Oligomerization of Ethylene in a Slurry Reactor Using a Nickel/Sulfated Alumina Catalyst

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During the oligomerization of ethylene over heterogeneous catalysts, the production of α-olefins may be lowered because of an accompanying deactivation of catalyst resulting from strong adsorption of products, by isomerization or by a tendency to copolymerize into branched products. The oligomerization of ethylene was studied using Ni(II)/sulfated alumina catalysts prepared with a nonporous fumed alumina (ALON) support. The influences of methods of catalyst preparation and activation upon oligomerization activity were screened using a gas−solid microreactor. On the basis of the test results obtained in the microreactor, a modified form of the superior catalyst was prepared and its performance was examined in more detail using a well-agitated gas−liquid−solid slurry reactor. This catalyst exhibited very good oligomerization activity with no apparent deactivation in the slurry reactor at temperatures at or below 298 K and at near-atmospheric pressure. Complete conversion of the ethylene with the production of mainly two oligomers, 1-butene and 1-hexene, was attained. After 34 h in the slurry, formation of a significant amount of two branched C_6 isomers was observed.

Introduction

Materials such as nickel oxide and nickel salts supported on silica and/or alumina have been used as catalysts for dimerization and oligomerization of ethylene (Matsuda *et al.*, 1979; Bonneviot *et al.*, 1986; Chauvin *et al.* 1988). The activities and selectivities of these catalysts are affected by strong adsorption of products, by isomerization of the primary oligomers, and by copolymerization of olefins into branched products (Alijaraliah *et al.*, 1992; Skupinska, 1991). Espinoza *et al.* (1987a) have shown that higher activity per Ni site can be achieved with selective exchange of nickel with sites of higher acid strength on silica−alumina. Chauvin *et al.* (1988) and Hugues et al. (1990) described a nickel oxide supported on γ-alumina modified with sulfate ions which was very active for propene dimerization. However, no mention of its activity for ethylene dimerization appears. Ethylene oligomerization over nickel-exchanged zeolite (NiNaY) has been investigated in a tubular flow reactor (Ng *et al.*, 1992; Heveling *et al.*, 1991). The majority of catalysts which have been described in the literature encountered rapid deactivation and an inability to achieve steady-state reaction performance (Goledzinowski and Birss, 1993; Espinoza *et al.*, 1987b; Ng *et al.*, 1992). Such variations in performance lead to ambiguous comparisons between the catalytic activities of these different catalysts.

In the work described herein, Ni(II)/sulfated alumina was prepared using a nonporous fumed alumina (ALON) support to which nickel was added by either impregnation or ion exchange. The influence of preparation and activation procedures upon the catalytic oligomerization activity was screened by initial testing of these catalysts using a batch gas−solid microreactor in which the ethylene pressure was monitored as a function of time. A modified catalyst containing 1.7 wt % Ni was prepared based on the results obtained from the batch microreactor with the objective of maintaining high activity with a lower nickel loading. This catalyst was further tested in a well-agitated slurry/solution reactor containing catalyst particles suspended in inert *n*-heptane liquid. Using the slurry reactor, both ethylene conversions and product distributions were obtained. Difficulties concerning the evaluation of catalyst performance because of the initial deadspace gas volume above the slurry and its initial pressurization with ethylene were eliminated in this study. On-line GC-FID analyses of the product gases leaving the reactor and a GC-MSD analysis of the composite solution within the reactor at the end of a run provided the basis for calculating the ethylene conversion and the product selectivities. The influences of mass of catalyst, temperature, holdup time on activity, selectivity, and stability of the catalyst were evaluated using a slurry/solution reactor.

Experimental Details

Catalyst Preparation. The ultrafine γ-alumina support (ALON, Cabot Corp.; BET area 102 m^2/g) is characterized by a high surface area for a nonporous material. The Ni(II) ions were added by either impregnation or ion-exchange methods. The reported nickel content of the catalyst is based on the initial mass of Ni used for the catalysts prepared by impregnation. For the ion-exchanged samples, Ni content is calculated by subtracting the amount of nickel remaining in the ion-exchanged solution from the initial amount of nickel used.

