determination of the hydrocarbon storage capacity, additional tests were conducted. For this purpose, the catalyst sample was conditioned and cooled down to a temperature of 383 K as in the previous measurements. After reaching this temperature, the HC dosage was started. The corresponding substances were dosed together with O₂, H₂O and N₂ as carrier medium for a period of 30 min. Then, the sample was purged with N₂ and H₂O for 10 min at 383 K. In order to make the measurements realistic and at the same time take advantage of the higher accuracy provided by the more precise CO₂ measuring equipment, after the purging a release phase with 10% O₂ and H₂O during a temperature ramp with a gradient of 5 K/min to a final temperature of 773 K was performed to remove potentially adsorbed HC from the catalyst surface.

At 773 K, the sample was subsequently conditioned with O₂ for a period of 10 min to ensure that no HC residues were stored on the sample. The sample was thereafter cooled to 383 K and the procedure was repeated. The HC concentration in the individual test corresponds to the concentration of the corresponding HC in a 200 ppm blend to achieve good comparability of the tests with the pure substance and to the investigations of the blend. The selected concentrations for the investigations of the hydrocarbon storage capacity are listed in Table 1. To stabilize the dosage of small amounts, ethanol and cyclopentanone were dissolved in a precisely

Table 1 Dosing of the different investigated hydrocarbons

Hydrocarbon	Sum formula	Conc. TPSR	Conc. HC-storage	Boiling point	Molar mass
1-Butanol	$C_4H_{10}O$	80 ppm	90 ppm	118 °C [27]	74.12 g/mol
2-Butanone	C_4H_8O	90 ppm	42 ppm	79.6 °C [28]	72.11 g/mol
Cyclopentane	C_5H_{10}	72 ppm	53/30 ppm	49 °C [29]	70.13 g/mol
Cyclopentanone	C_5H_8O	69 ppm	28 ppm	131 °C [30]	84.12 g/mol
Ethanol	C_2H_6O	160 ppm	100/57 ppm	78 °C [31]	46.07 g/mol
Blend 1	–	110 ppm	200 ppm	–	–
Blend 2	–	90 ppm	200 ppm	–	–

Fig. 1 Schematic illustration of the determination of HC storage. **A** The adsorbed amount (hatched area) is calculated by subtracting the area of the sum of all outgoing substances from the area of the dosed concentration. The released amount is calculated by the addition of released species (red area). **B** The quantities calculated from the integrals of the adsorbed and released quantities are then averaged and referred as the stored HC amount

defined amount of water and dosed as a solution. The separately dosed amount of water was adjusted accordingly. The amount of adsorbed HC at each point in time is the difference between the amount of dosed HC and the amount of measured HC. The measured HC quantity corresponds to the sum of the measured HC amount per product formed (Fig. 1 products 1–3) and the unreacted HC (outlet HC). Using ethanol as an example, at each point in time it is measured what proportion of the dosed ethanol effluents and what proportion of the ethanol is converted into the three products acetaldehyde, acetic acid, and CO_2 , and the sum of these is subtracted from the dosed amount to calculate the amount of HC stored into the catalyst. The total quantity adsorbed is finally the sum of the quantities stored at each point in time. Mathematically, this corresponds to the integral over the dosing period of the difference between the dosed quantity and the measured quantities (hatched area in Fig. 1). After the dosing phase, the catalyst is heated continuously with 5 K/min to 773 K. During this time, HC that was previously stored is released. The amount of HC released is the sum of the measured HC amounts of the individual products formed

and the unreacted HC (outlet HC). In order to determine the total amount stored, the sum (or integral) can be formed over the time from the end of the dosing to the end of the heating of the catalyst (red area in Fig. 1A). The curves in Fig. 1B indicate the total quantity already stored or released up to the corresponding point in time, i.e. the value of the integral up to this point in time. It is assumed that the quantity released and the quantity stored are identical, which is also illustrated by Fig. 1B. In order to account for potential measurement inaccuracies, the average of the measured adsorbed and released quantities is taken to determine the actual stored HC quantity. In order to increase the accuracy of the results, a large number of storage and release phases were carried out, resulting in the error indicators shown in Figs. 2 and 3.

