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The development of an environmental friendly catalytic system for the conversion of olefins

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Abstract

An elegant method is described for the synthesis of ZSM-22. By controlled addition of seeds and applying stirring during the crystallization, the phase purity and the crystal size can be controlled. The H-ZSM-22 is tested in the dense phase oligomerization of propene at 180–250°C and 70 bar. It is found that adding small amounts of water significantly increases the activity and decreases the deactivation of the catalyst. Secondly, it is shown that catalyst activity is higher after calcination at 400°C versus 550°C and that smaller crystal sizes positively affect the catalyst activity. Both observations are ascribed to the presence of active sites located near the zeolite outer surface accounting for a major part of the catalytic activity.

Keywords: Zeolites; Ton; Olefin oligomerization

1. Introduction

In 1935, Ipatieff et al. [1] of Universal Oil Products Company (UOP) introduced a process in which propene/butene mixtures are converted over supported phosphoric acid into a distillate range product. Since its introduction the process has been further optimized and developed. Besides fuel oil production, other applications were developed, such as the selective production of C_6–C_{12} olefins, which are intermediates for the synthesis of plasticizers [2]. The main disadvantages of the UOP catalyst are its short catalyst life, the absence of any possibility to tailor the catalyst properties to product demand, and problems arising on spent catalyst removal from the reactor and environmental issues related to disposal.

Some alternative systems are commercially available, but most of them are based on the use of transition metals, which requires (expensive) feed purifications (IFP Dimersol, Hüls Octol) [3,4], or they mainly aim at making synthetic fuels (MOGD) [5,6].

This paper describes the development of a new environment friendly catalyst based on acid zeolites with sheaf-like morphology, and especially TON-type zeolites as drop-in catalysts replacing the supported phosphoric acid (SPA). The zeolitic material combines high activity at moderate reaction conditions (180–250°C) with excellent product selectivity. In this work, it will be shown that key parameters for the catalyst performance are the zeolite morphology, activation, and the reaction conditions applied.

2. Experimental

2.1. Synthesis and analysis

The chemicals used in the synthesis of ZSM-22 were Ludox AS40 silica sol, $Al_2(SO_4)_3 \cdot 18H_2O$

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(Baker), KOH pellets 87.5% (Baker) and 1,6-diaminohexane (Janssen Chimica).

Samples were synthesized as follows [7]:

(1) Preparation of Solution A was done by dissolving in water the ingredients in the following order and quantities:

$Al_2(SO_4)_3 \cdot 18H_2O$ (Baker)	3.50 g
KOH pellets (87.5%) (Baker)	7.85 g
1,6-diaminohexane (Janssen Chimica)	16.70 g
H_2O	177.16 g
Rinse water	23.95 g

(2) Solution B has the following composition:

Ludox AS40 (40% SiO_2)	72.02 g
H_2O	100.03 g
ZMS-22 seed crystals	(variable)

The Ludox and the water were weighed in a glass mixing beaker. The Ludox/water mixture was homogenized by mixing for a few seconds. Solution A and the rinse water were added to Solution B. The resulting mixture was stirred for 15 min. The molar composition of the synthesis mixture was:

$$1.28\,K_2O/3.00\,R/0.110\,Al_2O_3/10\,SiO_2/402\,H_2O$$

in which R=1,6-diaminohexane.

The crystallization was done in autoclaves used in either static or stirred mode.

2.1.1. *Crystallization, washing, and recovery*

The autoclaves are placed in a room temperature oven, then the oven was heated within 2 h to 160°C. Crystallization time was varied between 54 and 97 h. After crystallization the samples were washed several times with water and then dried at 105°C for 3 h. The SiO_2/Al_2O_3 of the ZSM-22 product was 55.

2.1.2. *Analysis*

X-ray powder diffraction was used to identify the crystalline phases present in the solid product. Powder diffraction patterns were obtained using a Siemens D500 powder diffractometer.

Scanning electron microscopy was used to obtain information on the crystal size and size distribution. The micrographs were obtained using a Philips SEM 515 (W-filament).

