Dimerization of α-methylstyrene over Nafion / silica composite catalysts

Alfred Heidekum [a], Mark Harmer [b] and Wolfgang F. Hölderich [a,*]

[a] *Department of Chemical Technology and Heterogeneous Catalysis, University of Technology Aachen, Germany*
[b] *E.I. DuPont de Nemours & Company, Wilmington, USA*

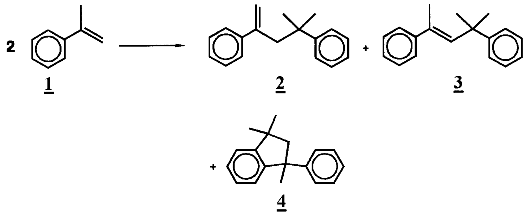
Received 17 June 1997; accepted 7 July 1997

The dimerization of α-methylstyrene (AMS) **1** over highly dispersed strongly acidic ion exchange resins based on Nafion® and entrapped in a porous silica matrix has been investigated in the continuous liquid phase. Over these new catalysts the dimerization rate is independent of the choice of solvent, which highlights the increased accessibility of the acid sites. Depending upon the reaction conditions different dimerization products are obtained. Complete conversion is achieved even at very high space velocities.

Keywords: α-methylstyrene, heterogeneous catalysis, Nafion, ion-exchange resin, solid acid, dimerization, continuous liquid phase, contact time

1. Introduction

The use of the acidic ion exchange resin Nafion® NR 50 in organic synthesis is described in several papers [1–4]. Due to the extremely low surface area of the polymer beads the activity of the polymer in some solvents and in gas phase reactions can be restricted. Reactions carried out in less polar solvents are less efficient. In polar solvents the polymer swells improving the material efficiently, due to an increase of accessibility [5]. On the other hand, entrapping nanosized Nafion® resin particles within a porous silica network extends the surface area by several orders of magnitude [6]. This new material shows improved performance in several acid catalyzed reactions, for example the successful isomerization of 1-butene [7]:



(1)

The products in the acid-catalyzed dimerization of AMS **1** are the unsaturated dimers 4-methyl-2,4-diphenyl-1-pentene **2**, 4-methyl-2,4-diphenyl-2-pentene **3** and the saturated dimer 1,1,3-trimethyl-3-phenylindan **4** according to eq. (1) as well as 4,6-dimethyl-2,4,6-triphenyl-1-heptene etc. as trimers. The unsaturated dimers are used as molecular weight controlling agents in the production of copolymers, such as acrylnitrile–butadiene–styrene resins (ABS) or styrene–butadiene rubber (SBR). The 1-pentene dimer **2** is an alternative substitute for tetrachloromethane or dodecylmercaptane and the hydrogenated forms of both isomers are of industrial value as components in lubrication compositions.

The homogeneous catalyzed dimerization with an aqueous solution of p-toluenesulfonic acid achieves high selectivity of about 92% to the desired dimer **2** [8]. However, the disadvantages of homogeneous catalyzed processes such as catalyst separation and disposal are well known. Therefore several solid acidic materials have been tested in this reaction. The use of ion exchange resin Amberlyst 15 achieves about 92% selectivity to **2** at 85% conversion in a discontinuous reactor [9]. With acid clay a batch process using carbonic acid ester as a reaction controlling agent gives a selectivity of more than 84% to **2** at conversion of 92.5% [10]. In the presence of microporous silicon aluminium phosphate a highly selective process is described carried out in the continuous gas phase [11]. The yield of **2** is about 92–95% at a low space velocity of about 1.2 h^{-1}.

In the present study we investigated the formation of the unsaturated dimers over the new strongly acidic Nafion® / silica composites in a continuous liquid phase with high space velocities in order to realize high space time yields.

2. Experimental

In batch experiments before the catalyst had been added, AMS and the solvent were preheated in a two-necked glass flask, equipped with a reflux condenser and a magnetical stirrer. Continuous experiments have been carried out in an up-flow stainless tube reactor with an

---

* To whom correspondence should be addressed.

internal diameter of 0.6 cm and a length of 12 cm. AMS was obtained from Fluka and dried over molecular sieve before use. Since the reaction is very fast and exothermic toluene was added for dilution and temperature control. The toluene was freshly destilled, stored under argon and pumped into the reactor by a metric pump. The composite catalysts have been prepared as described previously [6]. The Nafion® resin content was varied from 13 to 40 wt% and the catalyst was dried at 140°C for 4 h under vacuum. The products were identified by GC-MS, GC-IR and the saturated dimer **4** additionally by ^{1}H- and ^{13}C-NMR. Products were analyzed by GLC.