2.4 TPSR Measurements

To examine the oxidative behavior of the different hydrocarbons (1-butanol, 2-butanone, cyclopentane, cyclopentanone, ethanol, and two blends) on the catalyst, temperature-programmed surface reaction (TPSR) experiments have been

Fig. 2 Specific quantity of stored hydrocarbons, determined from stored and released quantity of the corresponding HC in mmol/l, stored HC in pure experiments (grey), stored HC in blend 1 (green), storage phase at $T = 383$ K and $GHSV = 60\,000\text{ h}^{-1}$, Gas composition: 8% H_2O , 8% O_2 , 0% CO_2 , HC: see Table 1, balance: N_2

Fig. 3 Specific quantity of stored hydrocarbons, determined from stored and released quantity of the corresponding HC in mmol/l, stored HC in pure experiments (grey), stored HC in blend 2 (orange), storage phase at $T = 383$ K and $GHSV = 60,000\text{ h}^{-1}$, Gas composition: 8% H_2O , 8% O_2 , 0% CO_2 , HC: see Table 1, balance: N_2

carried out. For all measurements, the feed gas contained 8% O_2 , 8% H_2O , and varying concentrations of the respective HC (see Table 1), with N_2 as balance. The used HC concentration was set to obtain a gas mixture corresponding to a relative air–fuel-ratio of 2.96 if there were additionally 8% of CO_2 . This enables a comparable amount of C and H to react on the catalyst in all experiments. For pre-experiment, the test procedure started with a catalyst pre-conditioning at 773 K with 8% O_2 and 8% H_2O to remove potentially adsorbed HC and to oxidize the catalyst surface. Afterwards, the catalyst was cooled down to 383 K and filled with the

respective HC. Once the FID signal has reached a constant value, the temperature was increased with a heating rate of 5 K/min to 773 K.

For concentration analysis by FTIR, various evaluation methods from the instrument manufacturer were modified for the investigation of exhaust gas components. In addition, FID and mass spectrometer data were used for verification.

2.5 TP-DRIFTS

Ceramic chips, that can be resistively heated through integrated electrodes, were coated with the catalyst material. The chips were then loaded with the pure HC or blend at the LGB. TP DRIFTS experiments were consecutively performed in a Vertex 70 FTIR spectrometer (Bruker Corporation, Billerica, MA, USA) equipped with a Praying Mantis mirror setup (Harrick Scientific Products, Inc., Pleasantville, NY, USA) and a custom-made DRIFTS cell. The temperature ranged between 323 and 673 K at a constant N_2 flow of 100 ml/min. Further details about the experimental conditions and sample preparation can be found in [24].

3 Results and Discussion

3.1 HC-Storage

Since the storage capacity depends on the properties of the corresponding HC, the results show differences between the species with different functional groups. In a first step, single component measurements were conducted. For cyclopentane, no HC storage capacity could be detected in the single component experiments. For 1-butanol, the largest absolute storage amongst all HC of 20.5 mmol/l could be observed. The second highest storage capacity was measured with cyclopentanone (12.5 mmol/l). For 2-butanone, a HC storage of 11.0 mmol/l was measured (Fig. 2). The measurements with ethanol resulted in an HC storage of 5.3 mmol/l for a dosage of 57 ppm and 9.5 mmol/l for a dosage of 100 ppm.

As already found by Wolkenar et al. [24], it could be shown that oxygenated molecules are better stored than molecules without oxygen in the molecular structure. A closer look at the results of the single component measurements shows that the storage for the investigated HC depends on the functional group as well as on the number of C atoms in the molecule. This results in a storage of 3 mmol/l per C-atom for ketones and 5 mmol/l per C-atom for alcohols. When comparing the stored quantities during the single substance measurements with the results of the mixtures, some differences are noticeable: Fig. 1 shows the storage of the blends compared to its pure constituents. In general, it can be said that all substances—with the exception of cyclopentane—were stored in blend 1 to a lower degree than in the experiments with the pure substances (Fig. 2). Large differences between the individual substance classes can be observed. While the difference between the stored ethanol in blend 1 and as pure substance is 15%, 2-butanone and cyclopentanone show a reduction of 38% and 62% respectively. In contrast to the studies with cyclopentane as a pure substance, a storage of cyclopentane can be observed with blend 1. However, the amount stored is small. Blend 2 shows a slightly different behavior (Fig. 3): although in this case the stored amount of the main component is also significantly lower (9%) compared to the stored amount in the test with the pure substance, the other components show a significantly improved storage behavior. Thus, the amount of stored ethanol and cyclopentane increases by 16% and 224%, respectively. When looking at the cumulative selectivities during storage and release phase, it is noticeable that ethanol in blend 2 not only shows the lowest conversion, but also that no partially oxidized products can be detected (Fig. 4).

