

1-Hexene dimerisation over a solid phosphoric acid catalyst

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$$\begin{bmatrix} \cos 90^\circ & \sin 90^\circ \\ -\sin 90^\circ & \cos 90^\circ \end{bmatrix} \begin{bmatrix} a_1 \\ a_2 \end{bmatrix} = \begin{bmatrix} 0 \\ 0 \end{bmatrix}$$

<http://www.xkcd.com/184>

Abstract

Solid phosphoric acid is a catalyst used for the upgrading of light olefins into fuels. To delve into the mechanism of olefin dimerisation over the catalyst, the oligomerisation of 1-hexene was investigated over a wide range of operating conditions. The reaction progression of 1-hexene dimerisation over solid phosphoric acid was interpreted by means of kinetic experiments for both a linear hexene (1-hexene) and a branched hexene (2,3-dimethylbutene). The reaction rate for both reagents was described by using an elementary kinetic model. From the experimental data it was shown that the rate of dimerisation of branched hexenes was faster than the rate observed for linear hexene dimerisation. To correlate the two sets of kinetic data, the reaction network was expanded to incorporate skeletal isomerisation of 1-hexene with dimerisation only taking place by the co-dimerisation of linear and branched hexenes and the dimerisation of branched hexenes. The fit of the kinetic equation demonstrated that the reaction rate of 1-hexene is essentially controlled by the rate of skeletal isomerisation. Due to the large activation energy for skeletal isomerisation, low reaction temperatures favoured the co-dimerisation of linear and branched hexenes whereas at higher temperatures, the reaction rate was dominated by the dimerisation of branched hexenes. The product distribution indicated that, because of the fast rates of both cracking and secondary dimerisation (*dimerisation of cracked products*), the product distribution instantaneously reached a pseudo equilibrium after the dimerisation of hexenes. Therefore the carbon distribution was found to depend only on the reaction temperature, not on the residence time in the reactor.

Solid phosphoric acid is a supported liquid phosphoric acid where the condensed state of the acid, e.g. ortho phosphoric acid (H_3PO_4) and pyro phosphoric acid ($\text{H}_4\text{P}_2\text{O}_7$), is dependent on the quantity of water present in the reaction mixture. With a decrease in water content, the distribution of acid shifts and the ortho phosphoric acid becomes more condensed ($\text{H}_4\text{P}_2\text{O}_7$, $\text{H}_5\text{P}_3\text{O}_9$ etc.), i.e. high water content \rightarrow low acid strength, low water content \rightarrow high acid strength. The experiments completed at various degrees of catalyst hydration and free acid loading showed that the rate of reaction over solid phosphoric acid was dependent on the acid strength of the catalyst. The effect of acid strength on the reaction rate was integrated into the rate constants by means of an exponential dependency on acid strength. It was also shown that both the product distribution and the degree of branching remained unaffected by acid strength. The constant product indicates that the rate of cracking is limited by the rate of

oligomerisation of hexenes, irrespective of the acid strength of the catalyst. Since the product from the dimerisation of 1-hexene could be used as fuel, the quality of the desired fuel would therefore depend solely on the reaction temperature, not on the hydration of the catalyst.

The work performed in this thesis has been published in two peer-review articles:

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2. Schwarzer R.B., du Toit E. and Nicol W. (2009) Solid phosphoric acid catalysts: The effect of free acid composition on selectivity and activity for 1-hexene dimerisation, *Applied Catalysis A: General*, 369, 83-89.

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Nomenclature

A	Linear hexenes isomers, mol/L
A_A	P_2O_5 weight percentage (i.e. acid strength)
B	Skeletal hexene isomers, mol/L
C_x	Concentration of molecule x, mol/L
D	Hexene depletion toward dimerised product, mol/L
E_a	Activation energy, kJ/mol.K
k_1	Kinetic constant for the rate of skeletal isomerisation, L/min.g
$k_{2,3}$	Kinetic constant for the rate of dimerisation and co-dimerisation, $L^2/mol.min.g$
$k_{x,o}$	Pre-exponential constant
k_{x,A_A}	Acid strength rate constant dependency
K_x	Distribution of molecule x with reference to the hexene depletion
K_{eq}	Experimentally determined equilibrium distribution of branched hexenes versus dimerised product
m_{cat}	Weight concentration of catalyst in the reaction mixture, g/L
$P_2O_5^\circ$	SPA base phosphoric acid strength, weight fraction P_2O_5
P_2O_5 (W %)	Acid strength of SPA
t	Time, min
T	Temperature, K
$W_{Free\ acid}$	Weight-free acid determined from titration, g
W_{H_2O}	Weight H_2O in the reaction mixture, g
V	Volume of reaction mixture, L

Abbreviations

AARE	Absolute average relative error
IB	Iso-butene
CD	Co-dimerisation of linear and branched hexenes
CFPP	Cold Filter Plugging Point
DLH	Dimerisation of linear hexenes
DBH	Dimerisation of branched hexenes
DMB	2,3-dimethyl-2-butene
<i>df</i>	Film thickness
FID	Flame ionisation detector
FT	Fischer-Tropsch
<i>i.d.</i>	Inside diameter
GC	Gas chromatography
MON	Motor Octane Number
2M1B	2-Methyl-1-butene
2M2B	2-Methyl-2-butene
MS	Mass-spectrometry
RON	Research octane number
SPA	Solid phosphoric acid
FA	Free acid

Figure symbols

◇	Concentration of branched hexenes
*	Concentration of linear hexenes
△	Concentration of oligomerised product

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