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# Influence of Remaining Acid Sites of an Amorphous Aluminosilicate on the Oligomerization of n-Butenes after Impregnation with Nickel Ions

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**Abstract:** Highly linear octene isomers can be produced from n-butene on industrial scale by using Ni-containing aluminosilicates as heterogeneous catalysts. These catalysts can be prepared by impregnating an aluminosilicate with a Ni(II) salt solution. This leads to a competition between acid-catalyzed and nickel-catalyzed reactions. In this study it is shown that some octene isomers are exclusively formed via an acid-catalyzed mechanism as a result of methyl group migration at the surface of a mesoporous catalyst. Specifically, the isomers 4,4-dimethylhexene (4,4-DMH) and 3-ethyl-2-methylpentene (3E-2MP) exhibit a systematic correlation compared to the amount of 3,4-dimethylhexene (3,4-DMH) formed at acid sites. By analyzing the ratio of 4,4-DMH and/or 3E-2MP to 3,4-DMH in the product spectrum before and after impregnation with a nickel precursor, the extend of acid site covered by nickel ions can be evaluated.

**Keywords:** oligomerization butene; amorphous aluminosilicate; octene isomer; acid sites; TPAD; nickel impregnation

# 1. Introduction

C4 molecules stemming from thermal or catalytic cracking are used to produce petrochemical intermediates and clean fuel additives on the industrial scale [1]. The C4 stream can be converted directly into gasoline by alkylation [2]. Depending on the composition, butadiene can be separated as a pure substance [3] and iso-butene can be selectively converted to, for example, methyl tert-butyl ether [4]. The remaining stream is mainly composed of butanes and n-butenes. The olefins can be converted to low-sulfur gasoline on acid catalysts [5]. Acid-catalyzed oligomerization of n-butenes has been known since the 1930s [6] and has been performed on numerous acid catalysts [7]. The reaction of olefins with protic acids forms a trivalent carbenium ion species, which can interact with the double bond of another olefin and form a C-C bond [8]. Highly branched oligomers are formed by this acid-catalyzed reaction [9]. Alternatively, n-butenes can be converted to linear oligomers with a selectivity of more than 99% [10]. Oligomerization activity over a homogeneous nickel system has been found for numerous reactants, from ethene to 1-octene [11]. When 1-butene is applied as reactant, selectivity to the formation of linear dimers was found to be over 80%. Formation of the linear products