Fig. 4 Selectivities of acetaldehyde, acetic acid, and CO_2 cumulated from ethanol storage and release in both blends and in the studies of the pure components at the corresponding concentration as they are also present in the respective blend. The black line shows the cumulative conversion of ethanol during the storage and release phases. Storage phase at $T = 383$ K and $GHSV = 60,000\ h^{-1}$, Gas composition: 8% H_2O , 8% O_2 , HC: see Table 1, balance: N_2

Fig. 5 Yield of acetaldehyde, acetic acid, and CO₂ released from ethanol during release phase relative to the whole amount removed from storage in both blends and in the studies of the pure components at the corresponding concentration as they are also present in the respective blend

In general, the data show that ethanol is converted worse in both blends than in the measurements with ethanol as pure substance. While the ratio between acetic acid and CO₂ in the released amount is about 1:1 in the measurements with pure ethanol (Fig. 5), both blends show a changed behavior: the substances released from ethanol in blend 1 contain significantly less acetic acid and a slightly increased amount of acetaldehyde. However, most of the stored ethanol is released as CO₂, although it is unclear whether this amount was stored as ethanol or as an intermediate or was converted to CO₂ on release. Blend 2 does not show any products from

partial oxidation even during the removal phase; in particular, it shows that about 20% of the ethanol stored is desorbed unreacted.

Also when looking at the substances released from the stored 1-butanol (Fig. 6), it can be seen that the proportion of unreacted 1-butanol is slightly increased compared to the comparative measurement without further components. On the other hand, the proportion of butyric acid is increased, while the fraction of CO₂ drops from 43 to 24%.

Similar results are also shown for cyclopentane and cyclopentanone. Although these are not as strongly increased

Fig. 6 Yield of butyraldehyde, butyric acid, and CO₂ released from 1-butanol during release phase relative to the whole amount removed from storage in blend 2 and during the study of the pure component

as for the two previously mentioned hydrocarbons, they are nevertheless significant, thus the amount of unreacted hydrocarbons in comparison of pure cyclopentane to blend 1 increases from 59 ± 6 to $71 \pm 1\%$. In the case of cyclopentanone, the fraction of unreacted hydrocarbons in the HC released increases from 47 ± 1 to $79 \pm 1\%$ in comparison of pure cyclopentane to blend 1. Only 2-butanone shows a different behavior. Thus, the amount of unreacted 2-butanone in the released quantity drops from $69 \pm 3\%$ in the comparative measurement with the pure component to a value of $56 \pm 2\%$ without the formation of any by-products being observable. In general, the observable deterioration of the conversion in the measurements with the blends could be explained by the deactivation due to the presence of carboxyl groups as they occur in the acids. This fact would also fit with the observations from the literature [32–36]. Only the enhanced conversion of 2-butanone in blend 1 seems to be in contradiction with the other observations. This fact could be due to a reaction pathway which proceeds only by the presence of the other blend components or their intermediates.

3.2 TPSR-Measurements

As already observed by Wolkenar et al. [24] during the TPSR investigations, some of the investigated HC react to CO_2 on this catalyst at the beginning of the initial storage phase at temperatures as low as 383 K. Figure 7 shows the CO_2 yield for each pure component during the storage before the TPSR starts.

It is not surprising that at the low temperature of 383 K cyclopentane is not converted to CO_2 in significant amounts due to its relatively high stability. Both alcohols, on the