(1) Impregnation Method. The ALON support was first dried at 773 K for 2 h under a stream of air, weighed, and then impregnated by mixing into an aqueous $Ni(NO_3)_2 \cdot 6H_2O$ (Fisher) solution containing the desired amount of nickel. The resulting slurry was then dried at 393 K for 4 h and again calcined at 773 K for 4 h.

(2) Ion-Exchange Method. A nickel ammonium complex was first prepared by dissolving $Ni(NO_3)_2 \cdot 6H_2O$ in ammonium hydroxide (Fisher) at pH 11. The dry ALON was then added to the nickel ammonium complex solution for ion exchange. After agitation for 12 h, the solid phase was filtered from the solution, washed with

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Table 1. Description of Catalysts Tested in a Batch Microreactor

catalyst notation and composition	BET area, m^2/g	nickel added, wt %	sulfate added, wt %	method of adding nickel
3.5NAS (Ni/sulfated alumina)	112	3.5	5.7	impregnation
3.5NA (Ni/alumina)	113	3.5	0	impregnation
0.9NAS/Ex (Ni/sulfated alumina)	109	0.9	5.7	ion exchange of Ni(II); then sulfated by impregnation
3.5NAS/Ex (Ni/sulfated alumina)	109	3.5	5.7	ion exchange of 0.9 Ni(II); then sulfate and add 2.6 Ni(II), both by impregnation

deionized water, dried at 293 K, washed again, and redried at 393 K for 4 h. A final calcination at 773 K for 4 h completed the ion-exchange procedure.

(3) Sulfation. The sulfation of either impregnated or ion-exchanged catalysts involved impregnation using an $(NH_4)_2SO_4$ solution (Fisher). The sulfation mixture was dried at 393 K and calcined at 773 K for 4 h. The catalysts used in this study are named in terms of their composition, the method of preparation, and the nickel content; *e.g.*, 0.9NAS/Ex denotes a nickel on a sulfated alumina catalyst with a nickel content of 0.9 wt %, prepared by ion exchange. Table 1 lists the catalysts which were evaluated in the batch microreactor.

Catalyst Testing with the Batch Microreactor. Use of a batch microreactor provided a simple and quick way of evaluating the influences of different activation procedures and the two methods of loading nickel ions. A mass of 0.1 g of catalyst powder (−100 + 120 mesh) was compressed into a thin (about 0.1 mm thick) wafer and placed in a batch IR cell, adapted for measuring the decline in ethylene pressure with reaction as a function of time, for each test. The pressure measurements were obtained following an initial ethylene pressure of 1.6 kPa with the cell at room temperature. The ethylene consumption rate was calculated based on the pressure drop and the equation of state for an ideal gas. The relative performances of the different catalysts were assessed by comparing their rates of consumption of ethylene at the standardized conditions.

The influence of three different catalyst activation procedures was evaluated after an initial outgassing of the catalyst for 2 h at 773 K under vacuum.

(1) Thermoactivation. This involved heating for 1 h at 773 K in a nitrogen environment (13 kPa).

(2) Oxygen Treatment. The catalyst was calcined with oxygen (13 kPa) for 1 h at 773 K, cooled to room temperature, and then evacuated for 1 h.

(3) CO Reduction. The catalyst was reduced using carbon monoxide (2.6 kPa) for 0.5 h at one of the temperatures 473, 573, 673, or 773 K, followed by evacuation for 1 h at the same temperature. It is worth noting that CO poisoning at 773 K has been reported as the result of formation of a CO complex with Ni^+ or Ni^0, such as $Ni(CO)_2$ (Cai *et al.*, 1993). However, the activity can be regenerated simply by evacuation of the CO-poisoned catalyst at 473 K (Cai *et al.*, 1993).

