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Olefins oligomerization: thermodynamics and kinetics over a mesoporous silica–alumina

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Abstract

Kinetic experiments of the oligomerization reaction were carried out in a spinning basket reactor, suitable for gas–liquid–solid systems. The catalyst used is an amorphous mesoporous silica–alumina (MSA) showing outstanding catalytic activity in the propylene oligomerization [G. Bellussi, C. Perego, A. Carati, S. Peratello, E. Previde Massara and G. Perego, Proceedings of the 10th International Zeolite Conference, Garmisch-Partenkirchen, Germany, 17–22 July 1994, Stud. Surf. Sci. Catal. 84 (1994) 85.].

The reaction rate of oligomerization, catalyzed by MSA extrudates [G. Bellussi, C. Perego and S. Peratello, US Patent 53 428 14, 1993.], has been described by a Langmuir–Hinshelwood–Hougen–Watson kinetic model and by considering the fugacity of reactants involved. The estimated activation energy (~18 000 J/mol) together with the experimental results suggest that the propylene oligomerization is limited by mass transfer inside the mesopores of MSA phase. © 1999 Elsevier Science B.V. All rights reserved.

Keywords: Kinetic experiments; Mesoporous silica–alumina; Olefins oligomerization

1. Introduction

The oligomerization of light olefins is industrially applied for the production of petrochemicals (nonene, dodecene) and fuels (polymeric gasoline, middle distillate) [3,4]. The interest of the latter is due to their low environmental impact (low heteroatoms and aromatics content).

Light olefins oligomerization is a highly exothermic reaction, heat of reaction is around 1046–1381 J/$g_{\text{reacted olefin}}$ [5], then it will be thermodynamically favored at low temperature. This explains why reactor design is dictated by heat-removal considerations. Main reactor configurations are “chamber” or “tubular”, in which heat is removed by dilution with the feed, between two catalytic beds, or by exchange through the wall, respectively.

Among a number of acid catalysts claimed to be able to catalyze such a reaction, it is worth to mention the following two:

- phosphoric acid supported on kieselguhr (Catpoly process [5]);
- ZSM-5 (MOGD process [6,7]).

The importance of the above processes is due to their known industrial application. There are, in fact, about 30 plants worldwide running with phosphoric acid supported on kieselguhr and one commercial scale equipment, using ZSM-5 zeolite, in a Mobil refinery [3]. The major diffusion of the first catalysts,

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with respect to the second, is mainly due to economic reasons. Notwithstanding the MOGD technology is both more efficient and flexible than that of Catpoly, it must be taken into account the high investment costs involved in revamping the old plants with the new technology. Anyway, owing both to the more stringent laws and increasing costs, concerning chemical product handling and disposal, supported phosphoric acid will be likely replaced in the future with more friendly catalysts such as zeolites.

We have recently developed a proprietary process for the oligomerization of light olefins to gasoline and jet-fuel catalyzed by a new amorphous mesoporous silico–alumina (MSA) [2,8]. This new amorphous mesoporous silica–alumina possesses remarkable catalytic activity in acid catalyzed reactions [1,9–12]. MSA shows the outstanding catalytic activity in oligomerization of light olefins, in comparison with other solid acid catalysts [1], mainly producing highly branched oligomers, according to its peculiar pore size distribution. By H-NMR studies it has been shown that, on average, the number of carbon atoms between branches is four for ZSM-5 and two for amorphous silica–alumina [13]. These oligomers have interesting properties: the gasoline boiling range fraction shows quite high RON (research octane number) with low benzene content; the kerosene boiling range fraction shows a very low smoke and freezing point, as reported in Table 1. Furthermore, MSA is surely a more environmentally friendly material with respect to supported phosphoric acid.

Several papers on oligomerization kinetic have been published where ZSM-5 zeolite is used as catalyst [14,15]. Here we report a kinetic study on propylene oligomerization, over MSA, which output has been devoted to the process development.