2.2. *Catalytic tests*

Catalyst performances were evaluated using a fixed bed, continuous flow reactor. A propene/propane mixture (50:50, w/w) was used as standard feedstock. The feed can be saturated with water by passing through a hydrator prior to its introduction into the reactor. After saturation at 40°C, the water content of the feed was around 0.15 mol%. The reaction was carried out in the supercritical phase at 70 bar and 195–225°C. The catalyst was used after acidification by conventional NH_4Cl or HCl treatment, and calcination in air at 400–550°C for 16 h. The catalyst powder was pressed in a laboratory press, sieved and the fraction between 0.2–1.1 mm was retained for the testing. Product analysis was done off-line by GC.

3. Results

3.1. *Synthesis of the ZSM-22 crystals*

3.1.1. *Purity*

When ZSM-22 is synthesized using the procedure outlined above, different phases can be obtained depending on the conditions applied. This is shown in Table 1.

The data in Table 1 suggest that, depending on the synthesis conditions, both pure ZSM-5 and ZSM-22 or mixed phases are obtained. Addition of small quantities of preformed ZSM-22 triggers the onset of ZSM-22 crystallization. When 100 wt ppm of ZSM-22 seeds are used, pure ZSM-22 is obtained. Alternatively, applying stirring during crystallization also has a positive effect on the purity of the ZSM-22 product. In this case, seeding has only a secondary effect.

3.1.2. *Morphology*

The members of the TON family are generally reported as having a sheaf-like morphology [8,10–13]. The crystal dimensions can vary from submicron to several microns. In the latter case, these (needle-shaped) materials are potentially toxic. The SEM analysis of ZSM-22 crystals from Table 1 are given in Table 2 and Figs. 1–3

From these data it can be derived that very small, nontoxic ZSM-22 crystals can be obtained by applying stirring during the synthesis.

Table 1
Effect of different synthesis parameters on the purity of ZSM-22

Catalyst code	Crystallization		Seeding	Stirring	Phases obtained	
	temperature (°C)	time (h)	(wt%) based on gel weight			cristobalite
A	160	72	None	No	Amorphous (trace of ZSM-5)	No
B	160	97	None	No	ZSM-5	No
C	160	72	0.04	No	ZSM-22+ZSM-5	Trace
D	160	54	0.10	No	ZSM-22	No
E	160	54	None	Yes	ZSM-22	No
F	160	54	0.10	Yes	ZSM-22	No

Table 2
SEM analysis of the ZSM-22 crystals

Code	Crystal morphology	Figure
C	Sheaf-like crystals with a length of approx. 15 μ	Fig. 1
D	Sheaf-like crystals with a length of approx. 4.5 μ	Fig. 2
F	Clusters of intergrown crystals of approx. 1 μ	Fig. 3

4. Catalytic experiments

4.1. *Effect of feed hydration*

The oligomerization of propene under the conditions just described was used as a standard reaction for evaluation of the performance of different ZSM-22 materials.