Catalyst Testing with the Slurry Reactor. The use of the laboratory slurry reactor enabled measurement of the longer term reaction behavior (essentially steady state except for the changes in amounts of dissolved oligomers accumulating in the *n*-heptane as the run proceeds) under conditions closer to those encountered in large-scale reactors. A catalyst formulation modified to contain about 1.7 wt % Ni content by ion exchange, denoted 1.7NAS2/Ex (1.7 wt % Ni and 5 wt % $(SO_4)^{2-}$), was used in the slurry reactor runs to measure its activity level and to evaluate the role of catalyst deactivation. The catalyst denoted by 1.7NAS2/Ex was prepared using the same procedure as that for 0.9NAS/Ex as described earlier but with different nickel and sulfate ion contents.

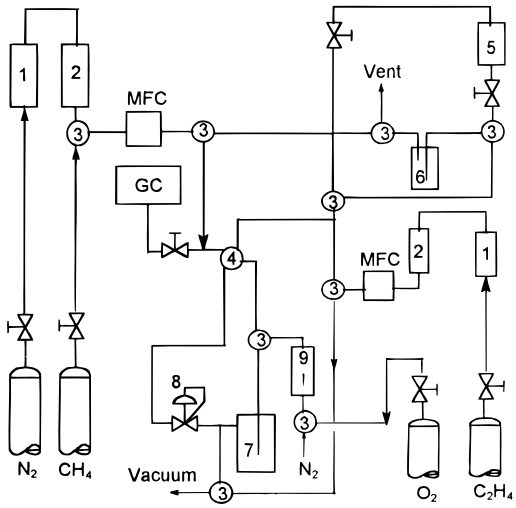

Figure 1. Schematic diagram of a slurry/solution reactor and equipment: (1) drier, (2) oxygen trap, (3) 3-way valve, (4) 4-way valve, (5) solvent tank, (6) solvent purification tank, (7) slurry reactor, (8) backpressure controller, (9) rotameter.

(1) Laboratory Slurry Reactor. Figure 1 provides a schematic diagram of the experimental equipment used in the slurry reactor operations. Ethylene was oligomerized within a Pyrex glass reactor, 70 mm i.d. and 80 mm height agitated by a magnetic coupling drive to a Rushton type impeller. Temperature differences within the reactor were less than 0.3 K as monitored by two thermocouples at different locations within the reactor. The ethylene gas feed flow rate along with the effluent gas flow from the reactor were continuous during the run, but the slurry mixture of *n*-heptane and catalyst powder was batch in operating mode. The slurry volume within the reactor increased slightly during typical runs, but this did not affect the ethylene consumption conditions significantly.

Prepurified nitrogen (Union Carbide, Linde grade) and ethylene (Union Carbide, CP grade) were purified additionally by passing through 13X molecular sieve and Alltech de-oxygen columns before flow regulation using mass flow controllers. The liquid solvent, *n*-heptane (Aldrich, 99%), was purified by bubbling nitrogen through the liquid overnight. In addition, nitrogen was also used to purge overnight the reactor inlet line. This eliminated any residual solvent vapor from the previous run that might contaminate the catalyst which was activated *in situ* within the reactor. After loading the −100 + 120 mesh catalyst powder, the thermoactivation procedure was carried out, following which the reactor was cooled to room temperature before introduction of 120 mL of the *n*-heptane solvent.

