True nickel-catalyzed oligomerization *versus* hetero-oligomerization: development of indicators for determining the mode of oligomerization as a function of reaction temperature

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Ni(II)-exchanged amorphous silica–aluminas are effective catalysts for the oligomerization of lower alkenes. The mode of the reaction and the product spectrum obtained depends largely on the reaction temperature employed. At low temperatures (~120 °C), mainly selective nickel-catalyzed oligomerization is observed (*true oligomerization*). As the reaction temperature is raised, the formation of hydrocarbons composed of non-integral multiples of the monomer increases (*hetero-oligomerization*). Plots of the ratio of integral multiples to non-integral multiples of the monomer versus reaction temperature are powerful indicators of the mode of oligomerization taking place. These plots are described by exponential relationships, and on a logarithmic scale, straight lines are obtained. The catalysts studied by us were grouped into two classes, those of (i) low to medium catalytic activity, and (ii) high catalytic activity. For group (i) catalysts (of relatively low nickel loading), the temperature of 180 °C marks the change-over from predominantly true oligomerization to predominantly hetero-oligomerization. For group (ii) catalysts (high nickel loadings), the contributions of true nickel-catalyzed oligomerization extends further into the high-temperature region (up to ~300 °C). The *Y*-intercepts of the plots can be taken as a measurement of the intrinsic selectivity of the catalysts (true versus hetero-oligomerization), while the value of the slopes quantifies the sensitivity of the selectivity to increasing reaction temperature (change-over from selective *true* to unselective *hetero-oligomerization*).

KEY WORDS: nickel; silica–alumina; heterogenous; true oligomerization; hetero-oligomerization; ethene; propene; 1-butene.

1. Introduction

In previous publications we have extensively reported on the oligomerization of ethene, propene and 1-butene into distillate-range products using nickel(II)-exchanged crystalline [1] and amorphous [2,3] aluminosilicate catalysts. In addition to high activity and selectivity, the nickel-containing amorphous silica–alumina catalysts show very high stability at low reaction temperatures and elevated pressures, i.e. at 120 °C, 3.5 Mpa and an mass hourly space velocity (MHSV) of 2 $g_{feed}\ g_{cat}^{-1}\ h^{-1}$ [2,3]. At low temperatures (~120 °C), mainly selective nickel-catalyzed oligomerization is observed, with the oligomers formed consisting of integral multiples of the monomer (*true oligomerization*). As the temperature is raised, the mode of the reaction changes and there is an increasing formation of products composed of non-integral multiples of the monomer (*hetero-oligomerization*).

Due to the stability of the carbenium ions involved, propene and butene are more reactive over acid catalysts, while ethene is readily oligomerized at low temperatures using transition metals such as nickel [4]. In general, acid-catalyzed oligomerization at high temperatures is less selective, and side reactions such as disproportionation, skeletal isomerization, and cracking lead to a more complex product spectrum [5,6]. For the formation of products with non-integral multiples of the monomer, the term *hetero-oligomerization* (as opposed to *true oligomerization*) was introduced by Langlois [7].

By monitoring the ratio of a primary oligomerization product (such as C_6 for ethene and propene, or C_8 for ethene and butene) to a secondary oligomerization product (such as C_5 for ethene and propene, or C_7 for ethene and butene) the relative contributions of true and hetero-oligomerization can be readily estimated, and in this communication we propose the use of logarithmic plots of the C_6/C_5 and/or C_8/C_7 ratios for determining the relative degrees of the mode of oligomerization taking place as a function of reaction temperature and nickel content of the catalysts.

2. Experimental

The types of catalyst are identical to those employed previously [2,3], except that the amount of nickel exchanged onto the amorphous silica–alumina carrier was varied (see table 1).