3. Results and discussion

3.1. Experiments in the liquid phase in a batch reactor

Table 1 shows the product distribution over two composite catalysts with different Nafion® contents and over the pure resin (Nafion® NR 50). Under these conditions all catalysts achieve virtually full conversion of AMS. Over the pure material the unsaturated dimer **2** is obtained predominantly whereas over both composite catalysts due to the higher activity and the consecutive nature of the reaction the saturated dimer **4** is formed exclusively.

These materials have already been investigated in a batch dimerization of AMS in different solvents. We have shown previously that by controlling the reaction conditions (shorter time) the main products **2** and **3** can be isolated in high yield (∼ 90%) [12].

3.2. Experiments in the liquid phase in continuous flow fixed bed

The reaction was studied in a fixed bed reactor varying the temperature, concentration of the starting material in toluene, space velocity and contact time.

3.2.1. Influence of temperature

In diagram 1 the product distribution is depicted for experiments at different temperatures. Even at 0°C and a space velocity of 6.8 h^{-1} nearly complete conversion is achieved. The selectivity to the dimeric products is less than 70% of which the unsaturated product **2** predominates having 63.4% selectivity. Raising the temperature always causes complete conversion but at the same time the selectivity to the unsaturated dimeric products drops due to the increased reaction rate of **2**, **3** to **4**. At 60°C the indane derivative **4** is produced almost exclusively with 95% yield. For comparison, an experiment carried out at 20°C using the pure polymer Nafion® NR50 as catalyst achieves less than 5% conversion after 1 h time on stream. In addition to the dimeric products the oligomers **5** such as different trimers or tetramers are formed. Raising the reaction temperature causes two effects:

- The oligomerization equilibrium is shifted to the side of the shorter compounds; the ceiling temperature of pure AMS is about 61°C [13].
- The reaction escapes via intramolecular alkylation to the very stable indane derivative **4**.

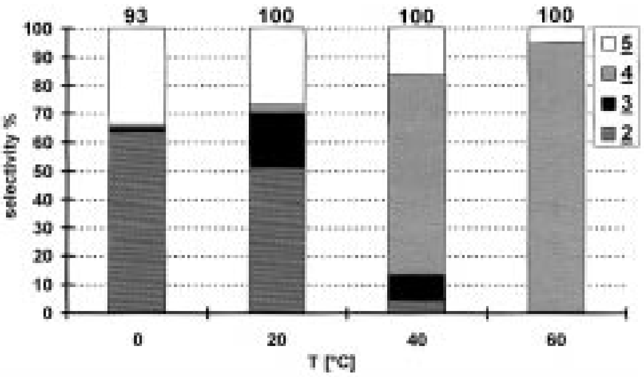


Diagram 1. Selectivities at different temperatures (oligomers **5**), TOS = 1 h. Reaction conditions: 50 wt% AMS in toluene, 1.5 g catalyst, WHSV = 6.8 h^{-1}. Figures above the columns = %conversion.

Table 1

Product distribution in the discontinuous liquid phase. Reaction conditions: $T = 60°C$, $t = 6.5$ h, catalyst loading 10 wt%, toluene in fourfold excess

Content of Nafion in the catalyst (%)	13	40	100
conversion (%)	98	100	97
product	**4**	**4**	**4**/**3**/**2**
selectivity (%)	91	99	24/15/47

3.2.2. Influence of space velocity

In diagram 2 experiments were carried out at different space velocities in a smaller amount of toluene. Again two effects are observed:

- The amount of the desired 1-pentene **2** is increased

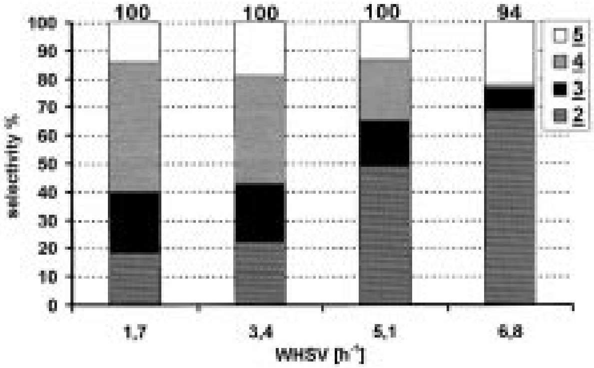
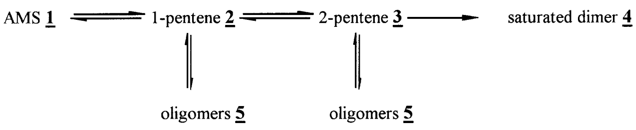


Diagram 2. Selectivities of the dimerization at different space velocities. Reaction conditions: TOS = 1 h, 20 wt% AMS in toluene, 1.5 g catalyst, $T = 20°C$. Figures above the columns = %conversion.

at higher space velocity. The conversion begins to decrease at WHSV $= 6.8\,h^{-1}$.