other hand, show at the low temperature of 383 K a sudden increase in CO_2 concentration at the beginning of the dosage. Subsequently, its concentration decreases steadily over time. This behavior has already been described in literature and points to an inhibition of the oxidation reactions due to carboxyl species formation e.g. formate with advancing storage of the HC at the active sites [24, 32, 33, 35]. Oh et al. described a mechanism which explained the formation of surface carboxyl species from C_3H_6 on a diesel oxidation catalyst with Pt [33]. I.e., the increase at the beginning is caused by oxidation of HC with the O_2 on the catalyst surface. With decreasing O_2 or with increasing HC loading and the resulting formation of carboxylic species on the surface, the CO_2 production decreases. Also, for both ketones, 2-butanone and cyclopentanone, this behavior is shown during CO_2 release at 383 K. After a short steep increase at the beginning of the dosage and a subsequent steady decrease, an almost stable CO_2 production settles out after a period of 3000 s. At this point, the descending order of the CO_2 yield is as follows: ethanol, 1-butanol, 2-butanone, cyclopentanone and cyclopentane. Thus, both alcohols lead to higher CO_2 yields than with/from the two ketones, and these in turn lead to a higher CO_2 production than the alkane cyclopentane. This can again be possibly explained by the fact that alkanes are more stable than ketones and the latter in turn are more stable than alcohols. Comparing both alcohols and both ketones, it can be observed that in both cases the short-chain molecules lead to a higher CO_2 production than the long-chain molecules. At 383 K, the maximum CO_2 yield during the 2-butanone dosage is about 2% lower than the maximum CO_2 yield at the same temperature in the experiment with cyclopentanone. A possible explanation for the

Fig. 7 CO_2 yield for different hydrocarbons from pure substance measurement, filtered by a Savitzky–Golay-Function of 3rd polynomial order and a window size of 90, $T = 383$ K and $\text{GHSV} = 60,000 \text{ h}^{-1}$, Gas composition: 8% H_2O , 8% O_2 , 0% CO_2 , HC: see legend, balance: N_2

Fig. 8 Weighted CO₂ yield, the blue line shows the expected CO₂ yield with the same conversion of HC in the blend as in the pure substance tests, black is the actual amount of CO₂ released from the blend. On the left side the HC is shown in the composition of blend 1

and on the right side of blend 2, filtered by a Savitzky–Golay-Function of 3rd polynomial order and a window size of 90, T=383 K and GHSV=60,000 h⁻¹, gas composition: 8% H₂O, 8% O₂, 0% CO₂, HC: see legend, balance: N₂

lower reactivity of 2-butanone compared to cyclopentanone could be steric hindrance.

Considering the results from the measurements with the blends, it is noticeable that the amount of CO₂ formed during the storage of both mixtures at 383 K does not correspond to the amount of CO₂ that would be expected from the weighted sum of the individual components based on the single experiments. While the difference between the expected and the measured amount of CO₂ for blend 1 is about 2%-points, there is a difference of 0.8%-points for blend 2. It is remarkable that in blend 1 the amount of CO₂ that would have to be produced from ethanol alone exceeds the actual measured concentration by slightly more than 1%-point (Fig. 8). These facts indicate that the presence of the other components leads to a reduced conversion of some of the hydrocarbons.

Depending on the dosed hydrocarbon, some reaction products could be detected in addition to the CO₂ already mentioned during the storage phase at 383 K. The formed products were acetaldehyde, acetic acid, butyraldehyde, butyric acid and small amounts of methane as well as CO₂.

One substance which could not be reliably identified by the specially developed FTIR evaluation method, was butyric acid, which is formed during the oxidation of 1-butanol. However, the formation of butyric acid could be qualitatively detected by MS. Therefore, the amount of butyric acid formed was determined from the difference between all known detectable substances that could be detected by FTIR measurement and the FID value for the total hydrocarbons. This calculated value was then corrected according to the dosed and measured C balance. While for the alcohols, 1-butanol and ethanol, significant amounts (> 50%) were already converted at 383 K and products from partial oxidations could be detected, both ketones showed no reaction products other than CO₂ at this temperature. For cyclopentane no significant conversion was observable at 383 K.

The typical reaction sequence of alcohol decomposition on Pt, Pd and other noble metals includes the formation of an alkoxide intermediate forming aldehyde, carbonic acid and CO₂ as reaction products [37–39]. Regardless of this, the acidity of the supporting Al₂O₃ can promote both the dehydrogenation and dehydration of ethanol and can thus

also lead to the formation of acetaldehyde and acetic acid [38–40]. It is known that Al_2O_3 has a poor adsorption behavior for ethanol because of its low specific surface area [41]. It is therefore assumed that the storage assigned to ethanol is mainly caused by adsorbed reaction products.

The steep gradient in the acetaldehyde concentration at the beginning of the TPSR could be an indication that a small part of the stored ethanol on the catalytic surface formed an intermediate that can be released as acetaldehyde. Aldehydes can be bonded to the surface via two possible mechanisms, one via both carbon and oxygen atoms of its carbonyl function group [$\eta^2(\text{C},\text{O})$ -conformation] and the other way via its oxygen atom only [$\eta^1(\text{O})$ -conformation] [37]. Oxygen-loaded surfaces support the $\eta^1(\text{O})$ -conformation of aldehyde intermediates which are more likely to desorb than to further decompose analogue to the $\eta^2(\text{C},\text{O})$ -conformation of aldehydes [37, 42].

