Oligomerization of propene on an alumoxane-grafted MCM-41 host with bis(cyclopentadienyl)zirconium dimethyl ($Cp_2Zr(CH_3)_2$)

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The anchoring of alumoxane, synthesized by the *in situ* hydrolysis of trimethylaluminum, on the internal pore walls of a mesoporous MCM-41 support generates a highly active and selective host for bis(cyclopentadienyl)zirconium dimethyl ($Cp_2Zr(CH_3)_2$) in the oligomerization of propene. The regioselective preference of the immobilized metallocene is preserved and a typical Flory–Schulz distribution for the propene oligomers is obtained.

Keywords: oligomerization, metallocene, MCM-41, methylalumoxane

1. Introduction

Since the metallocene/alumoxane system [1,2] is known to polymerize α-olefins in a stereospecific way [3–6], much attention has been directed to the steric and electronic design of the metallocene structure. On the other hand, substitution or reduction of the excessive amounts of methylalumoxane (MAO) still remains one of the important challenges. One solution to this problem is the anchoring of the alumoxane structure onto the silanol groups of a mesoporous material [7]. Moreover, it seems more appropriate to finely distribute the MAO phase in these type of materials by *in situ* hydrolysis of trimethylaluminum (TMA) [7] rather than by physisorption of the commercial compound [8,9]. We recently demonstrated that physisorption leads to well-defined islands of MAO with characteristic internal clustering of the alumoxane species, which ceases the catalytic potential in alkene oligomerizations of the metallocene at low alumoxane concentrations [7].

In this communication, we report a new application of the heterogeneous alumoxane system synthesized by *in situ* hydrolysis of TMA in the mesopores of a siliceous host. Oligomerization of α-olefins, performed at low Al/Zr ratios, has hardly been published in literature [10–12] and a proper heterogenization has never been discussed before. The MAO phase on the pore walls of the MCM-41 is accessible for the metallocene component which does not require supplemental MAO in the oligomerization of propene. At low Al/Zr ratios, the MAO-MCM-41 host is more active than the homogeneous system. Moreover, narrowing the pore size of the host increases the propagation rate (or growth factor α) of the metallocene catalyst, which opens up shape-selective properties for the host. The developed heterogeneous system is promising for the production of commodity alkenes such as plasticizers or surfactants [13].

2. Experimental

The MCM-41 molecular sieves were synthesized according to known procedures [7,14,15]. Anchoring of alumoxane onto the mesoporous host was accomplished by controlled *in situ* hydrolysis of trimethylaluminum (TMA) as described earlier in detail [7]. The water-saturated MCM-41 sample was suspended in 270 ml toluene in a 600 ml stainless-steel reactor (Parr Instruments), which was flushed with nitrogen and cooled to 273 K under continuous stirring for 1 h. TMA (Aldrich) was diluted in 20 ml toluene and added slowly to the suspension, resulting in a water/Al ratio of 1. The MAO-MCM-41 was filtered, washed with toluene, and dried under inert atmosphere. Physisorption of MAO (85 g of a 10 wt% solution in toluene, Aldrich) on 0.77 g of the calcined MCM-41 sample was performed for 3 h at room temperature under inert atmosphere.

Finally, 0.18 mmol of $Cp_2Zr(CH_3)_2$, obtained from the metallocene dichloride by alkylation with TMA in a typical Al/Zr ratio of 100, was added under nitrogen atmosphere diluted in 10 ml of toluene to the suspension of *in situ* prepared MAO-MCM-41.

The catalytic reactions were performed in a water-cooled batch reactor continuously fed with methane (491 ml/min), propene (1,400 ml/min) and nitrogen (40 ml/min) at an overall pressure of 0.7 MPa. The solvent and the gases used during the oligomerization reactions were carefully dried over molecular sieve 5A (Merck). After reaction, the alumoxane structure and the remaining TMA are decomposed prior to analysis. The propene oligomers were analyzed by HP 5890 gas chromatography with FID detection using a Chrompack CP-SIL-5 CB column. The dimer

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products were analyzed isothermally at 313 K, whereas the propene tri-, tetra- and pentamers were saturated prior to analysis on a hydrogen/cold trap (TCT injection system from Chrompack) using a Pd catalyst at a temperature of 453 K and trapped downstream in a fused silica tube cooled at 183 K. Consecutively, the collection trap is heated rapidly to 473 K and the oligomers are analyzed isothermally at 323 K. The different isomers are assigned based on Kovats retention indices and GC-MS experiments. The growth factor α is derived from the correlation $\log(W_m/m) = (m-1)\log\alpha + 2\log(1-\alpha)$, with W_m the weight fraction of the oligomer and m the oligomerization degree.