– On the other hand the amount of oligomers grows in the same way as the selectivity to **2** increases.

It seems that the substantial source of oligomers is the amount of the unsaturated dimer **2** which is in equilibrium with the oligomers as well as the other unsaturated dimer **3**:



3.2.3. *Influence of concentration*

The reduction of the amount of oligomers can be achieved via diluting the reaction solution. In diagram 3 the product distributions of runs carried out at the same temperature and the same space velocity but at different concentrations of the starting material in toluene are shown. At higher concentration of the starting material in toluene the selectivity to **2** decreases at the same time the quantity of oligomers is raised. With the subsequent reduction of the quantity of AMS **1** from 50 to 20% a constant decrease of the amount of oligomers occurs. In addition the selectivity to the non-desired products **2** and **3** is also decreased, which is probably due to a better temperature control in the reactor. This seems to be a further hint that the amount of oligomers is influenced by the selectivity to **2**.

However, increasing the concentration of the starting material at constant space velocity leads to a longer contact time on the catalyst. This parameter also influences the product distribution.

3.2.4. *Influence of contact time*

At higher reaction temperatures the reaction rate of the consecutive reactions significantly increases. Therefore, the space velocity has been enhanced significantly. Experiments carried out at 40 and 60°C and a space velocity of $13.6\ h^{-1}$ are shown in diagram 4. In order to study the influence of the contact time the catalyst has been mixed with glass beads of similar particle size before starting the run. In conclusion the mixed catalyst leads to a catalyst fixed bed in the reactor twice as long as the one without glass beads. The product distribution indicates a considerable influence of the contact time. At both temperatures the shorter fixed bed causes smaller conversion and simultaneously higher selectivity. At 60°C the amount of oligomers is very small although the selectivity to the dimer **2** is more than 60%.

In experiments carried out at higher temperatures only the indane derivative **4** is obtained as a single product even at very high space velocity. For example, at 100°C and a space velocity of $61.2\ h^{-1}$ the indan derivative **4** is obtained at about 97%, which is a space time yield of about $59.4\ kg\ (kg\ h)^{-1}$.

3.2.5. *Lifetime of the catalyst*

The selectivity to the dimeric products of the reaction considerably influences lifetime of the catalyst. In particular the oligomeric compounds distinctly tend to deactivate the catalyst.

Diagram 5 demonstrates the product distribution over a longer reaction period. The selectivity to all oligomeric compounds is in an area of about 10%. As a result, at constant selectivity to the dimeric products the activity of the catalyst drops by about 15% at least after 10 h. Though, in order to improve the lifetime of the catalyst the selectivity to all dimeric products has to be increased at least. To achieve a high selectivity at elevated temperature the contact time has to be adjusted very seriously. In addition to that, the selectivity will likely be raised by further reduction of the concentration of the starting material in the solvent.

4. Conclusions

Using highly dispersed Nafion® in silica catalyst

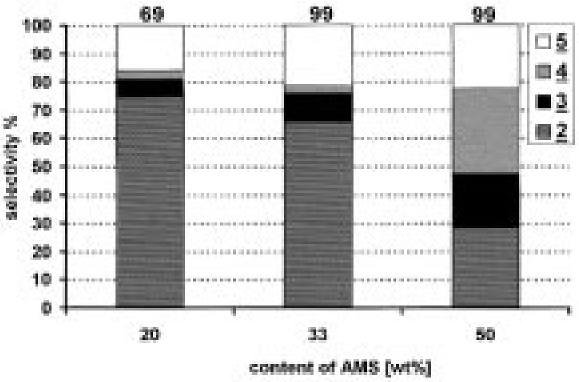


Diagram 3. Selectivities of the dimerization at different concentrations. Reaction conditions: TOS = 1 h, WHSV $= 6.8\ h^{-1}$, 1.5 g catalyst, $T = 20°C$. Figures above the columns = %conversion.