Due to the performed pre-treatment of the sample with 8% O_2 , a high oxygen loading of the surface can be assumed. On the other hand, after starting the temperature ramp at 398 K, we observe an increasing acetaldehyde concentration after $t = 4000$ s (Fig. 9), while the observed ethanol concentration drops. We therefore attribute this behavior to a higher formation rate of acetaldehyde rather than thermal desorption. As the temperature rises, there is also an increased formation of acetic acid. The maximum acetic acid concentration is reached at 473 K. This is in accordance with the results of Avgouropoulos et al. when using unpromoted Pt/ Al_2O_3 [38]. This increase in acetic acid concentration shows that a large part of the stored ethanol reacts on the surface to acetic acid and then is released with increasing temperature. In addition to acetaldehyde and acetic acid, a small amount

of methane can also be detected in the ethanol test. It is noticeable that the release of methane is only observable in the temperature range of 394–630 K with two maxima at ca. 433 K and 555 K.

The methane peak and the shoulder of CO_2 at 433 K could also be an indication for a decarbonylation of an aldehyde intermediate species on Pd^0 sites generating equimolecular amounts of methane and CO which would be followed by the oxidation of CO to CO_2 [40, 43]. These Pd^0 species could be generated by ethanol oxidative dehydrogenation [40]. However, it must also be noted that the quantities of methane formed are very small. 1-butanol shows a similar behavior on the catalyst as ethanol. The formation of the corresponding aldehyde and the corresponding carboxylic acid can also be observed here. However, no compounds with a small number of carbon atoms could be observed in the reaction of 1-butanol except CO_2 . While the investigations with cyclopentanone and cyclopentane did not reveal any oxidation products apart from CO_2 , the investigation of 2-butanone yielded acetic acid and methane.

The formation of acetic acid from 2-butanone has been known in the literature for a long time [44–46]. Among others, Jahan et al. reported how the selectivity of acetic acid is increased by the presence of water [44, 46]. The investigations with 2-butanone as pure component showed that over the entire dosage range of 383–773 K, an acetic acid and methane yield of 2.5% and 0.5% respectively was achieved. A steep increase in acetic acid concentration of 15% at 500 K indicates that stored 2-butanone is converted to acetic acid on the catalyst surface and this formed acetic acid is largely released when the temperature is increased. At

Fig. 9 Temperature-programmed surface reaction (TPSR) from $T = 383$ to 773 K and GHSV = $60,000 \text{ h}^{-1}$, Gas composition: 8% H_2O , 8% O_2 , 0% CO_2 , 160 ppm ethanol, balance N_2 . All data filtered by a Savitzky–Golay-Function of 3rd polynomial order and a window size of 90. Left axis: Normalized hydrocarbon concentration, versus time since start of TPSR; right axis: mean catalyst temperature versus time

Table 2 Light-off temperatures

Hydrocarbon	LO-temp/pure	LO-temp./blend 1	LO-temp./blend 2
1-Butanol	< 383 K	–	422 K
2-Butanone	473 K	495 K	–
Cyclopentane	576 K	601 K	558 K
Cyclopentanone	505 K	542 K	–
Ethanol	< 383 K	430 K	483 K
Weighted sum	–	485 K	476 K

temperatures above 645 K, no more acetic acid production could be detected.

When comparing the single hydrocarbons and the blends, large differences in the conversion on the catalyst are revealed. The light-off temperature (LO-temperature) is the temperature at which the conversion of a substance reaches 50%. All measured LO-temperatures and the sum product for both blends are listed in Table 2. The example of ethanol shows that in the presence of the other blend components, the LO-temperature of ethanol is increased. While in blend 1 the LO-temperature for ethanol is increased by 47 K to a value of 430 K, the presence of 1-butanol and cyclopentane in blend 2 causes an increase by 100 K to 483 K (Fig. 10). In the literature, LO-temperatures of 423–523 K for the conversion of ethanol have been observed for Pd/Al₂O₃ catalysts by Liu et al. [41]. The decrease in ethanol conversion is already apparent at 383 K. The analysis of blend 1 shows that the conversion of ethanol to acetaldehyde and acetic acid is significantly lower (average conversion of 45%) than the measurement with pure ethanol (average conversion of

64%). This discrepancy increases further at the dosage of blend 2, so that at a temperature of 383 K only an average ethanol conversion of 17% can be observed.