2,5-dimethylhexene and 2-methylheptene was found for homogeneously catalyzed dimerization of iso-butene or co-dimerization of iso-butene with 1-butene [12]. If the ligands are varied in regard to their acidic properties, the activity of the homogeneous catalysts rises with the increasing acidity of the ligands [13]. In this context, a nickel hydride species was identified as a catalytically active species. The DIMERSOL process was developed for industrial application of the homogeneously catalyzed oligomerization of propene and butene using a catalyst system of the Ziegler-Natta type, based on a nickel derivative and activated by means of an organometallic compound [14]. In the OCTOL process for the selective dimerization of n-butenes to highly linear octenes, which are suitable for the manufacture of isononyl alcohol plasticizers, nickel loaded aluminosilicate was used as a heterogeneous catalyst [15]. Over homogeneous and heterogeneous catalysts the mechanism of coordinative oligomerization is assumed to be comparable [16]. The oligomerization process is essential for production of olefinic precursors with respect to synthesis of plasticizer alcohols. The obtained octenes are hydroformylated in a homogeneously catalyzed process by applying synthesis gas to form C9 aldehydes, then afterwards hydrogenated to form alcohols, and esterified, for example with phthalic acid, to form PVC plasticizers [17]. Both, the product quality of the plasticizers and the activity of the hydroformylation catalysts depend on the linearity of the octenes. At high linearity, the formation of terminal aldehydes is preferred [18]. Consequently, suitable catalysts for n-butene oligomerization processes have to fulfill several requirements. Nickel oxide on silica exhibits only very low activity regarding the oligomerization of n-butenes; this can be increased through application of  $Al_2O_3$  [19]. The role played by the aluminum is a subject of controversial discussion. For instance, after impregnation of Ni(NO<sub>3</sub>)<sub>2</sub> solution on aluminosilicate and subsequent calcination, the formation of nickel-aluminum phyllosilicates has been demonstrated. Furthermore, it was shown that the formed amount of nickel-aluminum phyllosilicates decreases with increasing aluminum content [20]. This is accompanied by stabilization of tri- and tetravalent nickel oxide species by aluminum [21], which in the presence of olefins (in the present case primarily 2-butene) are reduced to catalytically active nickel hydride species [22]. In addition, using in situ electron paramagnetic resonance (EPR) spectroscopy correlated with XANES/EXAFS, the formation of a Ni<sup>I</sup>/Ni<sup>II</sup> redox pair was detected during the dimerization of n-butenes, which are present as single sites [23,24]. For the formation of this species, a reaction cycle has been proposed, which requires the interaction of olefins with Ni<sup>II</sup> in the direct vicinity of a Brønsted acid site. Both are approaches for a better understanding of the catalytically active species which presuppose the presence of aluminum. This necessarily leads to a competition between acid-catalyzed and nickel-catalyzed conversion of n-butenes. In respect to the optimization of heterogeneous catalysts for the OCTOL process, both the amount of nickel and the Ni/Al ratio were increased with each catalyst generation, which led to enhanced yields of linear octene isomers [25]. Accordingly, the increased amount of nickel minimizes the acid-catalyzed conversion of n-butenes, but it cannot be suppressed completely. Due to the influence of remaining acid sites, the number of octene skeletal isomers is significantly increased [26]. Recently it was shown that, in addition to amorphous aluminosilicates, highly structured microporous zeolites [27–29] or ordered micro/mesoporous materials [30] suit as supports for the nickel species. A strong metal-support interaction in such catalyst systems leads to the mutual influence of the active nickel and acid sites providing the observed positive trends in catalytic activity and selectivity. Novel catalyst systems based on cobalt oxide on N-doped carbon [31] or cobalt-zeolite catalysts [32] show promising results for a high selectivity to linear products. However, preparation of these catalysts on an industrial scale tends to pose various challenges. Neither in the scientific literature nor in the patent literature any indications that such systems have been examined for possible industrial applications, even on a mini-plant scale, can be found. Therefore, nickel-containing catalysts are still in use for heterogeneous oligomerization in the chemical industry. At present, they are still the industrial systems of choice.

In this work, the influence of nickel on the distribution of octene isomers formed by oligomerization of n-butenes is investigated. The change in product distribution is achieved by in situ impregnation of an amorphous aluminosilicate with an organic nickel compound in a differential loop-type reactor. The findings were verified by analyzing the oligomerization of ex situ impregnated nickel aluminosilicates in a fixed bed reactor. By applying these information, a criterion is established characterizing the number of remaining acid sites after impregnation of an aluminosilicate with nickel ions as well as their effects on the oligomerization process.

