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"In everything you do, put God first, and he will direct you and crown you with success"

Proverbs 3: 6

THE OLIGOMERISATION OF 1-ALKENES TO HIGH VISCOSITY OILS

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A thesis submitted to the faculty of Chemistry, University of the Witwatersrand, Johannesburg, in fulfilment of the requirements for the degree of Doctor of Philosophy

Sasolburg, 1997

Dedicated to Kobus and Liam

Declaration

I declare that this thesis is my own, unaided work. It is being submitted for the Degree of Doctor of Philosophy in the University of Witwatersrand, Johannesburg. It has not been submitted before for any degree or examination in any other university.

(Signature of candidate)

----- day of ----- 1997

Abstract

The Phillips catalyst which has been used for the polymerisation of ethylene has interested many researchers and has been extensively studied over the past 40 years. By contrast there is little literature available on the *oligomensation* of alkenes in the presence of this catalyst and no intensive studies have been reported in the open literature to determine the effect of various reaction conditions on the oligomerisation reaction and on the characteristics of the oligomerisation product.

In this study a chromium impregnated extrudated support was developed and tested for the oligomerisation of, specifically, 1-hexene. Deactivation of the catalyst was rapid, and a possible explanation for this was found by means of various characterisation techniques. The active chromium sites were found to deactivate due to the formation of inactive Cr_2O_3 .

Both a "one-factor-at-a-time" and a statistical design approach were used to determine the effect of various reaction conditions on the 1-hexene oligomerisation reaction. The statistical design approach was novel in the sense that it has not been applied to the $\text{CrO}_3/\text{SiO}_2$ catalysed oligomerisation reaction previously. Many significant conclusions could be drawn from the results obtained. One of the most interesting effects observed was that an increase in the reaction temperature resulted in the formation of a yellow coloured oligomer product. An explanation for this coloured product could not be found with certainty, although a predominating presence of olefins in the oligomer was identified in the high temperature product.

The presence of a large number of 1-hexene isomeric oligomer products was observed as a result of extensive isomerisation after the oligomensation reaction had taken place. The Ziegler-Natta head-to-tail mechanism was identified as the mechanism predominating during the Cr/SiO_2 catalysed oligomerisation of 1-hexene.

Attempts were made to assess the use of zeolites for the oligomerisation of 1-hexene. The zeolites proved not to be suitable for the oligomerisation reaction due to a very high selectivity for dimer formation. The catalysts also had short cycle times. Zeolites were also sensitive towards oxygenates in the reactant stream and were deactivated by the presence of heavy products in the pores.

Opsomming

Die Phillips katalisator wat gebruik word vir die polimerisasie van etileen het al verskeie navorsers interesseer en is veral die afgelope 40 jaar intensief bestudeer. Daar is egter weinig literatuur beskikbaar oor die oligomerisasie van alkene in die teenwoordigheid van hierdie katalisator, en geen intensiewe ondersoek is al gedoen om die effek van verskeie reaksie kondisies op die reaksie en die eienskappe van die produk te bepaal nie.

'n Soliede draer is in hierdie studie ontwikkel waarop die chroom impregneer is en in hierdie vorm vir aktiwiteit in die oligomerisasie van spesifiek 1-hekseen getoets kon word. Deaktivering van die katalisator het egter vinniger plaasgevind as wat verwag was, en 'n moontlike verklaring hiervoor is gevind by wyse van verskeie karakteriseringstegnieke. Die aktiewe chroom punte het deaktiveer weens die vorming van onaktiewe Cr_2O_3 .

Beide 'n "een-faktor-op-'n-tyd" en 'n statistiese optimiserings-benadering is gevolg om vas te stel wat die effek is van verskeie reaksie kondisies op die oligomerisasie reaksie. Die statistiese benadering was uniek in die sin dat dit nog nie voorheen toegepas is op die $\text{CrO}_3/\text{SiO}_2$ gekataliseerde oligomerisasie reaksie nie. Een van die mees interessante verskynsels wat waargeneem is was die effek van 'n toename in die reaksie temperatuur op die produk eienskappe. Hoe temperature lei tot die vorming van 'n oligomeer produk met 'n geel kleur. 'n Verklaring vir hierdie verskynsel kon nie met sekerheid verkry word nie, alhoewel 'n hoë konsentrasie olefiene in die oligomeer waargeneem is in die hoë temperatuur produk.

Die teenwoordigheid van 'n groot hoeveelheid 1-hekseen isomeriese oligomeer produkte is waargeneem weens 'n groot mate van isomerisasie wat plaasvind na afloop van die oligomerisasie reaksie. Die Ziegler-Natta kop-aan-start meganisme is identifiseer as die oorheersende meganisme tydens die Cr/SiO_2 gekataliseerde

oligomerisasie van 1-hekseen.

Pogings is aangewend om die gebruik van zeolite vir die oligomerisasie van 1-hekseen te toets. Die zeoliete was nie geskik vir die oligomerisasie reaksie nie weens 'n baie hoe selektiwiteit vir dimeer vorming. Die katalisatore het ook kort siklus tye gehad. Zeoliete was ook gevoelig vir die teenwoordigheid van oksigene in die reagens voer en was deaktiveer deur die teenwoordigheid van lang oligomeerkettings in die porieë.

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