The experimental arrangements and procedures were as reported earlier [2]. The oligomerization reactions were performed in fixed-bed microreactors and a

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Table 1
The catalysts used in this study (Slopes, *Y*-intercepts, and correlation coefficients (r^2) for the straight lines obtained in figures 2 (<180 °C) 5, and 6)

Catalyst[a]	Figure	Feed	Ratio	Slope (1/°C)	*Y*-Intercept	r^2
NiSA-II (0.12)	2	Ethene	C_6/C_5	−0.013	3.41	0.98
NiSA-II (0.63)	2	Ethene	C_6/C_5	−0.050	10.58	0.92
NiSA-II (0.76)	2	Ethene	C_6/C_5	−0.059	12.34	0.90
NiSA-II (1.56)	5	Ethene	C_6/C_5	−0.022	8.11	0.96
NiSA-II (1.56)	5	Propene	C_6/C_5	−0.034	9.70	0.96
NiSA-II (1.56)	6	Ethene	C_8/C_7	−0.017	7.22	0.90
NiSA-II (1.53)	6	1-butene	C_8/C_7	−0.019	7.90	0.94

[a] The number in parenthesis denotes the mass percent nickel exchanged onto the silica–alumina support.

(MHSV) of 2 $g_{feed}\ g_{cat}^{-1}\ h^{-1}$ was employed. If not otherwise indicated, a pressure of 3.5 MPa was applied.

3. Results and discussion

3.1. The catalysts used

All the nickel catalysts used in this study were obtained by ion-exchange of the amorphous silica–alumina. Silica–alumina type II (SA-II) [2] was used, which has a SiO_2/Al_2O_3 mole ratio of 50 and a specific surface area of 420 $m^2\ g^{-1}$. All catalysts utilized are listed in table 1. Some relevant physical and chemical properties were given in Ref. [2]. The naming of the samples follows the procedure used previously [2,3] and the number in parenthesis represents the mass percent nickel present.

3.2. C_6/C_5 ratios far catalysts of low to medium oligomerization activity

As discussed in Ref. [2,3], silica–alumina supported nickel catalysts show two pronounced activity maxima, one at low and one at high reaction temperatures. In the low-temperature region, volcano-type activity curves with a maximum around 120 °C are observed, provided the catalysts are examined over a sufficiently large temperature range (that is from about 40 to 180 °C). This is demonstrated in figure 1 for the three catalysts NiSA-II (0.12), NiSA-II (0.63) and NiSA-II (0.76) and with ethene as feed. The two temperature regions of high catalyst activity are clearly evident. The response of the resulting C_6/C_5 ratios to reaction temperature is shown in figure 2. The dependence is best described by exponential functions, and on a logarithmic scale, as demonstrated in figure 2, straight lines are obtained. The lines intersect at the base of the volcano curves on the high-temperature side at ~180 °C. At temperatures > 180°, the $\ln(C_6/C_5)$ values for all three catalysts fall on the same line with a slope close to zero. It can be seen that thermodynamic equilibrium is not fully attained, as at equilibrium $\ln(C_6/C_5)$ would be approximately zero [6]. From the above observations, it can be concluded that 180 °C marks the change-over from predominantly true oligomerization to predominantly hetero-oligomerization. It should be noted, however, as elaborated upon in Ref. [1–3], that the contribution of nickel to ethene conversion in both temperature regions is definitely more significant than that of the support itself. For ethene as feed, the silica–alumina support shows hardly any activity at temperatures below 240 °C [2,3].

As demonstrated in figure 3, the value of the *Y*-intercepts of the three straight lines for the NiSA-II catalysts with 0.12%, 0.63% and 0.76% nickel, shown in figure 2, increases with increasing nickel content of the catalysts. The intercepts can be taken as a measure of the intrinsic selectivity of the catalysts (true versus hetero-oligomerization). A higher nickel loading,

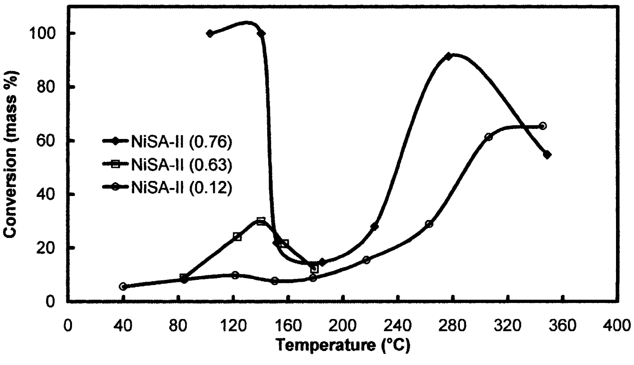

Figure 1. Oligomerization of ethene: Conversion as a function of temperature for nickel catalysts of different metal loadings.