Nitrogen sorption isotherms were recorded at 77 K with an Omnisorp 100 CX from Coulter, while X-ray diffraction measurements were performed on a Siemens D5000 equipment with a Cu K_α source ($\lambda = 0.15419$ nm, radiating at 40 kV and 50 mA) and operating with a scan rate of 1°/min.

3. Results and discussion

Alumoxane formation in the mesopores of the host changed the average pore size from mesoporous (2.75 nm) to microporous (2.4 nm) dimensions and sharply decreases its surface area (from 880 to 470 $m^2\,g^{-1}$), as evidenced by sorption measurements (figure 1). Capillary condensation within the pores of the MAO-MCM-41 is thereby strongly reduced. One may expect effects of the pore size in the catalytic reactions, performing shape-selective features on a molecular level. The d_{100}-spacing decreases from 3.99 to 3.79 nm and, although the main X-ray diffraction peak is broadened, the hexagonal arrangement of the mesoporous material remains intact. ^{29}Si-, ^{27}Al- and ^{13}C-MAS-NMR of the MAO-MCM-41 provide further evidence for the formation of alumoxane and proper anchoring on the mesoporous host, while elemental microanalysis points to a homogeneous distribution of the alumoxane species over the tubular channels of the mesoporous host [7].

Table 1
Oligomerization of propene on $Cp_2Zr(CH_3)_2$/MAO-MCM-41 in toluene at 333 K.

Run	Support material (MCM-41)[a]	Al/Zr[b]	Conc. Zr (μM)	Activity[c]	α
1	Ludox, C_{16}	40	0.60	3.02	0.48
2	Ludox, C_{16}	40	0.12	5.04	0.38
3	Ludox, C_{16}	20	0.60	1.78	0.47
4[d]	Ludox, C_{16}	40	0.60	1.43	0.30
5	Cab-O-Sil, C_{10}	40	0.60	3.13	0.55
6[e]	–	40	0.60	2.29	0.50
7	Physisorbed MAO	40	0.60	–	–

[a] The MCM-41 materials were synthesized with the indicated silica sources and surfactants.
[b] Based on the Al content of the MAO-MCM-41.
[c] Oligomerization activity of the zirconocene (10^5 g mol-Zr^{-1} h^{-1}) after 75 min reaction time based on gas chromatographic propene conversion with methane as internal standard.
[d] A flow of hydrogen (500 ml/min) was added to the feed.
[e] Reference experiment with homogeneous MAO (10 wt% in toluene, Witco).

The results of the oligomerization of propene with a non-bridged metallocene catalyst, $Cp_2Zr(CH_3)_2$, on MAO-MCM-41 are summarized in table 1. Encapsulation of the metallocene compound into the pores of the alumoxane anchored host produces a highly active and selective oligomerization catalyst. Under identical reaction conditions, the MAO-MCM-41 is catalytically more active than the corresponding homogeneous system (entries 1 and 6). Proper anchoring and distribution of alumoxane onto the pore walls of the host seems to limit bimolecular deactivation reactions as well as cluster formation of the alumoxane. The true heterogeneity of the catalytic system was confirmed by the negligible oligomerization activity of the supernatant of MAO-MCM-41.

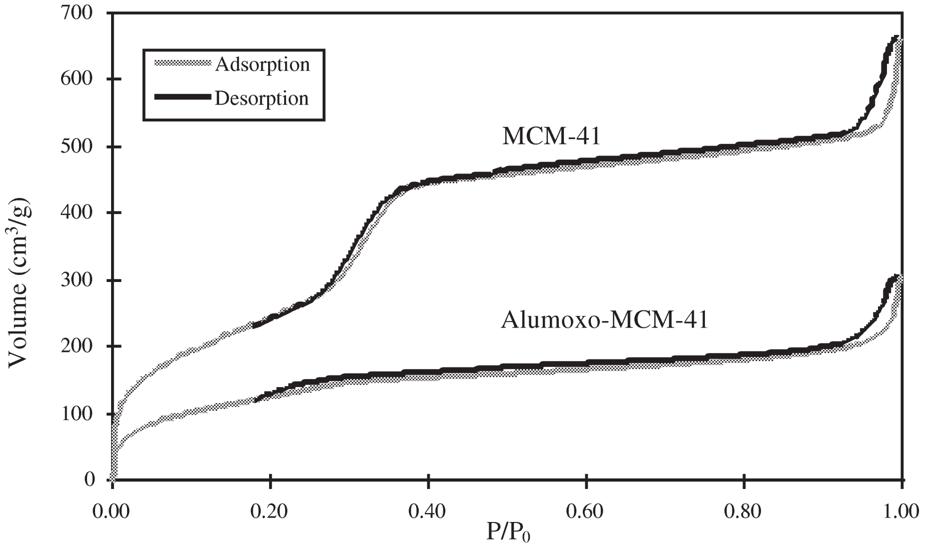

Figure 1. Sorption isotherm of MCM-41 upon alumoxane anchoring.