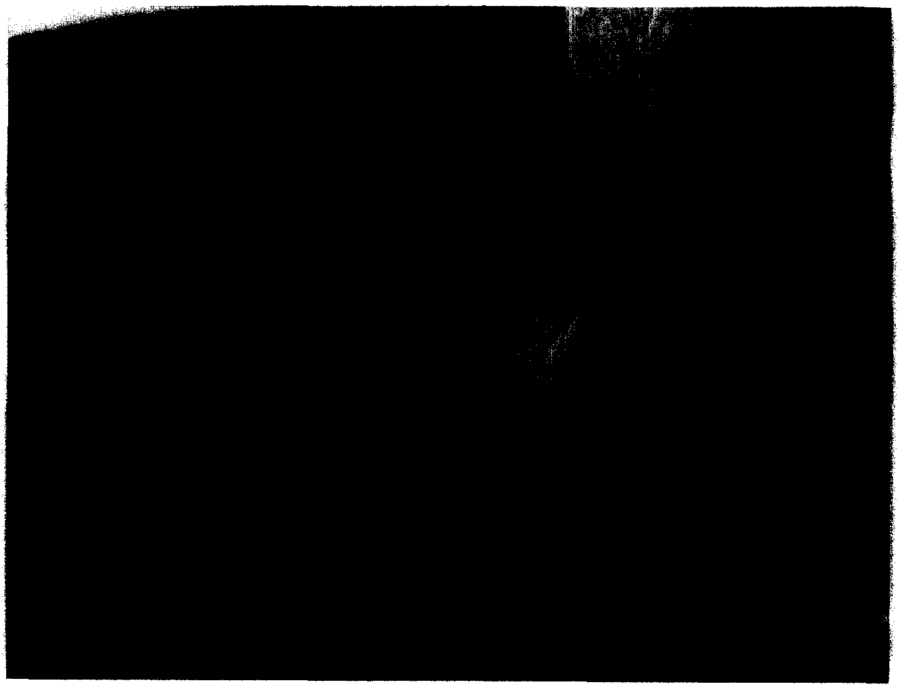

Fig. 1. SEM picture of ZSM-22 code C.

Fig. 2. SEM picture of ZSM-22 code D.

Fig. 3. SEM picture of ZSM-22 code F.

The H-ZSM-22 catalyst was prepared using code E crystals, calcined at 550°C in oxygen for 16 h, exchanged with NH_4Cl and calcined again at 550°C for 16 h.

The propene feedstock was passed through the catalyst at 205°C, 0.7 MPa and MHSV=1.3–1.6 $\mathrm{wt\,wt^{-1}\,h^{-1}}$. After 2 days the temperature was increased to 230°C in order to overcome the rapid catalyst deactivation. After 7 days on stream, the feedstock was passed through a hydrator set at 40°C. The water content of the feed was increased from <0.02 to 0.15 mol%. The activity of the catalyst is given in Table 3.

In the second experiment, the same fresh catalyst was evaluated on propene feed, but hydration was applied as in the beginning of the test. The reaction temperature was varied between 150 and 180°C. After 7 days on stream, hydration was bypassed. The results of this test are shown in Table 4.

The data from the first experiment show that the H-ZSM-22 catalyst deactivates rapidly in the absence of water. The conversion drops from 76 to 53% despite a temperature increase from 205 to 230°C. However, when 0.15 mol% of water is added to the feed, the activity of the partially deactivated catalyst increases significantly and conversions >80% are obtained.

In the second experiment, using a hydrated propene feed, conversions are obtained well above those of the first experiment, although a lower reaction temperature and higher feed rate were used. When the hydration is bypassed, after 7 days on stream, the catalyst deactivates rapidly.

Both experiments clearly demonstrate that the pressure of small quantities of water positively affect the oligomerization activity of the H-ZSM-22 catalyst. In addition, the experiment shows that the deactivation in the absence of water is reversed by adding water.

Table 3
Oligomerization of propene over H-ZSM-22 (code E) at 70 bar; effect of adding the feed hydration

Hydration (°C)	No hyd	No hyd	No hyd	No hyd	No hyd	40
Temperature (°C)	205	205	230	230	230	230
Space velocity ($\mathrm{wt\,wt^{-1}\,h^{-1}}$)	1.26	1.62	1.44	1.40	1.60	1.59
Hours on stream	20	44	68	92	164	188
Catalyst life (wt product/wt catalyst)	9.5	13.1	29.2	42.3	72.4	87.2
Propene conversion (wt%)	76.78	18.69	94.91	79.97	53.11	78.99

Table 4
Oligomerization of propene over H-ZSM-22 (code E) at 70 bar; effect of cutting the feed hydration

Hydration (°C)	40	40	40	40	40	40
Temperature (°C)	180	180	150	170	170	180
Space velocity ($\mathrm{wt\,wt^{-1}\,h^{-1}}$)	1.90	1.83	1.99	1.56	1.81	1.97
Hours on stream	10	34	58	64	130	154
Catalyst life (wt product/wt catalyst)	9.3	30.3	44.5	48.6	96.7	117.4
Propene conversion (wt%)	98.33	97.09	60.08	87.09	81.38	88.79

Table 5
Oligomerization of propene over H-ZSM-5 (Catalyst B) at 70 bar and MHSV=1.9 $\mathrm{wt\,wt^{-1}\,h^{-1}}$; effect of adding feed hydration

Temperature (°C)	230	230	230	250	250	250
Hours on stream	6	21	45	53	69	94
Propene conversion (wt%)						
without hydration	65.42	24.45	17.75	69.29	55.24	NA
with hydration	99.73	53.71	33.82	98.45	NA	91.34

Table 6
Activation procedures for ZSM-22

Catalyst code [a]	Calcination after synthesis	NH_4Cl exchange	Activation	Catalyst color [b]
F	550°C – 16 h	Yes	550°C – 16 h	White
G	None	Yes	400°C – 16 h	Grey

[a] The parent ZSM-22 was as synthesized code F.