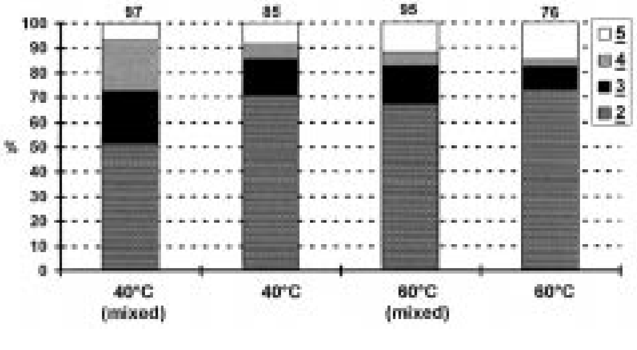


Diagram 4. Selectivities at contact times of $\tau = 6.7$ and $\tau = 13.3$ min (mixed catalyst). TOS = 1 h; reaction conditions: 20 wt% AMS in toluene, 0.75 g catalyst (mixed with 0.75 g glass beads of similar particle size); WHSV $= 13.6\,h^{-1}$. Figures above the columns = %conversion.

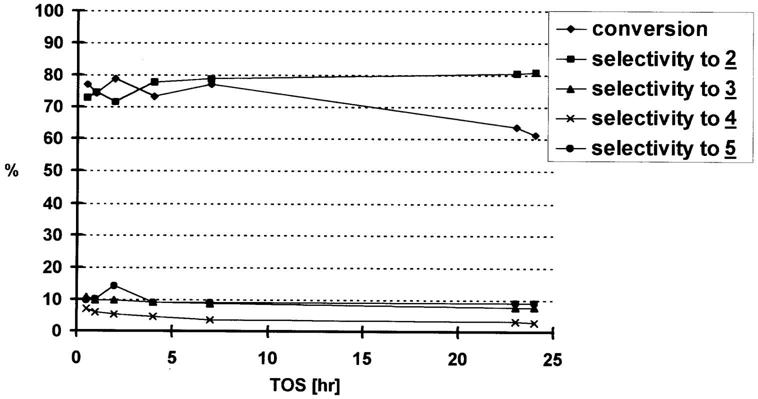


Diagram 5. Dimerization over longer reaction period. Reaction conditions: 20 wt% AMS in toluene. 0.5 g catalyst mixed with 1 g glass beads, WHSV = 20.4 h^{-1}, $T = 40°C$.

shows much higher activity in the dimerization of AMS than the pure Nafion® NR50, which is due to the improved accessibility of the acid sites in this material. In the continuous liquid phase the industrial favored dimeric products **2** and **3** can be obtained in a selectivity of more than 86% at conversion > 95%. In general the product distribution is mainly influenced by the contact time and the concentration of the starting material in the solvent. The amount of oligomeric products likely causes the decrease of the activity with time on stream.

Acknowledgement

We thank Du Pont de Nemours, Wilmington for financial support and the kind delivery of the catalyst material.

References

[1] G.A. Olah, P.S. Iyer and G.K.S. Prakash, Synthesis (1986) 513.
[2] F.J. Waller and R.W. van Scoyoc, ChemTech (1987) 438.
[3] G.A. Olah, R. Malhotra, S.C. Narang and J.A. Olah, Synthesis (1978) 672.
[4] H. Konishi, K. Suetsugu, T. Okana and J. Kiji, Bull. Chem. Soc. Jpn. 55 (1982) 957.
[5] T.D. Gierke, G.E. Munn and F.C. Wilson, J. Polym. Sci. Polym. Phys. 19 (1981) 1687.
[6] M.A Harmer, W.E. Farneth and Q. Sun, J. Am. Chem. Soc. 118 (1996) 7708.
[7] Q. Sun, M.A. Harmer and W.E. Farneth, J. Chem. Soc. Chem. Commun. (1996) 1201.
[8] H. Nishizawa, T. Saito, T. Itoh and K. Mashita, EP 0 641 756 (1994).
[9] B. Chaudhuri and M.M. Sharma, Ind. Eng. Chem. Res. 28 (1989) 1757.
[10] M. Inaba, S. Inui, H. Kurokawa and F. Mizutani, EP 0644 169 (1994).
[11] R. Thome, A. Tißler, B. Unger and G. Öhlmann, DE 43 31 116 (1995).
[12] Q. Sun, M.A. Harmer and W.E. Farneth, J. Catal. 164 (1996) 62.
[13] K.J. Ivin, Angew. Chem. 85 (1973) 533.