## 2. Results and Discussion

### 2.1. Change of Octene Isomer Distribution by In Situ Impregnation in a Differential Loop-Type Reactor

The effect of nickel on the performance of an oligomerization catalyst can particularly be observed by the linearity of the octene skeletal isomers that are formed. Usage of a mesoporous catalyst prevents any influence of the isomer distribution through shape selectivity [33] and minimizes limitation of diffusion [34]. Two types of mechanism to oligomerize ethylene, namely acid-catalyzed and coordinative mechanism, are well known from nickel-containing, mesoporous aluminosilicates [35]. Beside the acidic behavior of the amorphous aluminosilicate, the surface-near aluminum can activate nickel for oligomerization. The catalytic testing was performed at 80 °C. Under these conditions, only a small conversion occurs via the strongly temperature-dependent acid-catalyzed mechanism. This underlines the activity of nickel for oligomerization. To distinguish between products of nickeland acid-catalyzed oligomerization of n-butenes an in situ impregnation in a loop-type reactor can be performed. Through the cycle pump of this reactor type a nickel-containing solution can pass serval times the catalyst bed to achieve an effective impregnation. A high nickel dispersity can be achieved by using organometallic precursors. The oligomerization products over time on stream are shown in Figure 1A for the oligomerization over acidic aluminosilicate and after in situ impregnation of the catalyst with Ni(cp)<sub>2</sub>. Before impregnation, mainly 3,4-dimethylhexene (3,4-DMH) was formed, but after impregnation the proportion of 3,4-DMH was reduced in favor of n-octene (n-O) and 3-methylheptene (3-MH). However, a significant quantity of 3,4-DMH is formed even after the addition of the nickel solution. The coordinative formation of 3,4-DMH is attributed to a reaction of 1-butene with 2-butene and/or dimerization of 2-butenes [25]. Investigations regarding the reactivity of the individual n-butenes via a coordinative mechanism indicated that the reaction of 1-butene is favored [36]. Accordingly, the formation of 3,4-DMH via a coordinative mechanism is depending on the proportion of 1-butene in the feed, the WHSV, and the reaction temperature. Due to a varying feed composition in industrial operation, the ratio of n-O to 3,4-DMH cannot be used as a criterion to assess the saturation of acid sites by nickel ions. Due to the presence of nickel, the conversion suddenly increases from 5 wt.% to over 30 wt.% after impregnation. At 300 h time on stream, the conversion reached a constant level of approx. 25 wt.%. This value is much higher compared to the acid-catalyzed conversion. Nickel can be considered highly active even at 80 °C. Figure 1A also shows that in acid-catalyzed oligomerization of n-butenes, approx. 10% other skeletal isomers are formed, which can no longer be observed after impregnation with Ni(cp)<sub>2</sub> despite a higher conversion-level. These skeletal isomers are described as side products below. Formation of these isomers can be attributed to skeletal isomerization [37]. Migration of a methyl group is based on the formation of stable cyclopropyl carbon cations [38]. On bifunctional catalysts with similar acidity it can be shown that zeolites with one-dimensional channel system and a pore diameter less than 0.7 nm, such as mordenite, do not catalyze skeletal isomerization of butane or pentane [39]. However, n-butene is isomerized to iso-butene on ferrierite with a slightly lower pore diameter to mordenite but with a two-dimensional channel structure [40]. An adequate size or structure of the pores is necessary for the formation of side products. Other investigations indicate that a methyl group migrates to Brønsted acid sites [41]. In this investigation a mesoporous aluminosilicate was used, to prevent any influence caused by pore size. Furthermore, it is known from literature regarding the oligomerization of ethylene that micropores are not necessarily conducive to the activity [42]. Mainly 2,3-dimethylhexene (2,3-DMH), 4,4-dimethylhexene (4,4-DMH), and 3-ethyl-2-methylpentene (3E-2MP) were discovered as side products. With oligomerization of n-butenes on solid phosphoric acid, these isomers were

also identified at reaction temperatures between 150 and 250  $^{\circ}$ C [43]. The proportion of these skeletal isomers in the product spectrum shown in Figure 1B indicates that none of these isomers are formed after impregnation. Hence, the absence of these C8 side products points out the complete saturation of the Brønsted acid sites by nickel ions.



**Figure 1.** Distribution of octene skeletal isomers before and after in situ impregnation with  $Ni(cp)_2$  at 140 h time on stream; (**A**) distribution of the main products and summarized side products for the respective conversion, (**B**) distribution of the side products stemming from the dimerization of n-butene.

Not all C8 side products are equally suitable for assessing the remaining Brønsted acidity. The acid-catalyzed oligomerization of n-butenes was repeated in the differential loop-type reactor by varying the reaction temperature. Every reaction temperature was considered for at least 150 h time on stream to reach a steady-state. Figure 2A shows the ratio of 4,4-DMH and (B) the ratio of 3E-2MP to the main product 3,4-DMH during acid-catalyzed conversion at different temperatures. Due to slight fluctuations in the feed composition, there is a slight change in the conversion of n-butenes. However, this has no influence on the ratio of 4,4-DMH and 3E-2MP to 3,4-DMH; a constant ratio was identified at all temperatures. On the other hand, the ratio of 2,3-DMH to 3,4-DMH in Figure 2C does not remain at a constant level at different temperatures. Consequently, the formation of 2,3-DMH is dependent on other factors, such as the proportion of 1-butene in the feed, and this cannot be used as a criterion to assess the remaining Brønsted acid sites. The 3E-2MP isomer behaves similarly to 4,4-DMH and, potentially, could also be used as a criterion.



**Figure 2.** Ratio of octene skeletal isomer after methyl group migration to the main product 3,4-dimethylhexene at different reaction temperatures in differential loop-type reactor for the acid catalyzed conversion of n-butenes; ratio of side products (**A**) 4,4-DMH; (**B**) 3E-2MP; and (**C**) 2,3-DMH to the main product 3,4-DMH.