[b] Both materials showed identical XRD crystallinity.

In Table 5, propene oligomerization data are given using the ZSM-5 material obtained by the static, nonseeded synthesis method (Catalyst B in Table 1). The catalyst was calcined at 550°C, NH_4 exchanged and activated at 450°C in air. The catalyst was tested side-by-side with and without feed hydration. As for the ZSM-22, feed hydration also positively influences the activity of the H-ZSM-5 catalyst. The H-ZSM-5 catalyst, however, shows a lower overall activity as compared to the H-ZSM-22, as indicated by the higher reaction temperatures required for the former.

4.2. *Effect of catalyst calcination*

In another set of experiments, H-ZSM-22 was tested after applying different activation procedures, as summarized in Table 6.

Both catalysts were tested on propene feed using the standard conditions including feed hydration. The conversions obtained are shown in Fig. 4. The data show that initial conversions for both catalysts are complete, but upon ageing Catalyst F (550°C treated) deactivates faster. After increase of the reaction temperature from 205 to 215°C, the difference remains.

4.3. *Effect of crystal size*

ZSM-22 has monodimensional, nonintersecting pores with small 10MR windows [9,16]. The acid form of the zeolite has been evaluated in several catalytic applications indicating a pronounced shape selective behavior [13,17,18]. The increased catalytic activity of small crystals has been reported [19].

The effect of the crystal size on the oligomerization of propene was studied by evaluating the ZSM-22 with varying crystal size obtained from the different synthesis methods (see Tables 1 and 2). In order to completely void the pores, all materials were calcined at

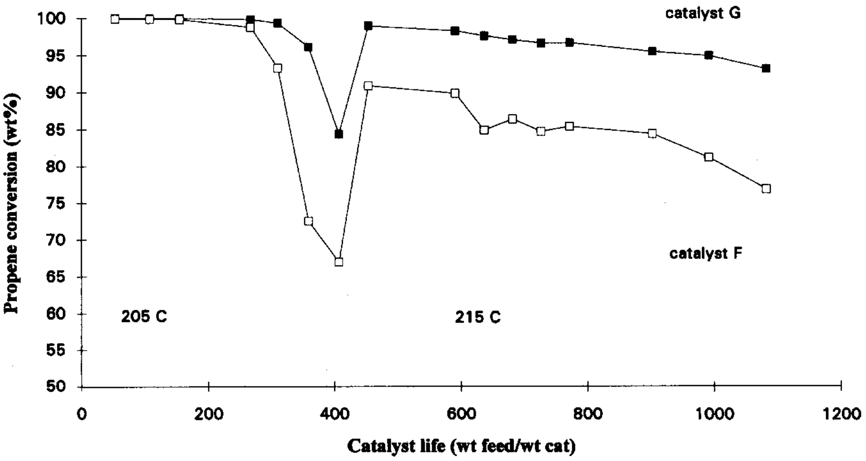

Fig. 4. Time-on-stream experiment on propene feed for H-ZSM-22 activated at 400°C (Catalyst G) and 550°C (Catalyst F).

Table 7
Catalyst lives for H-ZSM-22 with different crystal sizes in the oligomerization of propene. Reaction conditions are MHSV=2 wt wt^{-1} h^{-1}, 70 bar, 180–235°C and feed hydration at 40°C

Crystal length [a] (μ)	Catalyst life (wt product/wt catalyst)
27±7	252
15±4	384
7±2	636
1±0.3	>1000 [b]

[a] Based on SEM analysis.

[b] Test was stopped at 225°C.

550°C for 16 h prior to acidification by NH_4^+ exchange. The catalysts were activated by a second temperature treatment at 550°C in air. Propene oligomerization was done using standard conditions and feed hydration.

