



# Communication A Novel Model Parameter for the Assessment of the Dimerization of n-Butenes over Ni-Containing Aluminosilicate Catalysts

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**Abstract:** Previous investigations on the dimerization of n-butenes over Ni-containing Al-MCM-41/ZSM-5 mixed-phase catalysts have shown a correlation between the conversion and the Ni/(Al + Ni) ratio as well as between the conversion and the metal–support interaction, which is represented by the reduction degree. In the present work, both approaches are combined to a novel model parameter, which allows to determine the proportion of active Ni species on the Al-Ni site pairs and thus provides crucial insights into formation of catalytically active nickel sites as well as their effects on the selective formation of low-branched dimers.

Keywords: n-butenes; dimerization; ISO index; model parameter; nickel catalysts; OCTOL process

## 1. Introduction

Against the background of increasing oil shortage as well as global efforts to improve the sustainability of industrial processes, the selective dimerization of butenes, yielding long-chain hydrocarbons, represents a potential for a more extensive utilization of C4 alkenes. The dimerization is applied, for instance, in the so-called OCTOL process, which uses a nickel-containing amorphous aluminosilicate as a catalyst [1,2]. The objective of this process is providing a dimer fraction with the lowest accessible degree of branching. Based on the selective formation of low-branched dimers, surfactants and plasticizers of high product quality can be produced, thus increasing the energetic and economic efficiency of the entire processing of the C4 cut [3].

Since the branching degree of the dimers, displayed by the ISO index, strongly affects the quality of the plasticizing agents, a precise control of this parameter is essential. The ISO index indicates the mean number of methyl branches per molecule: n-octenes (n-O) contribute 0, methylheptenes (MHp, mainly 3-methylheptenes) contribute 1 and dimethylhexenes (DMHx, mainly 3,4-dimethylhexenes), contribute 2 to the ISO index of the C8 fraction [4] (cf. Figure 1). Currently, applied catalysts of the OCTOL process tend to generate dimer mixtures with an ISO index  $\geq$  1.1. Since there is a lack of knowledge regarding the formation of effective catalytically active nickel sites, a potential for further improvement exists.

Despite numerous studies on the formation of catalytically active nickel sites, full clarification regarding the targeted generation of these on the catalysts surface has not been achieved [3]. However, there is agreement on the positive effect of aluminum atoms or acid sites, respectively, on the formation of selective acting nickel sites due to an improved metal–support interaction and the resulting favoring aluminosilicates over silicates or alumina as a support material [5–10].



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**Figure 1.** Oligomerization of n-butenes to linear n-octenes, branched 3-methylheptenes, highly branched 3,4-dimethylhexenes, and long-chain oligomers.

With respect to literature, a vast number of nickel-loaded aluminosilicates of various structure and texture have been investigated regarding their suitability as catalysts for the selective dimerization of short chain olefins [3]. In addition to nickel-containing meso-porous aluminosilicates, analogous zeolitic systems proved to be promising catalysts as well. Besides the high catalytic activity and selectivity to linear dimers, however, these often show rapid deactivation due to diffusion-limiting effects caused by the microporous structures [11,12]. Therefore, in previous work [1], biporous aluminosilicates consisting of a mesoporous MCM-41 and a microporous ZSM-5 phase were synthesized, which combined the positive catalytic properties of both materials regarding long-term stability, catalytic activity, and target product selectivity.

The catalytic performance of these samples was attributed to an interaction of nickel sites with vicinal aluminum atoms or acid sites, resulting in the formation of Al-Ni site pairs, since a correlation between Ni/(Al + Ni) ratio, catalytic activity, and selectivity was found. By means of XPS it was demonstrated that with increasing Ni/(Al + Ni) ratio the nickel sites tend to form larger agglomerates in vicinity to aluminum atoms, which are much more stable than single nickel atoms. At the same time the enlarged number of nickel atoms in vicinity to aluminum atoms leads to a reduced electronic influence of the aluminum atoms or acid sites on the nickel atoms, which results in an enhanced formation of nonlinear dimers based on the unfavorable electronic state of nickel sites [1,2].

Moreover, a relation between total acidity, reduction degree, and conversion was shown, suggesting that increased metal–support interactions, indicated by a decreased reduction degree, favor the formation of electron deficient catalytically active nickel sites [7]. Both approaches were supported by a broad characterization and catalytic tests of the former investigated samples [1].