In general, it can be stated that the other hydrocarbons in the presence of the other blend constituents also show a significantly reduced turnover. The only exception is cyclopentane in blend 2 with an increased turnover leading to a small decrease of the LO-temperature of 18 K (Fig. 11).

3.3 TP-DRIFTS

Figure 12a and b show the TP-DRIFTS difference spectra of blend 1 and 2, respectively, in the temperature range between 323 and 673 K.

Since no oxygen is fed, no further oxidation reaction is expected to occur during TP-DRIFTS experiments. Observed bands are thus attributed to surface species that have formed during the LGB experiments, including reaction intermediates and products. Several characteristic features in agreement with our previous experiments can be observed [24]. The absorption band at 3700 cm⁻¹ becomes stronger with increasing temperature. This corresponds to the $\nu(\text{OH})$ of surface hydroxyl groups of the alumina support which are generated after the desorption of the HC [47]. Blend 2 exhibits additionally a broad band between ca. 3500 and 3100 cm⁻¹ which has previously been ascribed to –OH interactions through intermolecular H bonding. The decrease of this band with increasing temperature is attributed to the desorption of previously condensed phases on the catalyst surface [24]. Characteristic absorption bands of the $\nu(\text{CH})$ stretches can be observed in the region of 3000 cm⁻¹ for both blends. A continuous decrease in absorption at these

Fig. 10 Temperature-programmed surface reaction (TPSR) from $T=383$ to 773 K and GHSV = 60,000 h⁻¹, Gas composition: 8% H₂O, 8% O₂, 0% CO₂, ethanol: 160 ppm (pure, green), 55 ppm (blend 1, blue), 25.9 ppm (blend 2, black), balance N₂. All data filtered by a Savitzky–Golay-Function of 3rd polynomial order and a window size of 90. Left axis: normalized hydrocarbon concentration, versus time since start of TPSR; right axis: mean catalyst temperature versus time

Fig. 11 Temperature-programmed surface reaction (TPSR) from $T=383$ to 773 K and GHSV = $60,000\text{ h}^{-1}$, Gas composition: $8\%\text{ H}_2\text{O}$, $8\%\text{ O}_2$, $0\%\text{ CO}_2$, cyclopentane: 72 ppm (pure, orange), 16.5 ppm (blend 1, blue), 23.9 ppm (blend 2, black), balance N_2 . All data filtered by a Savitzky–Golay-Function of 3rd polynomial order and a window size of 90. Left axis: Normalized hydrocarbon concentration, versus time since start of TPSR; right axis: mean catalyst temperature versus time

Fig. 12 A–B TP DRIFTS difference spectra of the blends at temperatures between 323 and 673 K. C–D Comparison between TP DRIFTS difference spectra at 673 K for each blend as measured in the experiment and as calculated from the pure substance spectra. Increasing absorbance values are due to newly formed species, decreasing values

are caused by desorbing or decomposing species. Bands at 2360 and 2320 cm^{-1} stem from unavoidable, minor changes of CO_2 presence in the IR spectrometer during the measurement which could not be excluded. The offset between individual spectra was added during data treatment for clarity

wavenumbers indicates desorption of the HCs. The intensity of these bands is determined by the amount of adsorbed substance as well as the CH-chain lengths.

The presence of water from either humidity or oxidation reactions is shown by its characteristic absorption spectrum in the region of 4000–3500 cm^{-1} and 2000–1250 cm^{-1} which sometimes overlay with the IR absorption bands of HC species.

The band at about 1700 cm^{-1} , which is more pronounced in blend 1 due to the presence of ketones, is attributed to the characteristic $\nu(\text{C}=\text{O})$ vibration of either the HC itself (blend 1, 2-butanone, cyclopentanone) or from partial oxidation products (e.g. aldehydes) of alcohols during the storage experiment [42, 48]. Partial oxidation of alcohols also results in the observed absorption bands at about 1590 and 1475 cm^{-1} in blend 1 that have previously been attributed to the asymmetric and symmetric stretching of acetate species, respectively, in the case of ethanol [49, 50]. Although ethanol is also present in blend 2, we do not observe strong bands from these reaction intermediates indicating that the oxidation of ethanol is not occurring in significant amounts. Thus, TP-DRIFTS experiments support the observed, unexpected inhibition of the ethanol oxidation reaction in the presence of 1-butanol and cyclopentane.