In a differential loop-type reactor, the products formed are continuously passed over the catalyst bed. This leads to a product inhibition and dilution of the fresh feed. The selectivity ratio mentioned in Figure 2, 0.023 for 4,4-DMH and 0.03 for 3E-2MP to the main product 3,4-DMH at 100 °C, can be seen as the maximum methyl group migration rate under differential conditions at this temperature. By using a fixed bed reactor the concentration of the formed products changed along the reactor length. This allows a higher ratio of C8 side to main products. In order to evaluate the amorphous aluminosilicate with respect to acid-catalyzed oligomerization, a reaction temperature of 100 °C is suitable. At this temperature, higher conversions are achieved and a variation of the conversion by feed rate is feasible.

# 2.2. Correlation between Yield of Side Products and Feed Rate in Fixed Bed Reactor

The formation of 3,4-DMH compared to the formation of side products at a constant temperature (100 °C) and varying conversion was investigated on acidic aluminosilicate in fixed bed reactor. The residence time of the olefins in the catalyst bed was influenced by varying the feed rate over a constant catalyst mass. This procedure is well established for assessing catalyst performance [44]. At a reduced feed rate, the mass of olefins per hour per gram catalyst was reduced, leading to increased conversion rates. Figure 3 shows the amount of 3,4-DMH in the discharge of the reactor compared to the amount of side products 4,4-DMH and 3E-2MP. The increasing amount of 3,4-DMH is due to the reduced feed rate. Increasing the residence time of the n-butenes over the catalyst bed favors dimerization with migration of a methyl group disproportionately. Therefore, the amount of side products compared to 3,4-DMH increases quadratically. The formulas given in Figure 3 for the correlation between 3,4-DMH and the respective side product apply only for the investigated reaction temperature (100 °C) and the distribution of the acid sites of the chosen acidic aluminosilicate. Both factors influence the ratio of dimerization with migration of a methyl group (scheme in Figure 3).



**Figure 3.** Absolute amount (in wt.%) of 4,4-dimethylhexene (4,4-DMH) and 3-ethyl-2-methylpentene (3E-2MP) at different feed rates versus absolute amount of 3,4-DMH in product stream at the constant mass of amorphous aluminosilicate in proton form, 100 °C reaction temperature and 30 bar (liquid phase); trend line with equations, coefficient of determination and scheme of the competing reactions.

The activity of a methyl group migration can be described by the ratio of the side to the main product. Based on the results in the differential loop-type reactor, a constant ratio of 4,4-DMH and 3E-2MP to 3,4-DMH could be found under steady state conditions (see Figure 2). In this case, a dependence of the ratio of the temperature could be found. It could be found an increased ratio with

increasing temperature. The catalytic testing in the fixed bed reactor were performed at a constant temperature of 100 °C. However, the results in Figure 3 indicate a correlation of feed rate and activity to methyl group migration. To clarify this dependence, the ratio of 4,4-DMH and 3E-2MP to 3,4-DMH is plotted against the residence time in Figure 4. A linear trend line with associated formula is also given. Both C8 side products are formed preferentially at higher residence time. The rise of the ratios is comparable for both side products. The number of products after methyl group migration of 3,4-DMH increases 0.003 times per minute of residence time. The ratio is independent of the catalyst mass because the yield of both side and main products is influenced by the same parameter.



**Figure 4.** Ratio of the side products 4,4-DMH and 3E-2MP to the main product 3,4-dimethylhexene (3,4-DMH) at different residence times, varied through feed rate in the fixed bed reactor (100 °C, 30 bar); (**A**) linear area up to 7 min; (**B**) ratio at residence time from 7 to 25 min.

At a residence time of 6.5 min a ratio of side to main products comparable to the experiment in the loop-type reactor could be found. As already were discussed, the methyl group migration suppressed by a high content of C8 molecules. Due to the increase in the concentration of products along the catalyst bed, such product inhibition will only occur in the back of the catalyst bed. Figure 4B shows that even at a residence time of 10 min, the ratio deviates from linear progression. However, it can be assumed that if the residence time is too high, there will be no further increase of this ratio since a higher proportion of products is already formed at the beginning of the catalyst bed. This suggest that studies on the formation of side product at nickel-containing catalysts should be carried out at residence times of between 7 and 8 min. In this case, quantifiable amounts of side products are formed at existing acid sites and the product inhibition does not yet significantly affect the migration of methyl groups.