In the context of this study, the combination of both approaches leading to a novel model parameter is presented for catalyst samples with a comparable nickel amount, but with a different degree of reduction depending on the Si/Al ratio.

## 2. Results and Discussion

It has been already clearly demonstrated [1] and recently confirmed again [9] that, for catalyst samples with an enhanced nickel content, a preference of the coordinative reaction mechanism of oligomerization over acid-catalyzed mechanism was identified. The summarized results of the catalytic testing are once more shown schematically in Figure 2.

n-butenes conversion increased due to the growth in the nickel content. In addition, the increase in the Si/Al ratio also led to enhanced conversions (Figure 2a). This is based on the higher number of active nickel sites or on better stabilization of the active nickel species in a zeolitic phase with balanced acidity. The lowest ISO indices were obtained for catalysts with middle Si/Al ratios and comparable Ni contents (Figure 2b). The reason for this could be the high crystallinity and uniformly distribution of Al-Ni site pairs on the surface [1].



**Figure 2.** (a) Conversion of n-buttenes and (b) ISO index as a function of the Si/Al ratio and nickel content. The colors encode the numerical value in %. (blue  $\rightarrow$  red): conversion (3  $\rightarrow$  26), ISO index (0.9  $\rightarrow$  2.0).

Especially considering the pronounced Brønsted acidity of some samples and the simultaneous dominance of the coordinative reaction mechanism, an involvement of the Brønsted acid sites on the activation or stabilization of catalytically active nickel species, compensating the acid catalytic effect, seems highly likely. However, not every aluminum atom or every Brønsted acid sites is capable of activating nickel sites or contribute to the formation of catalytically active nickel sites. Strong and medium-strong acid sites, or aluminum atoms leading to the formation of these, are suitable to contribute to the formation of catalytic active sites, which selectively form less branched dimers. The weaker the acid sites are, the greater the proportion of branched dimers formed. Furthermore, by the strong interaction of nickel sites with the Brønsted acid sites, the electronic state of the nickel atoms and thus the product selectivity is changed [1,2].

To investigate the reducibility of the nickel species, TPR experiments have been carried out. The hydrogen consumption, corresponding to the absolute amount of reduced nickel, was detected for the reduction up to 550 °C for each sample. Based on the nickel content determined by ICP-OES and the hydrogen consumption, the reduction degree (proportion of reduced Ni) was calculated for each sample (cf. Table 1). In general, the samples with Si/Al ratios of 40 and 70 exhibit a decreased reduction degree compared to samples with a Si/Al ratio of 10. This could be attributed to the stronger interactions between the crystalline support material and the resulting stronger metal–support interactions. Hoang et al. [13] presumed that the stabilizing effect is due to an interaction of nickel with Brønsted acid sites of the ZSM-5 support material. In previous work [1], a relation between total acidity, reducibility, resulting in an enhanced catalytic activity. Based on this, correlation reduction degree can be used as an indirect proportional measure for the metal–support interactions.

 Table 1. Characterization and catalytic data of the synthesized catalysts.

Catalyst Sample	Si/Al Ratio	Ni Content [wt%]	Reduction Degree [%]	Ni/(Al + Ni) Ratio	Ni/(Al + Ni) (1/red)	Conversion [%]	ISO Index
OS-10-3	9.6	4.5	83	0.34	0.004	3.4	1.2
OS-10-5	9.4	7.2	82	0.45	0.006	8.8	1.3
OS-40-3	30.6	4.1	64	0.58	0.009	14.7	1.0
OS-40-5	29.9	6.6	25	0.69	0.028	21.2	1.0
OS-70-3	47.2	4.6	76	0.70	0.009	13.9	1.0
OS-70-5	52.7	6.6	15	0.80	0.052	25.9	1.2

In order to gain a deeper understanding of the generation of selective acting nickel sites, the proportion of catalytically active Ni species on the Al-Ni site pair can be estimated by combining the Ni/(Al + Ni) ratio and the reduction degree. For this purpose, the Ni/(Al + Ni) ratio was multiplied by the reciprocal of the reduction degree. The latter is indirectly proportional to the metal–support interaction and should therefore represent the ability to form active nickel sites or activate them, respectively, as it was shown in the previous study [7]. The product of the Ni/(Al + Ni) ratio and the reciprocal of the reduction degree (1/red) can thus be used to represent the proportion of active Ni species on the Al-Ni site pair.