A constant reaction pressure was maintained by using a downstream backpressure controller. When the solvent temperature reached the designated run temperature, the reactor was carefully pressurized using ethylene without agitation of the vessel contents. This

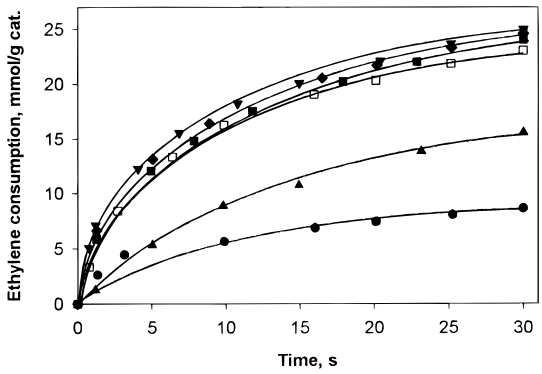

Figure 2. Influence of the activation procedure upon the catalytic activity of 3.5NAS catalyst in the gas−solid batch microreactor at room temperature. thermoactivation, ▼; oxidation, ▲; CO reduction at 473 K, ■; 573 K, ◆; 673 K, □; 773 K, ●.

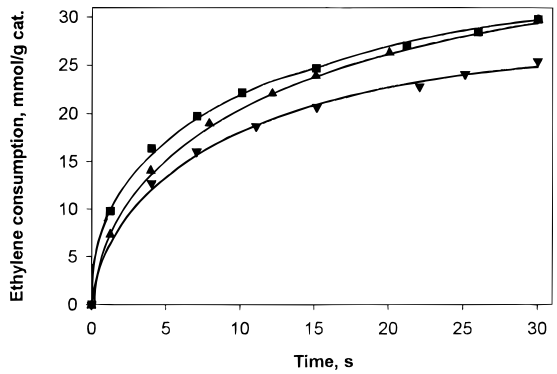

Figure 3. Influence of the method of preparation of the catalyst upon the catalytic activity in the gas−solid batch microreactor at room temperature: 3.5 NAS/Ex, ■; 0.9NAS/Ex, ▲; 3.5NAS, ▼.

enabled the run to be started when the agitator was turned on (450 rpm), with negligible reaction before startup. The ethylene and 1-butene contents of the effluent gas stream were monitored at 13 min intervals by the on-line gas chromatograph.

(2) Analysis of Gas and Liquid Products. The GC separation and quantification of effluent gas components were obtained using a capillary HP-PLOT/Al_2O_3 column (0.53 mm i.d., 5.0 μm film thickness, 50 m length). Methane was added as an internal standard before sampling and separation using a Hewlett-Packard 5890 Series II gas chromatograph fitted with a flame ionization detector. The peak integrations, composition calculations, and effluent flow calculations of ethylene and 1-butene were performed using the Hewlett-Packard GC Chemstation internal standard method.

The reaction products (dissolved in the liquid *n*-heptane) were collected as a composite liquid sample representative of the complete run, and a 0.5 μL sample was injected into a capillary J&W Scientific column (0.25 mm i.d., 0.25 μm film thickness, 30 m length, DB1 phase). The same gas chromatograph used for gas samples but using a parallel Hewlett-Packard 5971A mass selective detector (MSD) and an internal standard, 1-undecene, provided separation and quantification of the component peaks in the liquid sample. The conversion of ethylene was defined as the ratio of the total ethylene consumed to the total ethylene fed during the run. The ethylene consumption was calculated from a material balance. The total ethylene and 1-butene exiting from the reactor were calculated by integration of ethylene and butene flows *versus* run time curves, respectively, based on GC-FID information. The selectivities for the oligomers produced were defined as the mass ratio of the amount of oligomer produced to the total ethylene consumed during the run. The total mass of 1-butene was calculated by adding the mass in the effluent gas to that dissolved in the liquid phase (based on both GC-FID and GC-MSD information).

Experimental Results

Catalyst Activation Procedure. Figure 2 shows the ethylene consumption plotted *versus* reaction time for the three activation methods: thermoactivation, oxidation, and CO reduction (the latter at various temperatures) based on one catalyst, 3.5NAS. These results were obtained using the batch microreactor. It is evident that two methods generated comparable results: thermoactivation and CO reduction at 573 K. The catalyst activated by CO reduction at 773 K resulted in the lowest activity of the different activation procedures. A similar phenomenon was reported in the literature, and the low activity was attributed to CO poisoning as a result of the formation of $Ni(CO)_2$ type surface species (Cai *et al.*, 1993). Being the simpler procedure, thermoactivation was selected for activating the catalysts to be tested.