## 2.3. Determination of Acid-Catalyzed Oligomerization on Nickel-Containing Catalysts

The correlation between 3,4-DMH and the side products in Figure 3 can be used to distinguish between acid- and nickel-catalyzed oligomerization of n-butenes over nickel-containing samples. By in situ impregnation an exclusive nickel-catalyzed oligomerization could be realized for a heterogeneous catalyst. The production of such catalyst in industrial scale is not feasible. To produce oligomerization catalysts on a ton scale, inorganic nickel salts are preferably used for an ex situ impregnation. As a result, lower dispersities are achieved and despite a high nickel content, not all acid sites are necessarily masked with nickel ions. The proportion of side products formed can be used to assess the saturation of acid sites with nickel by catalytic data. Figure 4A shows the part of main products 3,4-DMH and n-O in the product spectrum. These catalytic testings were performed at 100 °C in liquid phase with a residence time of 7.8 min. As the nickel content is increased, the amount of 3,4-DMH decreases whereas

the amount of n-O formed increases. This indicates an increasing part of coordinative oligomerization of n-butenes as the nickel content increases. The side products in the product stream in Figure 4B show that the catalyst with a nickel content of 14 wt.% does not form any C8 side products. This suggests that, with this catalyst, oligomerization of n-butenes takes place completely via a coordinative mechanism.

The results from Figure 5 can be used to calculate the mass of formed octene isomers per gram catalyst with varying nickel content. These values are summarized in Table 1. Regarding the nickel-free aluminosilicate, a high yield of the highly branched octene isomer 3,4-DMH can be observed. The overall yield of octenes decreases slightly by the presence of nickel. However, a higher yield of the more linear octene isomers can be observed. In comparison to the oligomerization of ethylene over nickel-containing, mesoporous aluminosilicate, the yield of oligomers is at least one magnitude lower [45]. This reduced activity can be attributed to the hindrance of C-C bond formation by the more sterically demanding butene molecules in coordination with active nickel species.



**Figure 5.** Part of octene isomers in product stream after oligomerization of n-butenes on amorphous aluminosilicates with varying nickel content between 0 and 14 wt.% in continuous operation (100 °C, liquid phase, average over 180 h on stream); (**A**) part of main products and (**B**) part of side products.

Catalyst Sample	m <sub>3,4-DMH</sub> /g <sub>cat</sub> per h	m <sub>3-MH</sub> /g <sub>cat</sub> per h	m <sub>n-O</sub> /g <sub>cat</sub> per h
Ni-free	2.4	0.1	0
1 wt.% Ni	1.2	0.5	0.2
6 wt.% Ni	0.9	0.6	0.2
14 wt.% Ni	0.5	1.1	0.3

**Table 1.** Mass of octene isomers formed over catalyst samples with different nickel content per gram catalyst per hour in a fixed bed reactor (100 °C, 30 bar, residence time of 7.8 min).

Based on the part of side products in Figure 5B, the amount of 3,4-DMH formed via a cationic mechanism can be calculated. Therefore, the correlation between side products and the acid-catalyzed main product 3,4-DMH can be drawn from Figure 4. This dependency can be regarded as a kind of calibration straight line. Based on the mentioned formula, the proportion of 3,4-DMH formed by acid-catalyzed oligomerization can be calculated. Since the 3,4-DMH can also be formed via a coordinative oligomerization, a residual acid-catalyzed reaction cannot be clearly assigned without the consideration of the side products. The measured part of 3,4-DMH formed over catalyst with different nickel content should be compared to the calculated values using the proportion of 4,4-DMH and 3E-2MP. The results are summarized in Table 2.

14 wt.% Ni

Catalyst Sample	Measured Content of 3,4-DMH in Product Stream, wt.%	3,4-DMH calc. via 4,4-DMH, wt.%	3,4-DMH calc. via 3E-2MP, wt.%
1 wt.% Ni	13.0	14.8	14.3
6 wt % Ni	96	9.6	94

0

0

5.1

**Table 2.** Comparison of measured content of 3,4-DMH in product stream with theoretical part of 3,4-DMH generated via carbenium mechanism calculated via the part of 4,4-DMH and 3E-2MP in the product stream, average over 180 h on stream.