Table 1
Some characteristics parameters for the oligomeric fuels

	Gasoline	Jet-fuel[a]
Density (g/cm^3)	0.73	0.77
Freezing point (°C)		<−60
Smoke point (mm)		38
Aromatic (vol%)		1.8
Sulfur (wt%)		0
RON	97–102	
MON[b]	84–86	
Cetane index		27

[a] After hydrogenation.
[b] Motor octane number.

2. Experimental

2.1. The catalyst

The MSA gel (active phase) was prepared as described in [1]. MSA has a BET surface area around 800 m^2/g and a narrow pore size distribution in the region of mesopores (ca. 20 Å of radius). Transmission electron microscopy (TEM) analysis confirmed the uniform mesoporous structure of MSA: the pores are uniform in size but randomly distributed in the space [1]. By extrusion small MSA particles (5–50 μm) are dispersed in the binder (γ-alumina), then formed in cylindrical pellets (extrudates) according to [2]. The so obtained MSA extrudates are characterized by a BET surface area around 550 m^2/g and a bimodal pore size distribution (Fig. 1): a narrower one, of radius centered around 20 Å due to MSA [1] and a broader one, of radius over 1000 Å due to γ-alumina. MSA extrudates, having diameter ranging from 2 to 4 mm and length ranging from 3 to 5 mm, were used to perform kinetic experiments.

2.2. Catalytic test

All the experiments were carried out in a spinning basket reactor [16], suitable for gas–liquid–solid systems (Fig. 2). The reactor, loaded with fresh catalyst

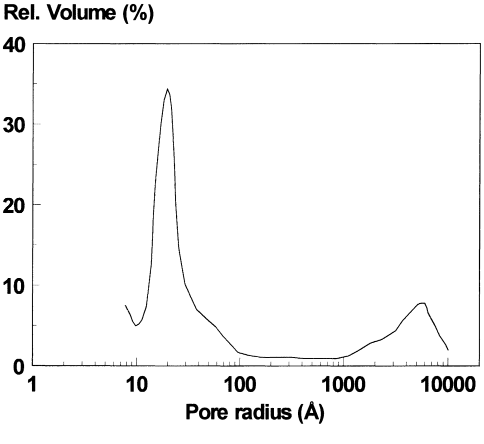

Fig. 1. Pore size distribution of MSA.

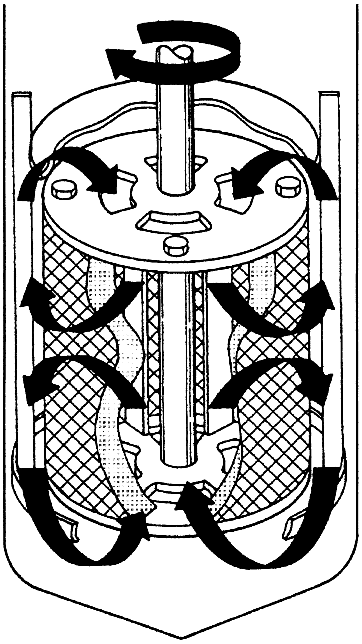

Fig. 2. Spinning basket section.

for each experiment, was fed with a liquid phase of propylene–propane mixture, by means of a high pressure HPLC type pump and maintained at the desired pressure by a back pressure control valve. The feed flow rate was measured by a balance weighting the feed vessel. The liquid oligomers and the gas phase were separated in a gas/liquid separator maintained at low temperature (T=−5°C). The gas phase line was connected with an on-line gas chromatograph, by which propylene conversion was measured, while the liquid oligomers were analyzed by an off-line GC simulated distillation (ASTM D-2887).

Several experiments were performed by changing temperature (100–200°C), pressure (2–4 MPa), propylene/propane ratio (form 30/70 to 70/30 wt/wt) and WHSV (1–20 g_{olefin}/h g_{MSA} referred to the binder-free MSA).

3. Results and discussion

According to [16], stirring speed tests were performed in order to find out the minimum stirring rate needed to eliminate external mass-transfer effects. As shown in Fig. 3, the minimum stirring rate results to be 800 r.p.m.