Three catalysts, one prepared by impregnation and two by ion exchange, were tested using the batch microreactor, and the results in Figure 3 show that ion exchange is the preferred method. For the ion-exchanged Ni loadings tested, after about 20 s of reaction time, both loadings, 0.9 and 3.5 wt % Ni, exhibited comparable activities. The latter results suggest that nickel loadings much less than 3.5 wt %, which has been reported in the literature, may be used. In the slurry reactor tests, a modified catalyst, 1.7NAS2/Ex with Ni content less than 3.5 wt % (1.7 wt % nickel and 5 wt % sulfate ion), was then used to evaluate the oligomerization process.

In the absence of sulfation, a Ni/Al_2O_3 preparation (3.5NA) did not exhibit catalytic activity adequate for oligomerization. Figures 2 and 3 also show that all of the catalysts tested under gas/solid reaction conditions exhibited a decline in activity with time. This behavior could be attributed to the decline in ethylene pressure with reaction and to strong adsorption of oligomeric products on the catalyst surface in the gas−solid type reactor. Some FTIR spectral evidence indicating the presence of adsorbed oligomerization products (not shown herein) supported this view. We speculated that the use of higher reaction pressures or the presence of a suitable liquid solvent phase might counteract this tendency of the catalyst to deactivate during the oligomerization reaction. Application of the latter idea led to our development of the slurry reactor. The use of *n*-heptane, a molecule not likely to appear as an oligomeric product, as the liquid phase in the slurry also generated a GC-MSD separation peak which did not interfere with the peaks from the other compounds eluting from the column. The *n*-heptane in the reactor not only provided the liquid phase for the slurry but also acted as a solvent for oligomeric products; hence, the reaction system really involved a slurry/solution reactor.

Results Using the Slurry/Solution Reactor. Using the 1.7NAS2/Ex catalyst, the effect of the mass of catalyst within the slurry was tested at 323 K. The results in Figure 4 indicate that an initial ethylene conversion of 100% is possible using a catalyst charge of 1.0 g under the experimental conditions used. It is clearly evident that the catalytic activity declines with

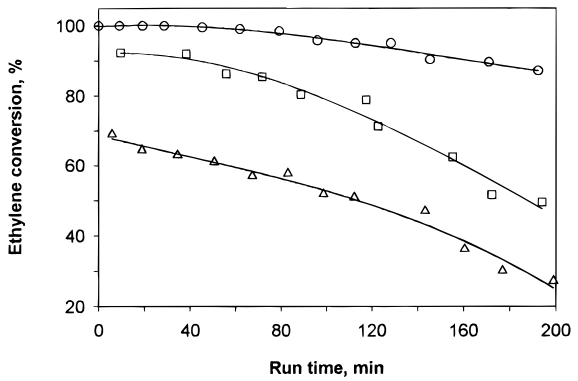

Figure 4. Influence of the mass of catalyst charged to the slurry reactor on ethylene conversion at 68.95 kPa and 323 K: 1.0 g ○; 0.5 g, □; 0.2 g, △.

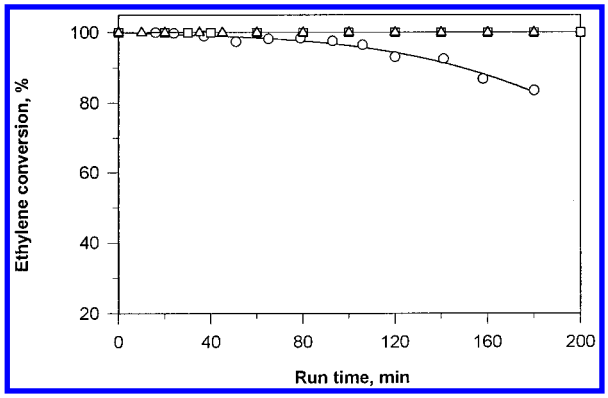

Figure 6. Influence of temperature upon the oligomerization of ethylene in the slurry reactor at 68.95 kPa with catalyst charge = 1 g (1.7NAS2/Ex): 279 K, △; 298 K, □; 323 K, ○.