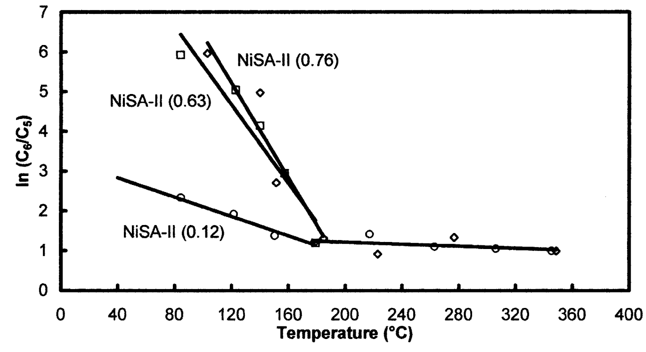

Figure 2. Oligomerization of ethene: $\ln(C_6/C_5)$ values as a function of temperature for the nickel catalysts of different metal loadings.

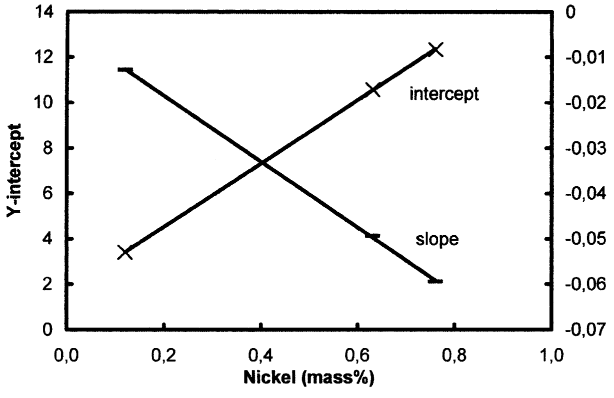

Figure 3. *Y*-intercepts and slopes of the graphs of figure 2 (<180 °C) as a function of nickel content of the catalysts.

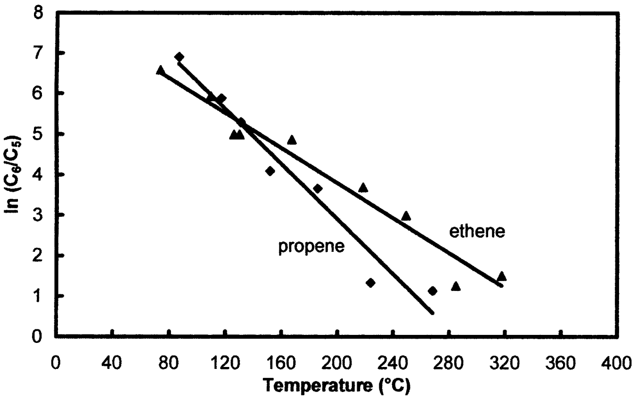

Figure 5. Oligomerization of ethene and propene over NiSA-II (1.56): $\ln(C_6/C_5)$ values as a function of temperature.

therefore, renders the catalysts not only more active, but also more selective towards true oligomerization.

Since the lines in figure 2 pass through a common point at ~180 °C, the slopes must too follow a linear relationship when plotted against nickel (mass%) (also shown in figure 3). The value of the slope serves as a measure of the change from true to hetero-oligomerization with increasing reaction temperature. At temperatures below 180 °C, catalysts of higher nickel loading show higher relative degrees of true oligomerization than catalysts of lower nickel content. The values for the slopes and intercepts are given in table 1, together with the corresponding correlation coefficients r^2.