Figure 12c and d show the comparison between the experimental difference spectra of blend 1 and 2 at 673 K, respectively, in comparison to a theoretical difference spectra calculated from TP-DRIFTS spectra of the pure substances (see Supporting Information). In the case of blend 1, we see particularly good agreement between theory and experiment. The broad band attributed to the intramolecular H-bonding between 3500 and 3100 cm^{-1} is more pronounced in the calculated case, which could be due to a more pronounced condensation in the case of the pure substance experiments. Interestingly, the case of blend 2 is reversed: the experiment—in contrast to the calculated spectrum—shows a very pronounced decrease in the broad band indicating the vanishing of formerly condensed species. Other absorption bands [$\nu(\text{CH})$, $\nu(\text{C}=\text{O})$] are relatively weakly pronounced. However, the region below 1400 cm^{-1} shows characteristic bands for cyclopentane (compared to pure substance spectrum). The bands observed in blend 2 (Fig. 12d) are more strongly pronounced compared to the experiment with pure cyclopentane, in which only very weak absorption bands were observed (Figure S1). These findings support the observations of the storage behavior at the LGB, in which cyclopentane alone showed very poor storage behavior, whereas the storage efficiency was drastically increased in blend 2. A possible explanation is that the nonpolar rests of both alcohols could lead to an improved accumulation of cyclopentane.

4 Conclusion

In the presented study, a series production Pt–Pd/ Al_2O_3 oxidation catalyst for lean-burn engines was investigated on a LGB with respect to its storage capacity and oxidative performance for five different HCs and two different blends. The storage investigations showed that generally in the presence of several HCs, these are stored in a smaller quantity than if they were dosed as pure components. The mixture of 1-butanol, ethanol and cyclopentane showed particular characteristics: the stored amount of 1-butanol was reduced in the presence of the other two substances, but the stored amount of ethanol and especially cyclopentane could be significantly increased by the presence of 1-butanol. The increase in ethanol storage can probably be explained by the formation of intramolecular H bonds between 1-butanol and ethanol. The high number of nonpolar groups of both alcohols could lead to an improved accumulation of cyclopentane. In addition, it could be shown that the stored amounts of 2-butanone and cyclopentanone in the blend are significantly reduced. This could indicate that both ketones compete for the same storage sites on the catalyst surface.

TPSR measurements were performed to investigate the oxidation behavior. The investigations showed that for both alcohols, 1-butanol and ethanol, a conversion of more than 50% occurred already at the start temperature of 383 K. Both ketones, 2-butanone and cyclopentanone, showed a LO-temperature of 473 K and 505 K respectively. With a value of 576 K, cyclopentane showed the highest LO-temperature. Cyclopentane was the only substance which could not be completely converted even at a temperature of 773 K.

In general, it can be said that the presence of other blend components increased all LO-temperatures. Only in the case of cyclopentane could a reduction in LO temperature be demonstrated in the presence of 1-butanol and ethanol. Significant differences were found in the conversion of ethanol in the presence of 1-butanol and cyclopentane, with ethanol conversion at 383 K being only 17% compared to > 50% in the pure substance tests. Considering the previously mentioned assumption that this blend leads to many H bondings between ethanol and 1-butanol molecules, the deteriorated ethanol conversion could be associated with it.

The TP-DRIFTS analyses confirmed the LGB measurements. The formation of acetaldehyde and acetic acid by partial oxidation of ethanol was detected in the pure ethanol and blend 1 experiments. Also, the particularities of the investigations with blend 2 were confirmed with TP-DRIFTS.

Supplementary Information The online version contains supplementary material available at <https://doi.org/10.1007/s10562-021-03771-w>.

Acknowledgements The current work was funded by the Deutsche Forschungsgemeinschaft (DFG, German Research Foundation) under

Germany's Excellence Strategy—Cluster of Excellence 2186, The Fuel Science Center"—ID: 390919832.

Funding Open Access funding enabled and organized by Projekt DEAL.

Declarations

Conflict of interest The authors declare that they have no conflicts of interest to this work.

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