Table 7 lists the catalyst lives obtained for four different crystal sizes. The catalyst life is defined as wt product/wt catalyst. The start-of-run temperature was 180°C, giving a conversion >80% for all materials. The temperature was then gradually increased to the maximal end-of-run temperature of 235°C in order to overcome the catalyst deactivation. An average conversion >70% was targeted.

The data show that the catalyst activity increases significantly when the crystal size is decreased. In case of the smallest crystals (Catalyst F in Table 6) the test was stopped after 1400 h on stream, although the end-of-run temperature was not attained yet.

4.4. *Product selectivities over H-ZSM-22*

The conversion and the oligomer selectivities as functions of the catalyst age, for Catalyst F, are shown in Figs. 5 and 6, respectively. The catalyst deactivates most rapidly at 205°C; after increasing the temperature, the conversion is increased and the deactivation becomes slower. At 225°C almost no deactivation is observed, and a conversion >95% is maintained.

The corresponding data in Fig. 6 show that the product selectivity depends on the overall conversion and catalyst age. The C_6 selectivity is generally the highest and increases with decreasing conversion and also with catalyst ageing. The C_{12} and C_{15} selectivities are inversely proportional to the C_6 selectivity. The C_9 selectivity is almost not affected by conversion and catalyst age.

Over the commercial phosphoric acid catalyst, the typical propene oligomer selectivity is:

$$C_6 : C_9 : C_{12} : C_{15} = 4 : 55 : 14 : 2 \text{ wt\%}$$

The sum of the oligomers is typically <70 wt%. For the H-ZSM-22, this sum, except for the first high conversion data at 205°C, equals 90% or higher. This

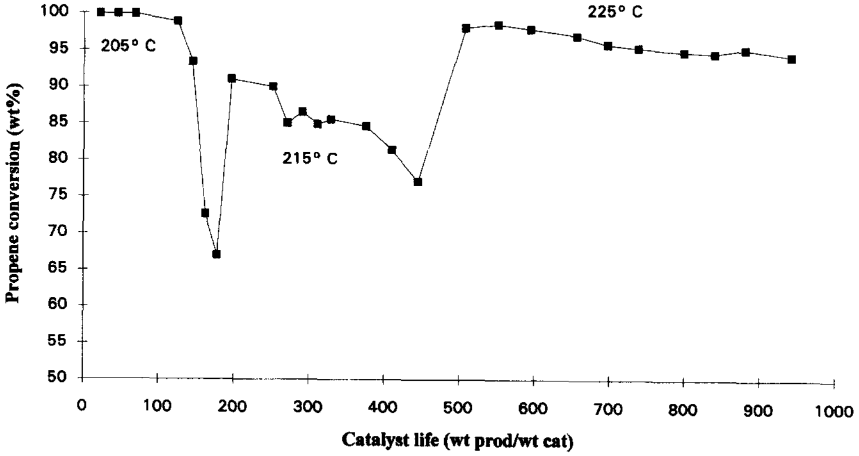

Fig. 5. Propene conversion as function of catalyst life for Catalyst F. Reaction conditions are MHSV=2 wt wt^{-1} h^{-1}, 70 bar, hydration at 40°C.

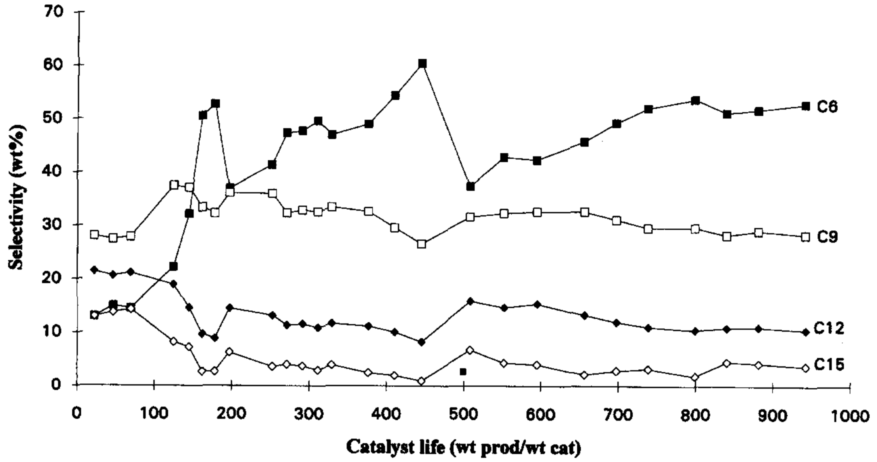

Fig. 6. Propene oligomer selectivities as function of catalyst life for Catalyst F, same reaction conditions as in Fig. 5.