After oligomerization, the catalyst with 1 wt.% nickel exhibits an average 3,4-DMH content of 13.0 wt.%. However, based on the amount of side products formed, it should be possible to detect 14.8 wt.% (calculated from 4,4-DMH) or 14.3 wt.% (calculated from 3E-2MP) in the product stream. Accordingly, the calculated part of 3,4-DMH was slightly overestimated. The correlation between 3,4-DMH and side products was determined on acidic aluminosilicate in continuous operation over approx. 500 h time on stream. As a result, it can be concluded that during the long time on stream acid sites are deactivated, probably by deposits of high boiling products. The deactivation of strong acid sites during the oligomerization of propylene is well known since decades [46]. The activity in steady-state is related to acid sites of moderate strength. Investigation of the oligomerization of 1-butene on beta zeolite with different acidities indicates that secondary reactions take place, such as hydrid transfer or migration of a methyl group on strong Brønsted acid sites [47]. These sites may also be responsible for the formation of side products during the oligomerization. Through deactivation, the correlation between 3,4-DMH and side products changes. Figure 6A shows the part of 3,4-DMH formed on the catalyst with 1 wt.% nickel over 180 h on stream. The industrial feed applied here shows fluctuations in the olefin concentration. In the first 80 h on stream, the resulting change in WHSV shows a direct change in the amount of 3,4-DMH that is formed. As the strong acid sites are increasingly deactivated from approx. 75 h on stream onwards, less 3,4-DMH is formed at a constant WHSV. Oligomerization of 1-butene on ZSM-5 containing Al and ZSM-5 containing Fe was investigated in the literature [48]. If in ZSM-5 aluminum is substituted with iron, this reduces the acidity, which was measured by the reduced conversion of 1-butene. However, the Fe-ZSM-5 system tends to show a lower deactivation. After initial deactivation of the strong acid sites, this catalyst exhibited stable conversion, probably due to moderately strong acid sites that do not catalyze the formation of deactivation products. Transferring these findings to the mesoporous aluminosilicate discussed here, deactivation should influence the formation of side products. Figure 6B shows the measured proportion of 3,4-DMH compared to the part of 3,4-DMH calculated from the side products. As deactivation of strong acid sites increases, activity for migration of methyl group decreases and fewer side products are formed. After 150 h time on stream, the calculated amount of 3,4-DMH is similar to the measured value. The reaction system approaches the stationary state that was already reached when determining the measured values from Figure 3. It can be concluded that an increased density of strong acid sites has a positive effect on the formation of side products.

For the sample containing 6 wt.% nickel, Table 1 shows a good correlation between the calculated and measured amounts of 3,4-DMH. It can be assumed that with this catalyst almost the entire amount of 3,4-DMH is formed via a cationic mechanism. This can be attributed to the small amount of active nickel sites for coordinative oligomerization. While with a coordinative mechanism 3,4-DMH is the product of dimerization of 2-butene or co-dimerization of 1-butene and 2-butene, 1-butene is preferably dimerized on active nickel sites [49]. Consequently, with a small number of active nickel sites, almost no 2-butene is coordinatively dimerized to 3,4-DMH as the nickel sites are constantly covered only with excessive 1-butene.



**Figure 6.** Catalytic results of n-butene oligomerization on the catalyst with 1 wt.% Ni at 100 °C; (**A**) 3,4-DMH in the product stream in continuous operation by varying the content of C4 olefins in the feed; (**B**) comparison between measured and calculated content of 3,4-DMH via side products in the product stream.

The number and strength of acid sites of a solid material can be determined via temperature-programmed ammonia desorption (TPAD). The density of acid sites determined with TPAD shows, for example, a very good correlation with the catalytic activity for isomerization of n-butane [50]. The desorption profiles of the aluminosilicates with and without nickel are shown in Figure 7. The desorption profile of the aluminosilicate in (A) shows a broad distribution of acid sites with different strength. The desorption of ammonia at temperatures above 500 °C indicates strong acid sites [51]. For the nickel-free aluminosilicate a desorption of 830  $\mu$ mol NH<sub>3</sub> per gram sample was measured. A total of 130 µmol/g strong acid sites could be assigned. By adding nickel to the surface, these acid sites are increasingly masked and a new, narrow signal becomes visible. The formation of metal ammonia complexes occurs by coordinative interaction between ammonia and metal cations at the surface of porous solids [52]. These complexes can decompose at temperatures above 450 °C [53]. Increased nickel content decomposes more complexes and increases the intensity of the resulting signal. The sample with 1 wt.% nickel in Figure 7B does not show this narrow signal. However, in this sample desorption is detected at temperatures above 500 °C, comparable to the nickel-free sample. This shows the presence of strongly acidic centers, which was already predicted by the interpretation of the catalytic data regarding the correlation between 3,4-DMH and 4,4-DMH. These acid sites are not masked by impregnating the aluminosilicate with only 1 wt.% nickel. Therefore, a significant amount of 4,4-DMH is formed, which decreases with time by deactivation of strong Brønsted acid sites until the steady-state (analogous to reference [46]).