Figure 3a shows the conversion of n-butenes on investigated catalysts depending on the calculated product as a characteristic value for estimating the proportion of catalytically active nickel sites on the Al-Ni site pair. As the size of this product increases, the conversion increases at the same time, due to the enhanced stability of the nickel sites caused by the increased Ni/(Al + Ni) ratio as well as the improved ability to activate the nickel sites based on the increased metal–support interaction. However, conversion seems to tend towards a limit value, as can be seen from the reduction of the increase as the characteristic value grows. It is quite conceivable that at very high Ni/(Al + Ni) ratios, the acidity of the support material is not sufficient to activate more nickel sites, and thus no further catalytically active nickel sites are generated. Furthermore, it is remarkable that all value pairs fit very well into the trend, whereas when plotting the conversion against the Ni/(Al + Ni) ratio, such a clear trend was not obtained [1].



**Figure 3.** (a) Conversion of n-butenes and (b) ISO index depending on the product of Ni/(Al + Ni) ratio and 1/red.

Figure 3b shows the ISO index as a function of the product of the Ni/(Al + Ni) ratio and the reciprocal of the reduction degree for the investigated catalysts. There is a relatively broad range of product values, leading to an improved interaction between Ni species and vicinal aluminum atoms or acid sites accompanied by a beneficial electronic state of the nickel sites and resulting in a low ISO index. If the product of the Ni/(Al + Ni) ratio and the reciprocal of the reduction degree is too low, unstable nickel sites with weak metal–support interaction are mainly present, which yield low conversions and low selectivities towards low-branched dimers.

The higher the value of this product, the better the metal–support interaction, leading to the formation of more stable electron-deficient nickel sites, which in turn are responsible for increased conversion and improved selectivity (cf. catalyst samples OS-40-3, OS-70-3, and OS-40-5). At very high product values, the proportion of nickel is very high leading to a decrease in the electron-deficient character of these and thus to increasing ISO indices (cf. catalyst sample OS-70-5).

## 3. Materials and Methods

#### 3.1. Catalysts Preparation and Characterization

In order to examine the influence of both the Si/Al ratio and the nickel content on the dimerization of n-butenes over Ni-containing Al-MCM-41/ZSM-5 mixed-phase catalysts, samples with a various Si/Al ratio and nickel amount were synthesized. Initially, 39.8 g hexadecyltrimethylammonium bromide (98+%, Merck-Millipore, Burlington, MA, USA) and 165.52 g tetrapropylammonium bromide (98%, Sigma Aldrich, Burlington, MA, USA) have to be solubilized in 840 mL DI-water and stirred for 20 min. This is followed by a stepwise addition of a precursor mixture composed of sodium trisilicate (Sigma Aldrich, Burlington, MA, USA), sodium aluminate (99+%, Sigma Aldrich) and nickel (II) nitrate hexahydrate (Chempur, Karlsruhe, Germany). While sodium aluminate and nickel (II) nitrate hexahydrate are used to adjust the Si/Al ratio and nickel content, respectively, the amount of sodium trisilicate (91.42 g) was kept constant for all samples.

After adding the precursors to the surfactant solution, the pH-value was adjusted to 10 by dropwise addition of 50 wt.-% sulfuric acid (95–97%, Merck, Darmstadt, Germany). The resulting gel was transferred into a PTFE-lined autoclave and aged at 150 °C for 48 h. An increasing pH-value (pH  $\geq$  14) during hydrothermal treatment allows a quantitative precipitation of nickel hydroxide. Subsequently, the obtained precipitate was filtered and washed a few times by using DI-water and ethanol. After drying at 100 °C, calcination was carried out in synthetic air at 540 °C for 12 h, revealing a template-free sample. The protonated form of the aluminosilicate was obtained by ion exchange with a 0.1 M ammonia nitrate solution (99+%, Sigma Aldrich) at 70 °C for three times, followed by another calcination step in synthetic air for 6 h at 450 °C. The resulting catalyst samples were stored in a desiccator prior to further investigations.