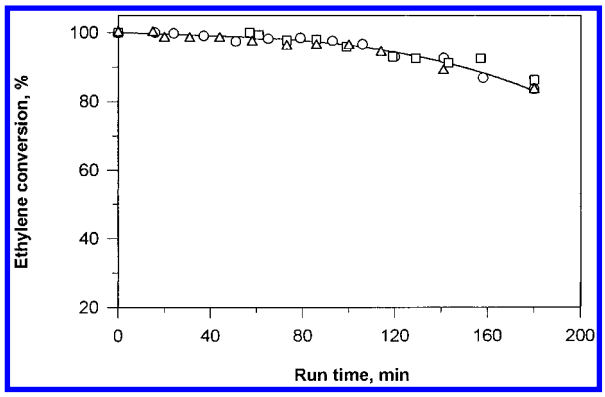

Figure 5. Reproducibility of three replicate runs in the slurry reactor at 323 K and 68.95 kPa. Catalyst charge = 1.0 g.

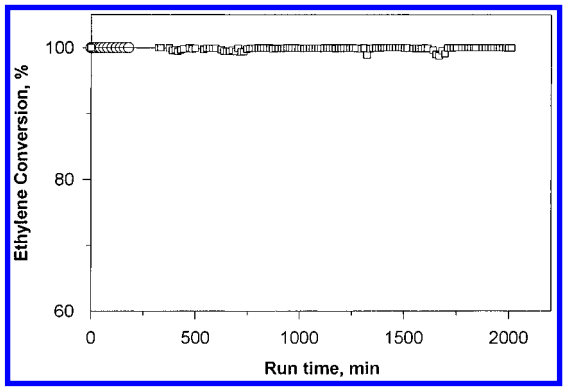

Figure 7. Stability of 1.7NAS2/Ex catalyst over prolonged reaction times at 279 K and 68.95 kPa, with an ethylene feed rate of 83 cm^3/min at STP. 3 h, ○; 34 h, □.

reaction time at 323 K and that this effect is more significant, the smaller the amount of catalyst employed. Accordingly, a catalyst charge of 1.0 g was used throughout the remaining runs described in this study.

Using 1 g of 1.7NAS2/Ex catalyst in the slurry reactor, Figure 5 shows the changes in ethylene conversion with time for three replicate runs at 323 K. It is evident that the equipment and procedures provide very good reproducibility in the measurement of ethylene conversions using the slurry/solution reactor. The dominant products encountered in the liquid phase were 1-butene (about 89 wt %) and 1-hexene (about 11 wt %). Although some decay in catalyst activity with run time is visible after 80 min, an average ethylene conversion of 95% was obtained over the run of 3 h duration. By lowering the reaction temperature from 323 to 298 K, and even to 279 K, Figure 6 shows that the deactivation of the catalyst can be eliminated over the 3 h run duration. The results for the replicated runs, the effect of temperature on the selectivities, and the result from one long 34 h run at 279 K are summarized in Table 2. During 3 h of reaction time, the products essentially remained 1-butene and 1-hexene throughout, and only at 279 K does one observe a minor shift in selectivity toward increased 1-butene. At 279−298 K and 3 h reaction time, only traces of C_4 isomers were detected. At 323 K and 3 h reaction time, traces of two C_4 isomers and two C_6 isomers were detected by GC-FID and GC-MSD analysis. The C_4 isomers did not match reasonably with any of the standard spectra in the HP MS database. Whether these two isomers are internal or branched isomers could not be identified. However, the search of the HP MS data base indicates that the spectra of the two C_6 isomers have a 95% match with (*E*)- and (*Z*)-3-methyl-2-pentene (Hewlett-Packard, 1993). Further identification of these isomers was not attempted.