The catalyst with 6 wt.% nickel shows no significant deactivation within the first 100 h time on stream and the amount of 3,4-DMH formed by acid catalysis can be calculated directly from the amount of 4,4-DMH (see Table 2). This sample also shows no desorption of ammonia in Figure 7B at 600 °C in contrast to the sample with 1 wt.% nickel. The strong acid sites were masked with nickel in the catalyst with a nickel content 6 wt.%. Through the course of the ratio of 3,4-DMH to 4,4-DMH over time, the deactivation of strong acid sites during the reaction can be interpreted. In industrial operation, this information is very helpful in order to be able to make predictions about the conditions of the catalyst and about the further run-time. Usually, no sample of the catalyst can be taken from the reactor during the industrial operation, so the interpretation of obtained catalytic data is extremely important.



**Figure 7.** Temperature programmed desorption of ammonia after removal of physisorbed compounds at 200 °C; (**A**) profile of amorphous aluminosilicate in proton form and (**B**) of impregnated samples with varying nickel content.

The catalyst with 14 wt.% nickel has a higher number of active nickel sites and, as a result, 2-butene is also coordinatively converted to 3,4-DMH with this catalyst as more nickel centers are available that are not completely covered by 1-butene. This is the reason why no prediction can be made about the part of acid catalysis based on the amount of 3,4-DMH as it can obviously be formed also by coordinative catalysis. This catalyst exhibits no formation of side products, which means that complete saturation of the acid sites with nickel ions can be assumed. This information would not have been available without consideration of the side products.

The interaction of nickel cations with the surface of acidic aluminosilicate results in a decrease of Brønsted acidity, whereas the Lewis acidity increases [54]. As already discussed, these new Lewis acid sites can form complexes with ammonia, which in case of nickel are decomposed at about 500 °C and cause a corresponding signal in the TPAD. The interaction of nickel with aluminosilicates can be described by the HSAB theory (hard and soft acids and bases). The nickel cations interacting as electrophilic compound with the electron-rich surface-oxygen in vicinity to aluminum [55]. A classical replacement of protons by nickel cations at Brønsted acid sites are conceivable [56] as well as the interaction of nickel cations with silanol groups [57]. In contrast to the oligomerization of ethylene a complete substitution of protons with nickel cations favors the oligomerization of butenes to the desired products.

#### 3. Materials and Methods

## 3.1. Catalysts

Acid-catalyzed oligomerization of n-butenes was investigated on granulated amorphous aluminosilicate (Grace, DAVICAT O 701, Columbia, MD, USA) with particle sizes between 1 and 2.5 mm, a Si/Al ratio of 6.4 and an average pore diameter of 11 nm. The average pore diameter was determined using nitrogen physisorption and evaluation according to Barret, Joyner, and Halenda [58] as well as porosimetry with mercury [59]. To assess the influence of nickel on the formation of different octene isomers, the amorphous aluminosilicate was impregnated by incipient wetness method with an aqueous Ni(NO<sub>3</sub>)<sub>2</sub> solution and then calcined at 550 °C for 10 h under a nitrogen stream. For impregnation, the volume of nickel solution was adjusted to suit the pore volume. The concentration of nickel ions in the solution was adjusted in the way that, after calcination, catalysts with a nickel content of 1, 6, and 14 wt.% were obtained.

### 3.2. Characterization

The acid strength distribution and number of acid sites of the used amorphous aluminosilicate were determined by temperature-programmed desorption of ammonia. The measurement was carried out with the TPDRO 1100 device from Thermo Scientific (Waltham, MA, USA). For this purpose, 1 g of the sample was weighed into a measuring cell and calcined at 550 °C. When the sample had cooled to room temperature, it was loaded with ammonia for 2 min. The physically and weakly adsorbed part of the ammonia was removed at 200 °C with argon. After the sample had cooled again, the desorption profile from 40 °C to 600 °C was determined with a heating rate of 5 K/min and a flow rate of 20 mL/min argon. The maximum temperature was maintained for 30 min. Detection took place via a thermal conductivity detector. To quantify the amount of chemically adsorbed ammonia, the sample was heated to the temperature of the desorption maximum and a defined quantity of ammonia was injected into the system with a gas syringe. The measurement signal was used as a calibration point for the respective temperature. The catalysts with different nickel content were characterized in the same way.