The elementary composition and quality of the solid-state products obtained were characterized using various analytical methods as previously described [1]. By means of inductively coupled plasma optical emission spectroscopy (ICP-OES), the Si/Al ratio and nickel content were determined. X-ray diffraction (XRD) was used for crystallinity analysis, as well as N<sub>2</sub>-physisorption for the measurements of specific surface area (S<sub>BET</sub>). Surface acidity and the nature of the acid sites were investigated with temperature programmed ammonia desorption (TPAD) coupled with Fourier transform infrared spectroscopy (FTIR). Magic-angle spinning nuclear magnetic resonance (<sup>27</sup>Al MAS NMR) was applied to distinguish the type of aluminum surface species, and X-ray photoelectron spectroscopy (XPS) was used in order to determine reaction-related electronic state of the nickel species.

Special attention was paid to a temperature programmed reduction (TPR) of each sample, which was first placed in the measurement cell and calcined in argon atmosphere at 550 °C, followed by a reduction. For the purpose of reduction, a gas mixture containing of 10 vol.-% hydrogen and 90 vol.-% argon was passed over the sample accompanied by an increase of temperature (10 K/min) to 550 °C. The degree of reduction was determined by the amount of hydrogen consumed.

The characterization data relevant for this study, such as Si/Al ratio, nickel content, and nickel reduction degree, are summarized in Table 1. The given designation of the as-prepared samples (OS-YY-X) reveal the synthesis procedure of the one-pot synthesis (OS), which was used for the whole sample series, the chosen Si/Al ratio (YY), and the amount of nickel (X) in the synthesis gel.

#### 3.2. Catalysts Testing

Catalytic tests were carried out in liquid phase at 3 MPa in a tubular reactor of 2 m-long stainless-steel pipe with an internal diameter of 6 mm. 12.5 g of pressed and classified catalyst pellets with a diameter of 0.8 to 2 mm were placed in the reactor. To fix the catalyst bed, the rest of the tube was filled with glass beads with a diameter of 2 mm. As a feed stream, so-called Raffinate II was used with an olefin-proportion greater than 80 wt.-%, containing cis- or trans-2-butene and 1-butene, as well as approximately 20 wt.-% iso- and

n-butane. The reaction temperature varied between 80 and 100  $^\circ\text{C}$  , while WHSV was kept at 9.5 L/h.

Product stream was analyzed by two gas chromatography systems (GC). One GC for analyzing C4 compounds and oxygenates and another one for the quantification of further oligomers. For both GCs, a Pd/C catalyst was placed in the GC liner and hydrogen was used as carrier gas. The applied hydrogenolytic gas chromatography led to a hydrogenation of the olefinic oligomers in order to reduce the number of signals and to focus on the skeletal isomers according to [14]. Depending on the preferred mechanism of oligomerization, an oligomer with different degree of branching is obtained. The degree of branching is indicated by the ISO index, which is the average number of methyl groups per C8 molecule in the isomer mixture and is defined as follows:

$$ISO index = [n(n-O) \cdot 0 + n(MHp) \cdot 1 + n(DMHx) \cdot 2]/n(C8)$$

The catalytic data, especially the conversions achieved and the calculated ISO indexes, can be found in Table 1.

## 4. Conclusions

Further investigations of Ni-modified Al-MCM-41/ZSM-5 catalyst systems on the dimerization of n-butenes lead to the conclusion that when preparing the most effective catalyst, in addition to the optimal values for the Si/Al and the Ni/(Al + Ni) ratio, the combined effect of the Ni/Al ratio and reduction degree must also be taken into account. For this purpose, it is recommended to use an additional model parameter presented for catalyst samples with a comparable nickel amount as a product from Ni/(Al + Ni) ratio with a different reciprocal of the reduction degree depending on the Si/Al ratio.

At low product values, unstable nickel sites with weak metal–support interaction are mainly present, which yield low conversions and high ISO indices. With increasing product size, the conversion and the selectivity towards linear dimers increases due to the improved stability of the nickel sites, as well as the enhanced ability to activate the nickel sites. At very high product values, electronic influence of the aluminum atoms on the nickel atoms is decreased, leading to an unbeneficial electronic state of the nickel sites accompanied by an enlarged yield of branched dimers. In general, aluminum atoms in the support material contribute to the formation of catalytically active Ni<sup>+</sup> ions, but the resulting dimers are able to leave the pore structure of the material unhindered. Our new evaluation model provides a very good additional criterion for comparison of such catalyst systems.

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