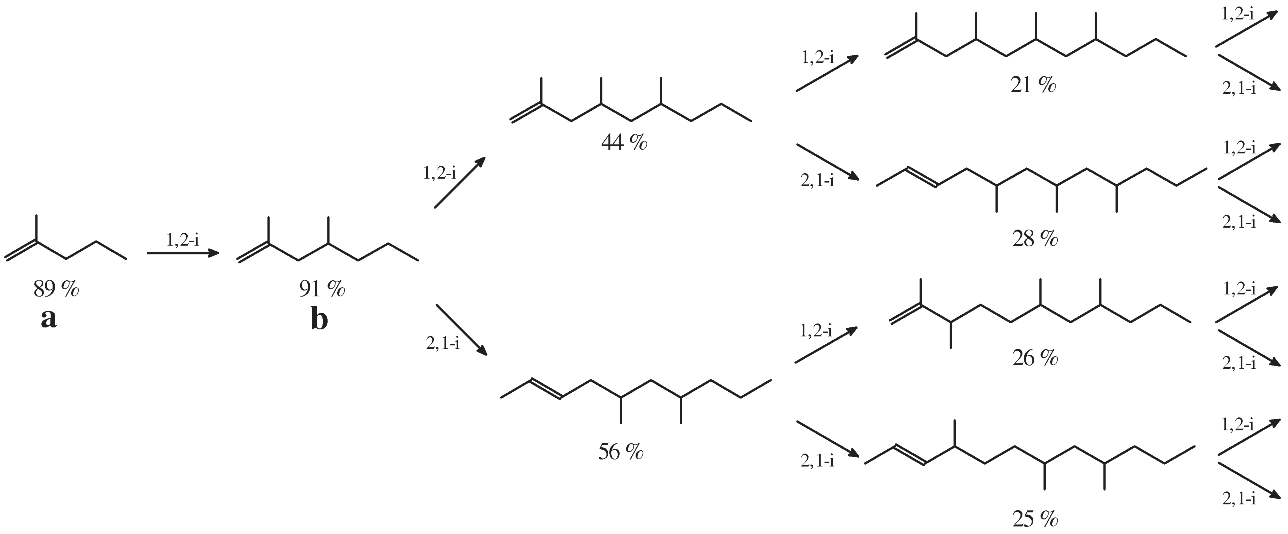

Figure 2. Overall oligomerization scheme for the $Cp_2Zr(CH_3)_2$/MAO-MCM-41 catalyst (entry 1) with indication of the isomer distribution in each oligomer fraction.

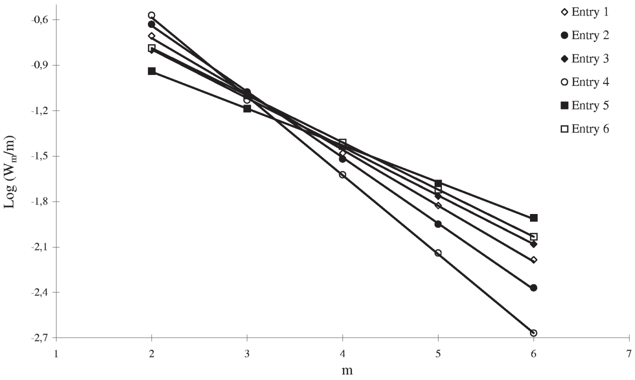

Figure 3. Flory–Schulz distribution of the propene oligomers for the MAO-MCM-41 with respect to the homogeneous conditions.

The product distribution of the propene oligomers is of the Flory–Schulz type (figure 3), a characteristic aspect of single-site catalysis [16]. Thus, the selectivity for the different reactions can be quantified by the growth factor α, representing the probability of the propagation step. α is calculated from the weight fractions of the different oligomers and ranges in our oligomerization set-up from 0.30 to 0.55. Anchoring of alumoxane on the mesoporous host slightly decreases the α-factor and thereby increases the weight fraction of propene di- and trimers (column 7). Physisorption of MAO (entry 7) onto the mesoporous host did not reveal any significant oligomerization activity in our set-up, which is a strong argument in favor of the *in situ* formation of alumoxane species.