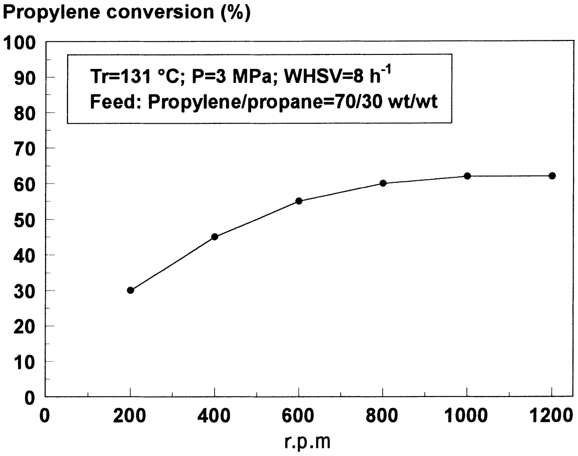

Fig. 3. Propylene conversion as a function of basket r.p.m.

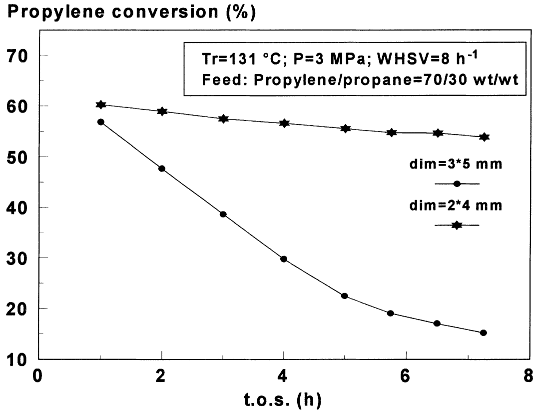

Fig. 4. Comparison between two extrudates having different sizes.

Since oligomerization reaction, catalyzed by solid acids, is affected by deactivation [17] and decay rate depends on catalyst particle size, the pellet size effect was also investigated. Propylene conversion as a function of time-on-stream (t.o.s.) is reported in Fig. 4 for two extrudates having different size. It is seen that higher extrudates size corresponds higher decay rate. Then, in order to obtain experimental data with small influence of deactivation, all the experiments were carried out with 2×4 mm extrudates. The initial activity, hence the initial reaction rate, was calculated by extrapolating the conversion curves at zero t.o.s.

The dependence of total conversion on contact time (defined as 1/WHSV), is reported at different reaction

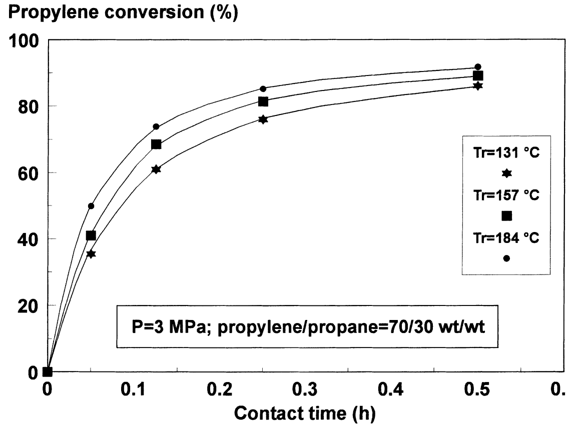

Fig. 5. Propylene conversion versus contact time, at different reaction temperature.

temperatures and total pressure in Figs. 5 and 6, respectively.

As expected, from thermodynamic and kinetic considerations, total conversion of propylene, hence reaction rate, increases when temperature and/or total pressure increase. The same trend is obtained when increasing the olefin concentration in the feed (Fig. 7).