3.3. C_n/C_{n-1} ratios for catalysts of high oligomerization activity

With nickel catalysts of high ethene oligomerization activity, such as NiSA-II (1.56), the volcano-type curve in the low-temperature region may be less obvious, as the feed conversion remains close to 100% for reaction temperatures >60 °C (see figure 4). However, as the activity pattern for nickel-catalyzed oligomerization follows the order ethane $\gg$ propene > 1-butene [3,4], the volcano curve can be hidden for ethane as feed, while it may become more pronounced for the less reactive alkenes such as propene and 1-butene. This is indeed clearly demonstrated in figure 4, where the conversion is plotted against reaction temperature for all three alkenes using NiSA-II (1.56) as catalyst. In the low-temperature region there is no volcano curve for ethene, but it can be readily seen for propene and 1-butene.

Again, the response of the C_6/C_5 ratios to reaction temperature is best described as an exponential relationship, but for NiSA-II (1.53–1.56), the straight lines of the logarithmic plots extend to higher temperatures (~300 °C, see figures 5 and 6). This is in agreement with the absence of a clear division between low- and high-temperature oligomerization, especially with ethene. It can be concluded, therefore, that with the catalysts of high nickel content the contribution of true nickel-catalyzed oligomerization extends further into the high-temperature region (beyond 180 °C) as compared to the catalysts with lower nickel loading (compare figures 2 and 5).

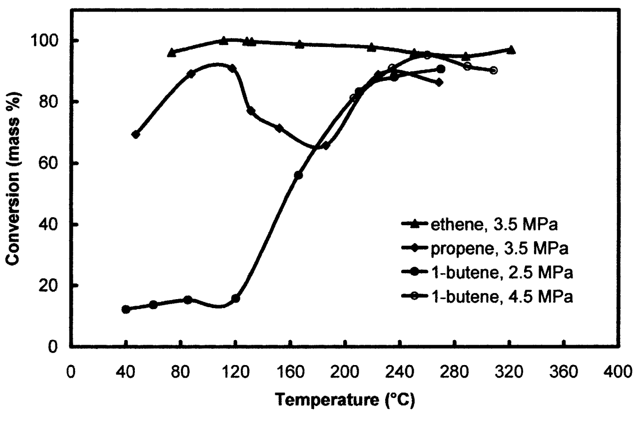

Figure 4. Catalyst NiSA-II (1.56): Conversion of ethene, propene and 1-butene as a function of Oligomerization temperature (2.5–4.5 MPa).

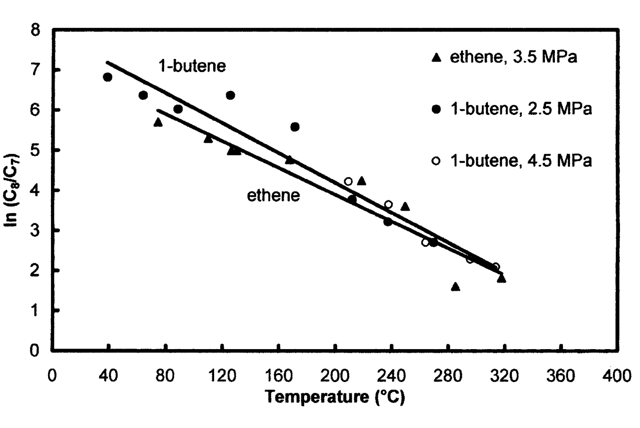

Figure 6. Oligomerization of ethene and 1-butene over NiSA-II (1.53–1.56): $\ln(C_8/C_7)$values as a function of temperature (2.5–4.5 MPa).

The lines in figure 6 (C_8/C_7 ratios from ethene and 1-butene oligomerization) have very similar slopes and intercepts (see also table 1). This is not surprising, since as we noted earlier [2,3], in the oligomerization of ethene considerable dimerization activity of the butene intermediates is exhibited by the NiSA-II (1.56) catalyst (see figure 4 in Ref. [2]). Hence, for ethene and 1-butene as feeds, a similar distribution for the products $> C_6$ is to be expected.