#### 3.3. Analysis of Products and Feed

The composition of feed and reaction product was determined online via a sample loop with two gas chromatography systems (GC). Distribution of the C4 fraction is determined separately by GC. Distribution of the octene isomers and the proportion of the C4 fraction over the complete product spectrum were analyzed by hydrogenating the evaporated components via a Pd catalyst in the GC liner with hydrogen as a carrier gas [60]. An inlet temperature of 190 °C was used to avoid cracking of oligomers in the liner. The distribution of the octene skeletal isomers is directly accessible through hydrogenolytic gas chromatography. The arrangement of the isomers was verified with the corresponding pure substances and based on literature values [61]. The supporting information provides more detailed information regarding the calculation of conversion and selectivity.

#### 3.4. Testing and In Situ Impregnation in a Loop-Type Reactor

Acid catalyzed conversion of n-butenes was tested in a differential loop-type reactor. The ratio of feed rate and cycle was set to 1:10 to ensure adequate back mixing [62]. Four grams of aluminosilicate was added to the reactor for this purpose. A mixture of n-butenes, iso- and n-butane was used as the feed. The feed was set to a weight hourly space velocity (WHSV) of 7.5 g olefin per gram aluminosilicate. To ensure a reaction in liquid phase, the reaction temperature was varied between 80 and 100 °C at a pressure of 30 bar. For in situ impregnation, 0.5 g bis(cyclopentadienyl) nickel(II) (nickelocene, Ni(cp)<sub>2</sub>) was dissolved in 100 mL dry n-heptane and stirred for 1 h. The solution was then filled into a pressure-resistant vessel under argon and fed via a by-pass into the reactor with fresh feed under reaction conditions. During impregnation at 80 °C, the feed and discharge of the reactor were closed and the mixture was stirred with circulation for 1 h. Following this, the feed and discharge were opened and the conversion and distribution of the C8 isomers were analyzed. A typical composition of feed and a diagram of the reaction apparatus can be found in the supporting information.

#### 3.5. Testing in a Fixed Bed Reactor

Oligomerization of n-butenes on acidic aluminosilicate and catalysts based on this with different nickel content were investigated in a fixed bed reactor in continuous operation. For this purpose, 12.5 g catalyst was filled into a tube with an inside diameter of 6 mm. Glass beads in front of and behind the catalyst filling acted as preheating and cooling zones. Oligomerization was carried out at 100 °C with 30 bar in the liquid phase with a WHSV of 7.5 g olefin per hour per gram catalyst.

#### 4. Conclusions

Heterogeneous catalysts for coordinative oligomerization of n-butenes are produced on an industrial scale through impregnation of acidic aluminosilicates with a nickel precursor. Remaining acid

sites can convert n-butenes via an acid-catalyzed mechanism and thus influence product distribution. It was shown that certain octene isomers are exclusively formed via an acid-catalyzed mechanism. Some octene side products, namely 4,4-dimethylhexene (4,4-DMH) and 3-ethyl-2-methylpentene (3E-2MP), are formed by a methyl group migration of 3,4-dimethylhexene (3,4-DMH) at strong acid sites. Sufficient pore size to form transition states is required. The amount of these side products depends on the reaction temperature, space velocity, and density of strong acid sites. For a specific acidic aluminosilicate, a distribution between side products and 3,4-DMH can be determined under different reaction conditions. By using this aluminosilicate for oligomerization after impregnation with a nickel precursor, the amount of 4,4-DMH and/or 3E-2MP indicates the degree of saturation of active acid sites with nickel ions. The proportion of 3,4-DMH formed through an acid-catalyzed mechanism can be calculated. This allows the effectiveness of an impregnation method and the influence of different nickel precursors and quantities to be determined by catalytic testing without any further characterization. Furthermore, information about the deactivation of strong Brønsted acid sites can be obtained by the shifting ratio of 3,4-DMH to 4,4-DMH over time. With increasing deactivation, the relative part of 4,4-DMH decreases. As a result, predictions can be made about the further catalyst activity in industrial operation. During continuous operation, where no catalyst samples can be taken, the assessment of how to proceed depends on such important catalytic information.

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