According to the Continuous Stirred Tank Reactor (CSTR) model [18,19], propylene reaction rate can be simply calculated by the following equation:

$$\begin{aligned} r_{C_3H_6} &= F^0_{C_3H_6}/W_{MSA} \times (Z_{in} - Z_{out})/42 \\ &= \mathrm{WHSV} \times (Z_{in} - Z_{out})/42 \qquad (1) \end{aligned}$$

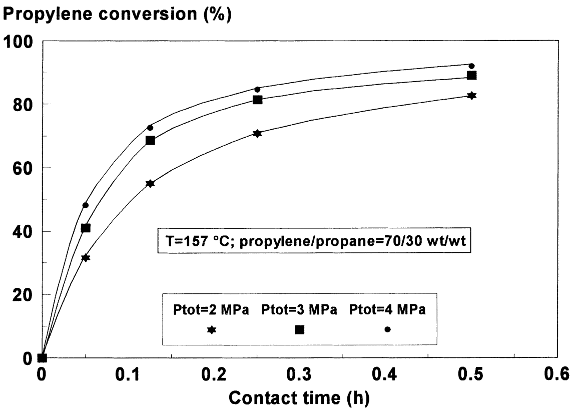

Fig. 6. Propylene conversion versus contact time, at different total pressure.

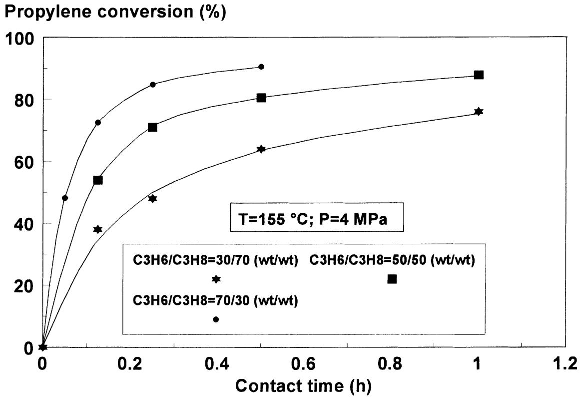

Fig. 7. Propylene conversion versus contact time, at different propylene concentration in the feed.

Where $r_{C_3H_6}$ is the propylene reaction rate ($\mathrm{mol}_{C_3H_6}$/h g_{MSA}), $F^0_{C_3H_6}$ the feed rate of propylene ($g_{C_3H_6}$/h), W_{MSA} the mass of MSA (g_{MSA}), Z_{in} and Z_{out} are the inlet and outlet propylene mass fraction, respectively (g/g) and 42 is the propylene molecular weight ($g_{C_3H_6}/\mathrm{mol}_{C_3H_6}$).

According to the Langmuir–Hinshelwood–Hougen–Watson approach (LHHW) [20] and considering as rate determining step the reaction between an adsorbed molecule of propylene, over a surface site (σ), and another one present in gaseous phase (Rideal–Eley mechanism):

$$C_3H_6 + \sigma \leftrightarrow \sigma\text{–}(C_3H_6) \quad \text{(equilibrium)}$$

$$\sigma\text{–}(C_3H_6) + C_3H_6 \rightarrow \text{oligomers} \quad \text{(rate determining step)}$$

it is possible to describe the propylene reaction rate by the following equation:

$$r_{C_3H_6} = k \times p_{C_3H_6} \times \vartheta_{C_3H_6} \qquad (2)$$

where k ($\mathrm{mol}_{C_3H_6}$/h g_{MSA} MPa) is the kinetic constant, $p_{C_3H_6}$ (MPa) the propylene partial pressure and $\vartheta_{C_3H_6}$ is the fraction of catalytic sites occupied by propylene molecules. If the first step is at equilibrium it results in

$$\vartheta_{C_3H_6} = b_{C_3H_6} \times p_{C_3H_6}/(1 + b_{C_3H_6} \times p_{C_3H_6}) \qquad (3)$$

then

$$r_{C_3H_6} = k \times b_{C_3H_6} \times p^2_{C_3H_6}/(1 + b_{C_3H_6} \times p_{C_3H_6}) \qquad (4)$$

where $b_{C_3H_6}$ (MPa^{-1}) is the adsorption–desorption equilibrium constant of propylene.