Comparison of the data for ethene and propene (figure 5) shows a more rapid decrease of the C_6/C_5 ratio with increasing reaction temperature in the case of propene. In contrast to ethene, propene can readily form secondary carbenium ions and as such is more prone to the less selective high-temperature acid-catalyzed oligomerization, which is thought to be the source of the products composed of non-integral multiples of the monomer [6,7]. Furthermore, the two lines in figure 5 intersect in the temperature region of ~130 °C where the change-over takes place (for propene) from the selective nickel-catalyzed oligomerization at low-temperatures to the region of the less selective hetero-oligomerization (see figure 4).

3.4. Discussion

The difference between catalysts of low to medium and those of high oligomerization activity can be rationalised by assuming that the chemical environment of the active nickel species varies with the extent of ion exchange of the amorphous silica–alumina carrier. It is well established that the exchangeable sites in silica–aluminas have a distribution of acid strengths [8]. According to ion-exchange principles, the nickel exchanges first with the sites of highest acid strength available. It follows, that in the case of our catalysts with low nickel loadings (corresponding to low to medium oligomerization activity), the nickel species are associated with the sites of relatively high acid strength. It is these nickel sites which are most active for ethane oligomerization at high temperatures (eg., 300 °C) [9,10]. Using nickel-exchanged NaY as model catalysts, it was demonstrated that the reaction follows first-order kinetics with respect to the nickel in the low-temperature region (at 150 °C) [1], while this was clearly not the case at high reaction temperatures (220–360 °C); at high temperatures a catalyst exchanged to a lower degree is relatively more active per nickel site than a sample with a higher nickel loading [11]. Interestingly, the oligomerization activity at the low-temperature maximum irreversibly diminishes after the reaction temperature has been taken to the point marking the start of the high-temperature activity region, that is to 220 °C for the NiNaY catalysts [1,11] and to 180 °C for the NiSA-II catalysts (figures 1,2). It appears then, that with the above indicated catalysts different nickel species catalyze the reaction in the low- and in the high-temperature regions. This is reflected in the selectivity pattern observed for the NiSA-II catalysts in figure 2, where a different temperature dependence for $\ln(C_6/C_5)$ is found below and above 180 °C.

In the case of the NiSA-II catalysts of high nickel loading, the ion-exchange involves more or all of the sites available on the silica–alumina carrier, which are of different acid strength. As a consequence, after ion-exchange a broader spectrum of potential catalytic sites is present, and the overall activity of the catalysts is higher (compare figures 1 and 4). As a net result, the volcano curves in the low- and high- temperature region, seen in figure 1 for the catalysts of low nickel loading, become levelled off (most strikingly for ethene, see figure 4), and the corresponding $\ln(C_n/C_{n-1})$ values fall on one straight line over the whole temperature range investigated, as can be seen in figures 5 and 6.

4. Conclusions

The results show that plots of integral multiples to non-integral multiples of the monomer Versus reaction temperature provide a good indication of the type of oligomerization taking place over nickel-exchanged silica–alumina catalysts. The dependence is best described by exponential functions, and on a logarithmic scale straight lines are obtained. As the reaction temperature increases the mechanism changes from predominantly nickel-catalyzed *true oligomerization* to predominantly acid-catalyzed *hetero-oligomerization*. At a particular reaction temperature, depending on the catalyst and the type of teed, the plots change into straight lines with slopes close to zero and the carbon number distribution tends to approach the thermodynamic equilibrium.

The plots and correlations shown in this paper make a valuable contribution to the understanding and the classification of oligomerization catalysts, in particular those which consist of an active metal species (such as nickel) on an oxide support. The slopes and intercepts calculated from these plots depend mainly on the amount of nickel exchanged onto the silica–alumina carrier, and to a lesser extent, on the type of monomer used. The *Y*-intercepts can be taken as a measurement of the intrinsic selectively of the catalysts, that is the relative degree of true to hetero-oligomerization at a low reaction temperature. The value of the slopes indicates the sensitivity of the selectively to increasing reaction temperatures (change-over from true to hetero-oligomerization).

For catalysts of relatively low nickel loading (0.12–0.76 mass%), both the activity and the intrinsic selectively of the catalysts increases with increasing nickel content. Catalysts of high nickel loading (1.53–1.56 mass%) have higher activities, buth their intrinsic selectively and the temperature sensitivity of the selectivity is comparatively lower.

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