To evaluate more thoroughly the endurance of the catalytic activity of 1.7NAS2/Ex, a 34 h run was completed. Figure 7 shows that the ethylene conversion remained at 100% over the entire 34 h period; however, the selectivities of 1-butene and 1-hexene gradually declined because of the increasingly long retention time of these components dissolved in the liquid *n*-heptane. The catalytic activity remained high throughout this run

Table 2. Ethylene Oligomerization Runs in a Slurry Reactor[a]

temperature, K	ethylene consumption rate, g/(g of catalyst·h)	overall ethylene conversion, %	average oligomer selectivity, %	
			1-butene	1-hexene
323	6.0	95.1	88.7	11.3
323	5.9	92.6	90.5	9.5
323	6.1	96.3	88.8	11.2
298	6.2	100	88.3	11.7
279	6.2	100	89.7	10.3
279[b]	6.2	99.8	95.0[c]	5.0

[a] Catalyst charge (1.7NAS2/Ex) = 1.0 g (−100 + 120 mesh). Pressure = 68.95 kPa. Ethylene feed rate = 83 mL(STP)/min. Volume of *n*-heptane in reactor = 120 mL. [b] Duration of run = 34 h. [c] Includes 28 wt % of C_4 and C_6 isomers (only traces of C_8 isomers).

but the extended reaction time enabled some of the dissolved 1-butene and 1-hexene to undergo secondary reactions, and their average selectivities declined to 67 and 5 wt %, respectively. The remaining 28 wt % of the converted ethylene had apparently become isomers of 1-butene (two isomers) and 1-hexene (two branched isomers) along with traces of C_8 isomers (none of which were 1-octene). No α-olefins with a carbon atom content exceeding six were encountered. The GC-MSD calibration included all α-olefins up to C_{18}, and no traces of α-olefins beyond C_6 were detected.

The 34 h run had to be terminated because the product solution in the *n*-heptane solvent increased the volume of liquid within the reactor to an overflow condition. This long run was terminated because the equipment did not provide for overflow of liquid from the reactor during a run.

A run attempted with 1-butene feed failed to produce 1-octene by dimerization. Hence, it seemed reasonable to speculate that the primary reactions proceed through some surface mechanism whereby the pattern/location of the active sites involved accommodates adsorption and reaction of ethylene with a second adjacent adsorbed species such as ethylene or 1-butene to form 1-butene or 1-hexene, respectively. Larger adsorbed α-olefinic molecules such as 1-hexene are apparently unable to react with ethylene to form higher α-olefins.

Discussion

The experimental results indicate clearly that 1.7 wt % Ni on 5 wt % sulfated ALON is a very active catalyst for the oligomerization of ethylene to 1-butene and 1-hexene at temperatures from 279 to 298 K. Nearly complete ethylene conversion with high selectivities to 1-butene and 1-hexene was attained in the slurry reactor. Our findings that ion-exchanging of the Ni(II) ions results in a better dispersion of the Ni enables lowering of the Ni content below that required for impregnation of Ni loading. This agrees with the observations of Espinoza *et al.*, (1987c). Without the increased acidity provided by sulfation of the alumina, Ni/alumina exhibits very inferior oligomerization catalytic activity. It is known that addition of sulfate ions to the surface of alumina induces the appearance of strong Lewis and Brönsted acid sites (Przystajko *et al.*, 1983). Chauvin *et al.* (1988) earlier indicated that the activity of the Ni/sulfated alumina catalyst in propene dimerization is a function of the acidity of the support. Kustov *et al.* (1984) have suggested that ethylene may oligomerize on the Lewis acid sites of Y-zeolite by a cationic mechanism and on the Brönsted acid sites of HZSM-5 by either a carbonium ion mechanism or an ethoxy group mechanism. However, the role of sulfation in forming a surface Ni complex or in stabilizing a particular surface Ni species is not yet well understood. Further studies are required.