Narrowing the pore size of the molecular sieve MCM-41, by altering the alkyl chain length of the surfactant, slightly increases the activity per Zr and α-factor of the oligomerization reaction (entry 5), providing shape selectivity of the host. A smaller pore aperture of the MAO-MCM-41 sterically hinders the incorporation of metallocene molecules, thereby increasing the average molecular weight of the products.

Table 2
Selectivity of the propene oligomers and distribution of the isomers within each oligomer length.

Composition (wt%)	Run 1	Run 5	Run 6
Dimer	**42.3**	**30.7**	**37.0**
2-M-1-$C_5^=$	89.0	87.6	88.8
4-M-2-$C_5^=$	9.2	10.9	7.3
2-$C_6^=$	1.4	1.1	3.6
2,3-diM-1-$C_4^=$	0.3	0.3	0.3
4-M-1-$C_5^=$	0.1	0.1	0.0
Trimer	**23.2**	**20.8**	**23.9**
2,4-diM-C_7	91.2	91.7	92.0
2,3,5-triM-C_6	5.0	6.7	5.1
4-M-C_8	3.1	1.1	2.4
2,3-diM-C_7	0.7	0.4	0.5
Tetramer	**12.5**	**14.2**	**13.3**
4,6-diM-C_{10}	55.6	55.7	56.9
2,4,6-triM-C_9	44.4	44.3	43.1
Pentamer	**7.9**	**10.1**	**8.5**
2,3,6,8-tetraM-C_{11}	28.1	27.8	28.0
4,6,8-triM-C_{12}	26.2	26.6	26.8
4,6,9-triM-C_{12}	25.1	25.8	25.2
2,4,6,8-tetraM-C_{11}	20.6	19.8	20.0
Hexamer	**5.3**	**7.6**	**5.9**
Higher oligomers	**8.7**	**16.7**	**11.4**

A smaller catalyst concentration (entry 2) increases the oligomerization activity and decreases the α-factor of the reaction, whereas a lower Al/Zr ratio (entry 3) reduces the catalytic activity and leaves the α-factor unchanged. Supplemental addition of hydrogen (entry 4) decreases the oligomerization activity, which might be due to a smaller concentration of propene in the reaction medium. However, hydrogen acts as a chain transfer agent, converting the propene monomer mainly in di- and trimer products, hereby sharply decreasing the α-factor.

In table 2, the isomer distribution of the propene oligomers is shown for entries 1, 5 and 6 of table 1. The

β-H termination reaction is a typical aspect of the non-bridged metallocene catalyst forming a vinylidene unsaturated endgroup. Although the α-factor is different for the three reactions, the isomer distribution is comparable, giving 2-methyl-1-pentene (**a**) and 2,4-dimethyl-1-heptene (**b**) as the main products for the di- and trimerization, respectively (figure 2). Hetero-oligomerization, with the formation of $C_5^=$ or $C_7^=$ isomers (for the dimer) and $C_8^=$ or $C_{10}^=$ isomers (for the trimer) was not observed, which implies that only β-H termination occurs with the subsequent insertion of an α-olefin into the Zr–H bond.

Starting from the fourth insertion, the regioirregular 2,1-insertion of propene strongly influences the isomer distribution, generating position-dependent branching or a shift of the unsaturation. Moreover, it seems that the tetramers are mainly composed of 2 isomers, the pentamers of 4 and the hexamers of 8. While regioregular 1,2-insertions are dominant in the beginning of the growing oligomer chain, the metallocene looses its regioselective preference after a few propagation steps and 1,2- or 2,1-insertions take place at random. This lack of regioselectivity results in an almost statistical composition of isomers within each oligomer number. Altering the geometric composition of the metallocene generates α-olefin oligomers with different branching positions.

Moreover, adjusting ethene to the α-olefin feedstock diminishes the amount of branching in the oligomer chain. In this respect, the effect of the ethene addition on the α-factor and on the isomer distribution has to be studied.

4. Conclusion

In conclusion, alumoxane anchoring on the pore walls of MCM-41 by *in situ* synthesis provides an excellent host for the $Cp_2Zr(CH_3)_2$ metallocene with respect to the homogeneous conditions. A Flory–Schulz distribution for the propene oligomers is observed and typical isomer compositions were obtained as a consequence of the chain-length-dependent insertion mechanism of the metallocene.

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