In the range of temperature, pressure, feed composition, product distribution and propylene conversion of the present study, both liquid and gaseous phases are present. Therefore, the overall propylene mole fraction in the reactor, calculated from the experimental propylene conversion determined by GC analysis, may be significantly different from the vapor phase mole fraction of propylene, due to the high non-ideality of the mixture. In other words the propylene exhibits a non-negligible solubility into the oligomer. According to Satterfield [21], the reaction rate of a mixture at vapor–liquid equilibrium does not depend on the physical state of the fluid which contacts the catalyst, as the chemical potential of each component is the same in the two phases even if the concentration is different.

These considerations justify the substitution of the partial pressure by the fugacity in the reaction rate expression. Then Eq. (4) becomes

$$r_{C_3H_6} = k \times b_{C_3H_6} \times f^2_{C_3H_6}/(1 + b_{C_3H_6} \times f_{C_3H_6}) \qquad (5)$$

where

$$f_{C_3H_6} = \varphi^{V}_{C_3H_6} \times y_{C_3H_6} \times P_{tot} = \varphi^{L}_{C_3H_6} \times X_{C_3H_6} \times P_{tot} \qquad (6)$$

In the Eq. (6) the meaning of the symbols is

- $\varphi^{V}_{C_3H_6}$ and $\varphi^{L}_{C_3H_6}$ are the fugacity coefficients in vapor and liquid phase, respectively;
- $y_{C_3H_6}$ and $X_{C_3H_6}$ are the propylene molar fraction in vapor and liquid phase, respectively.

The use of the fugacity in the reaction rate equation supplies an easy way to model reactors, such as adiabatic bed reactors, in which the reaction mixture enters as a gaseous phase and a liquid phase is formed as the conversion proceeds along the reactor.

This simplification in reactor modeling complicates the kinetic parameters estimation. A T–P flash calculation, in fact, is required to associate to each experimental reaction rate value a propylene fugacity value. The composition of the mixture to be flashed is related to the propylene experimental conversion by the following equations, that embody the reduction of the number of moles in the oligomerization reaction:

$$X_{C_3H_6} = (1 - \eta_{C_3H_6})/[(1 - \eta_{C_3H_6}) + 42/44 \times (1 - Z_{in})/Z_{in} + 42/M_w \times \eta_{C_3H_6}] \qquad (7)$$

where $X_{C_3H_6}$ is the molar fraction of propylene in the mixture, $\eta_{C_3H_6}$ the propylene conversion, Z_{in} the inlet propylene mass fraction and M_w is the average molecular weight of the oligomers produced.

Furthermore, owing to the fact that in many experimental conditions propylene and propane are above their critical temperature (92°C), an equation of state is necessary to calculate the fugacity coefficients. The equation used in the present study is the RKS equation of state [22].

The relationship between the kinetic constant and temperature is described by the Arrhenius equation:

$$k = k^0 \times \exp[-E_a/R \times (1/T - 1/T^0)] \qquad (8)$$

or

$$\ln(k) = \ln(k^0) - (E_a/R) \times (1/T - 1/T^0) \qquad (9)$$

where k^0 is the kinetic constant at temperature T^0, E_a is the activation energy (J/mol) and R is the gas constant (8.314 J/mol K).

Experimental data were well fitted by the kinetic model proposed, considering propylene fugacity instead of partial pressure. The model parameters were estimated by using a non-linear least-square analysis [23], by which an apparent activation energy of about 18 000 J/mol and an average error of 4% were estimated (Fig. 8). The goodness of fitting was also verified for each experiments: as an example Fig. 9 reports the comparison between experimental and calculated conversions for two kinetic experiments,