Table 8

Average isomer structure from propene at 90%$^+$ conversion over H-ZSM-22 (Catalyst F), H-ZSM-5 (Catalyst B) and solid phosphoric acid

C_9 Isomers [a]	H-ZSM-22 (wt%)	H-ZSM-5 (wt%)	Solid phosphoric acid (wt%)
Linear	2.7	0.3	0.3
Mono-branched [b]	32.7	9.9	10.2
Di-branched [b]	56.7	81.5	83.1
Triple branched	7.9	8.5	6.4
Average degree of branching [c]	1.7	2.0	2.0

[a] After hydrogenation of the olefin to the corresponding paraffin.

[b] Branches can be methyl or ethyl groups.

[c] Calculated as the sum of the fraction of isomers multiplied by the number of branches.

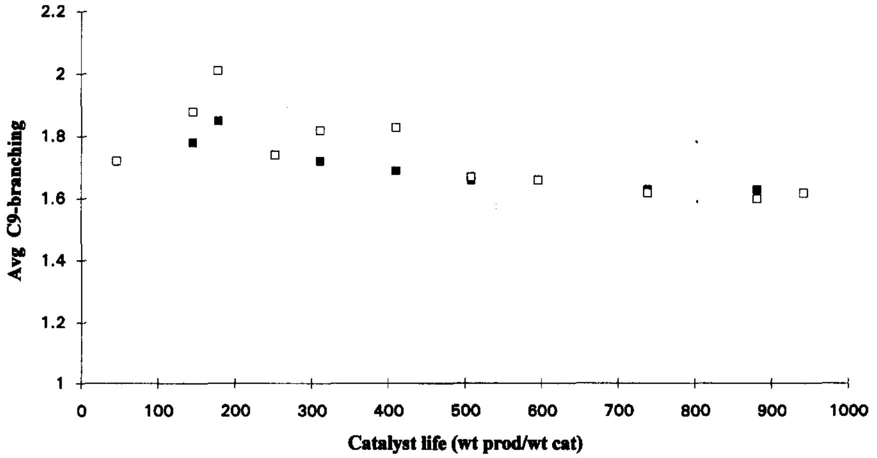

Fig. 7. Nonene isomer structure as function of catalyst life for Catalyst G (filled squares) and Catalyst F (open squares).

indicates a very low cracking-hetero-oligomerization activity of the H-ZSM-22.

The average isomer structure of the propene trimer was analyzed by GC. Table 8 compares the isomers obtained over H-ZSM-22 (Catalyst F), H-ZSM-5 (Catalyst B) and solid phosphoric acid.

The data show that over H-ZSM-5 and solid phosphoric acid, nonenes with a similar isomer structure are formed. Di-branched isomers are the main product and almost no linear nonenes are formed.

On the contrary, over H-ZSM-22, significantly more mono-branched and linear nonenes are formed at the expense of the di-branched isomers. The amount of triple branched isomers is comparable for the three catalysts. As a result, the average branching degree of the nonenes is the lowest for the H-ZSM-22.

In Fig. 7, the average C_9 branching is plotted against the catalyst life. Data are shown for the H-ZSM-22 heat treated at 400°C (Catalyst G) and 550°C (Catalyst F). The data suggest that upon ageing, the catalyst becomes more selective to less branched isomers. Comparison of Figs. 5 and 7 indicates that the branching increases only slightly when the conversion is dropped significantly.

5. Discussion

During the crystallization of ZSM-22 other phases can be formed such as ZSM-5, cristobalite, ferrierite and ZSM-48 [12,20–22]. The extent to which these are formed depends on the crystallization conditions applied.