Other studies have shown the formation of Ni^+ species from well-dispersed Ni^{2+} ions on the surface of alumina (Bonneviot *et al.*, 1986) or on zeolites (Bonneviot *et al.*, 1983; Elev *et al.*, 1984) by photoradiation under a hydrogen atmosphere or even on contact with an olefin. They also suggested that these Ni^+ species are the active sites for the olefin dimerization reaction. It would be of interest to correlate the number of Ni^+ sites on the surface of sulfated alumina with the different activation procedures. Our study shows that both thermoactivation (as described herein) and CO reduction at 573 K generate a more active catalyst than do oxidation or CO reduction at temperatures other than 573 K. Considerably lower activity after CO reduction at 773 K was observed in agreement with Cai *et al.* (1993).

The strong adsorption of reaction products on the surface of the catalyst has also been suggested as the cause of catalyst deactivation during oligomerization (Aljaraliah *et al.*, 1992; Skupinska, 1991). In our results, this deactivation effect was visible earlier in the course of reaction within the gas−solid system at room temperature than in the slurry/solution reactor at 323 K. The use of lower temperatures in the slurry/solution reactor resulted in the suppression of this deactivation effect; thus, one may surmise that the strong adsorptions involve activated adsorption. Furthermore, by carrying out the oligomerization in a liquid solvent medium as well as at lower temperatures, the deactivation of the catalyst was very limited. In this study, all experiments were carried out at near-atmospheric pressure. Increasing the pressure slightly to about 200 kPa did not show any difference in performance.

The selectivity results show that the formation of the products, 1-butene and 1-hexene, dominates, with little tendency for formation of higher oligomers during a 3 h contact time between these dissolved oligomers and ethylene in the presence of the catalyst. At temperatures above 298 K and/or contact times above 3 h, isomers of C_4 and C_6 α-olefins and traces of C_8 branched olefins increasingly appear. Presumably, such branched species may be involved in deactivation by strong adsorption. Successful production of α-olefins in large yields requires the elimination of wasteful formation of secondary products, and the formation of these latter products likely contributes to the deactivation of the catalyst.

This study demonstrates that a 1.7 wt % ion-exchanged Ni/5 wt % sulfated alumina, thermoactivated, is an efficient and stable catalyst at temperatures of 298 K or less for the oligomerization of ethylene to 89% 1-butene and 11% 1-hexene in a *n*-heptane-based slurry/solvent reactor.

Conclusions

1. A highly active and selective ethylene oligomerization catalyst may be prepared by ion-exchanging Ni(II) onto an alumina support. Although 1.7 wt % Ni was added to the support, smaller amounts may also be used. The lower limit of Ni content to enable good performance in the slurry reactor was not established. Thermoactivation at 773 K generated a catalytic activity level comparable to that resulting from CO reduction at 573 K.

2. By conducting the oligomerization of ethylene in a slurry reactor with a *n*-heptane liquid phase, the catalyst was not deactivated by strongly adsorbed oligomerization products during a run of 34 h duration. At a reaction temperature of 279 K, 100% conversion of ethylene and selectivities of 90% and 10% for 1-butene and 1-hexene, respectively, were achieved after a 3 h run.

3. Operation at temperatures above 298 K results in some deactivation of the catalytic activity and in the appearance of secondary products. After excessive contact time of the dissolved oligomers with catalyst (even at 298 K), some degradation of the two linear α-olefins into other isomeric forms occurs. The production of α-olefins with eight carbons or higher was never observed under any of the conditions tested.

4. Based upon this work, a continuous process seems possible for the production of 1-butene and 1-hexene from ethylene using the Ni/sulfated alumina catalyst in a slurry/solution type reactor. A totally continuous operation with an inlet feed flow of *n*-heptane liquid and corresponding withdrawal of the reactor liquid phase containing the dissolved oligomers remains to be evaluated.

Acknowledgment

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