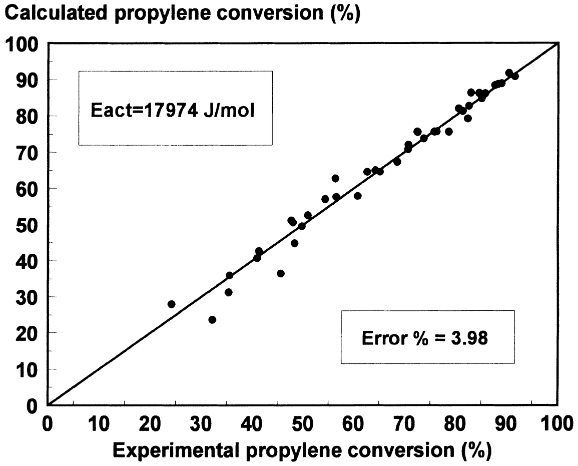

Fig. 8. Result of fitting. Calculated conversion versus experimental.

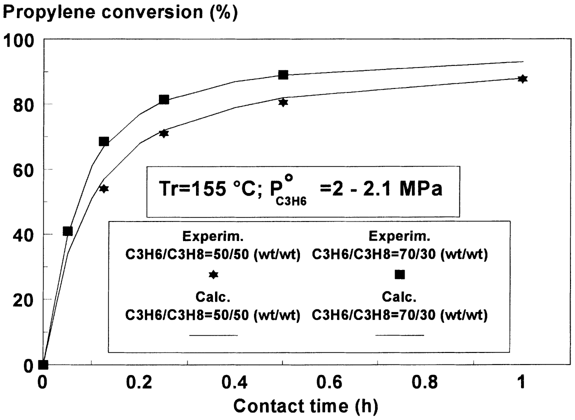

Fig. 9. Result of fitting. Calculated conversion (curves) and experimental (symbols) versus contact time.

performed by keeping constant the initial propylene partial pressure but varying the feed composition.

An apparent activation energy of about 18 000 J/mol suggests that the propylene oligomerization is limited by mass transfer.

In order to verify if such a limitation was confined mainly in the mesopores belonging to MSA phase, a kinetic test was carried out by using pure MSA granules having the same size as the extrudates.The granules were obtained by crushing and sieving to 6–8 mesh the MSA gel.

In Fig. 10 a comparison between pure MSA granules and extrudates is reported. Such a comparison was performed by keeping constant the amount of MSA active phase present in the reactor. Taking into account that pure MSA granules have a monomodal pore size distribution, centered around 20 Å of radius [1], while extrudates have a bimodal pore size distribution (Fig. 1), the lower activity of the granules, with respect to the extrudates, is in agreement with the hypothesis that mass transfer limitations can be ascribed mainly to the MSA domain.

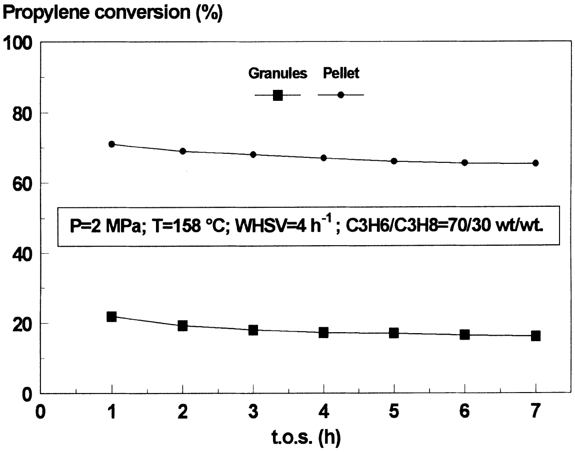

Fig. 10. Catalytic activity comparison between pure MSA (granules) and pellets (extrudates).

4. Conclusions

The reaction rate of oligomerization, catalyzed by MSA extrudates, can be well described by a LHHW kinetic model considering, as the rate determining step, the reaction between an adsorbed molecule of propylene, over a surface site, and another one coming from the gaseous phase. The kinetic model has been improved by taking into account the liquid–vapor equilibrium, that is, by using propylene fugacity instead of partial pressure.

The estimated activation energy (~18 000 J/mol) together with catalytic results, suggest that the propylene oligomerization is limited by mass transfer inside the mesopores of the MSA phase.

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