The formation of the other zeolitic phases depends mainly on the composition of the synthesis gel, namely the SiO_2/Al_2O_3 ratio, the alkalinity and the type of alkali cation used. Also higher temperatures tend to favor the formation of these other phases.

The formation of cristobalite typically results from the presence of temperature gradients or hot spots in the autoclave. This can be minimized when stirring is applied, but care has to be taken to avoid the presence of mixture pockets whose temperature would allow the formation of cristobalite.

The method for ZSM-22 synthesis described in this paper allows to overcome these ZSM-22 purity problems especially for larger scale syntheses, where efficient stirring may become more difficult. The method consists of controlled addition of preformed ZSM-22 crystals to the synthesis gel. As shown in Table 1, the same gel will produce, under static conditions, either pure ZSM-22 or ZSM-5 or mixed phases, depending on the presence and the amount of ZSM-22 seeds. When at least 0.10 wt% of seeds are added, pure ZSM-22 is formed.

When stirring is used, pure ZSM-22 is more easily obtained, and addition of seeds becomes of secondary importance.

Besides the effect on crystal purity, the data in Table 2 show that stirring also significantly affects the dimensions of the ZSM-22 crystals formed. A synthesis gel producing pure ZSM-22 crystals with a needle length of 15μ, when crystallized under static conditions, will produce crystals smaller than 1μ when adequate stirring is applied. Secondly, the SEM pictures indicate that the sheaf-type morphology of the smallest crystals has disappeared; the crystals are present as agglomerates of very small particles.

When the H-ZSM-22 catalyst is tested in the oligomerization of propene, a rapid deactivation is typically observed due to deposition of heavy oligomers in the zeolite pores.

However, when a small amount of water is added by saturation of the feed at 40°C, the catalyst activity is recovered and the deactivation is significantly decreased.

As the reaction temperatures used are too low to cause dehydroxylation of the framework, it is proposed that water decreases the production or accelerates the desorption of the heavy oligomers [14,15].

The effect of water on the oligomerization activity of zeolites is not restricted to ZSM-22, but has also been observed on H-ZSM-5.

The catalyst performance is also influenced by the calcination/activation procedure applied. As shown in Fig. 4, catalyst activity decreases when the calcination temperature is increased from 400 to 550°C. In addition, the acidification by NH_4^+ exchange can be done on the synthesized material without prior removal of the template. This behavior is tentatively explained by the existence of acid sites located near or at the crystal outer surface. This is in line with the observations reported earlier on Pt-ZSM-22 [17], where it was proved that the isomerization of *n*-decane involves acid sites located near the pore mouths.

The involvement of active sites at the outer surface can also explain the influence of the crystal size observed. However, a reduced mass transfer limitation inside the pores of the smaller crystals cannot be excluded.

The propene product selectivity over the H-ZSM-22 indicates that the catalyst has a lower tendency to crack and hetero-oligomerize than solid phosphoric acid. As a result more true oligomers are formed. In addition, the H-ZSM-22 is more selective to dimers as compared to trimers. Both effects are further pronounced upon ageing of the catalyst. This is explained by a progressive decrease of catalyst activity, reducing the possibility to crack oligomers or further convert the dimers. The deactivation is probably the result of fouling of the acid sites decreasing the zeolite acidity. The isomers produced over H-ZSM-5 and solid phosphoric acid, indicating a pronounced shape selective behavior of the monotubular pore system of the ZSM-22. The observation again is accentuated by catalyst ageing. Referring to the role of the outer surface mentioned earlier, this seems to confirm that acid sites near the pore mouths are involved [17].

6. Conclusion

H-ZSM-22 is a promising catalyst to replace solid phosphoric acid catalyst for the oligomerization of propene to C_6–C_{12} olefins. The zeolite can be synthesized in a pure form with controlled crystal size when seeding and stirring are applied. The oligomerization reaction is found to occur at or near the outer surface as indicated by the influence of the crystal size and calcination conditions. The products formed over H-ZSM-22 have a high selectivity to true oligomers especially dimers. In addition, the isomer structure analysis shows an increase of the linearity of the oligomers as compared to ZSM-5 or solid phosphoric acid products. It is tentatively proposed that active sites located at the pore mouths account for this shape selective behavior.

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