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Thermo-catalytic degradation of low density polyethylene over clinoptilolite — the effect of carbon residue deposition

Summary — Thermo-catalytic degradation of low density polyethylene (PE-LD) was studied in the presence of the natural zeolite — clinoptilolite. The effect of carbon deposition on the catalyst activity was also investigated. It was observed that the PE-LD degradation process over clinoptilolite proceeded at shorter time and lower temperature. The catalyst activity tests were carried out in argon in a stainless steel batch reactor at temperature, up to 410 °C at ambient pressure. The decomposition products were classified into three groups: gases, liquids and solid-like residues. The liquid products were analysed by gas chromatography coupled with mass spectrometry GC/MS method. A shift towards lower molecular mass products was observed in reactions with fresh clinoptilolite. The application of this catalyst in thermal degradation of PE-LD leads to lower alkane to alkene ratios and inhibits the formation of cyclohydrocarbons. The presence of carbon deposit on the surface of re-used clinoptilolite leads to higher ratio of saturated to unsaturated hydrocarbons, but neither did it significantly change reaction temperature nor the phase composition of the reaction products.

Key words: clinoptilolite, thermal degradation, catalytic degradation, low density polyethylene, carbon deposit.

TERMOKATALITYCZNA DEGRADACJA POLIETYLENU MAŁEJ GĘSTOŚCI W OBECNOŚCI KLI-
NOPTYLOLITU — WPLYW DEPOZYTU WĘGLOWEGO NA AKTYWNOŚĆ KATALIZATORA

Streszczenie — Przeprowadzono badania dotyczące zastosowanie naturalnego zeolitu — klinoptylolitu jako katalizatora reakcji rozkładu termicznego polietylenu małej gęstości (PE-LD), a także wpływu depozytu węglowego na powierzchni tego katalizatora na jego aktywność w badanej reakcji. Stwierdzono, że klinoptylolit jest bardzo efektywnym katalizatorem termokatalitycznej degradacji PE-LD umożliwiającym obniżenie temperatury reakcji, skrócenie czasu jej trwania jak i zwiększenie selektywności reakcji w kierunku produktów ciekłych. Testy katalityczne prowadzone były w reaktorze ze stali nierdzewnej w atmosferze przepływającego argonu, pod ciśnieniem atmosferycznym do temperatury 410 °C. Otrzymane produkty reakcji termokatalitycznej degradacji PE-LD podzielono na trzy grupy: gazowe, ciekłe i stałe. Ciekłe produkty analizowane były za pomocą chromatografu gazowego sprzężonego ze spektrometrem mas (GC/MS). Stwierdzono, że zastosowanie „świeżego” klinoptylolitu w badanej reakcji sprzyja otrzymywaniu lżejszych węglowodorów, zmniejsza stosunek ilościowy alkanów do alkenów i niemalże eliminuje cykloalkany z produktów ciekłych. Kilkakrotne zastosowanie tej samej próbki katalizatora w reakcji rozkładu PE-LD skutkuje zwiększeniem stosunku ilościowego węglowodorów nasyconych do nienasyconych w produktach degradacji oraz niewielkim wzrostem zawartości węglowodorów cyklicznych, ale nie wpływa znacząco na czas i temperaturę prowadzenia procesu, a także na skład fazowy otrzymanych produktów.

Słowa kluczowe: klinoptylolit, degradacja termiczna, degradacja katalityczna, polietylen małej gęstości, depozyt węglowy.

Low density polyethylene (PE-LD) is applied in almost every area of human activity. An increase in the application of this material results in an increase in the amount of waste produced from it. Due to its physico-chemical properties such as large volume at a relatively low weight and prolonged lifetime, it has become a significant environmental hazard [1].

Just as other plastic materials PE-LD can be biodegraded [2] or recycled using three methods: mechanical, chemical or energy recovery [1]. Mechanical recycling by remelting and shaping waste plastics does not generate any pollution, but results in low quality of the product. It is also very difficult to separate various used plastics from dust, metal or wood. The energy recovery method for waste plastics causes air pollution. So the essential procedure for plastics recycling is

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the recovery from them fundamental chemicals or fuels.

In recent years catalytic degradation of polyolefins has been regarded as the most promising method suitable for commercial implementation. Several factories in Poland (e.g. Koźmin Wielkopolski, Wola Krzysztoporska, Kartoszyn) were producing fuel oils from waste plastics until the introduction of excise tax in January 2007. Now the catalytic degradation of polyolefins in Poland is not economically viable unless legal changes are made or the cost of the process lowered. This can be achieved by using an appropriate catalyst.

Clinoptilolite belongs to the group of natural minerals of volcanic origin, which could be found all over the world. Its structure is similar to a honeycomb with a series of channels and cavities. This type of the structure is responsible for its ion exchange capacity and selective sorption properties [3–5]. The chemical composition of clinoptilolite is similar to that of clay minerals. The literature reports that clay-based catalysts are effective in thermo-catalytic degradation of polymers.

Thus the aim of the present work was to test the activity of clinoptilolite in the degradation of PE-LD to fuel oils.

Commercial clinoptilolite is relatively expensive, so the effect of four times usage as well as the carbon deposit on the surface on its activity in PE-LD degradation was also investigated.

EXPERIMENTAL

Materials

Clinoptilolite (Si/Al molar ratio = 5.1, $S_{\text{BET}} = 22 \text{ m}^2 \cdot \text{g}^{-1}$, pore volume = $0.05 \text{ cm}^3 \cdot \text{g}^{-1}$) was obtained from Erem, Poland. PE-LD (pellets, density $0.925 \text{ g} \cdot \text{cm}^{-3}$ at 25°C) was obtained from Sigma Aldrich.

Methods of testing

The activity tests were carried out in an in-house designed stainless steel batch reactor at atmospheric pressure. The reactor was initially purged with argon. PE-LD degradation was studied with or without the catalyst — clinoptilolite. 50 g of PE-LD was used for thermal degradation reactions while 5 g of clinoptilolite was added for catalytic degradation runs. The substrates were placed in the reactor and heated to the required temperature with rate $5^\circ\text{C} \cdot \text{min}^{-1}$, and held until no further liquid products were obtained. The outlet of the reactor was connected to a condenser cooled to 15°C . After every reaction the solid residues (0.3 g of catalyst and solid reaction residue) were collected for further investigations.

Thermal analysis thermogravimetry coupled with differential thermal analysis: and mass spectrometry (TG-DTA-MS) was carried out in argon (for PE-LD de-

gradation) or air (for carbon deposit oxidation) up to 700°C using a Setaram thermobalance unit (Setsys 16/18) connected to Balzers quadrupole mass spectrometer (Thermostar). About 15 mg of the sample was subjected to thermal treatment with a heating rate of $10^\circ\text{C} \cdot \text{min}^{-1}$.

The reaction products were classified into three groups: gases, liquids and solid residues. The yield of liquid products was determined as the amount of liquid collected in a receiver, and the yield of residues as the waxy compounds and catalyst remaining inside the reactor after the experiment. The yield of gas products was calculated as the difference between the loaded amount of polymer and catalyst and the yield of liquids and residues.

Solid phase extraction (SPE) (C18 sorbent based on octadecylsilane bonded irregular silica gel particles) was used to prepare samples for gas chromatographic/mass spectrometry (GC/MS) analysis by retaining the interfering substances and eluting the product of interest. The SPE columns were conditioned with 2 cm^3 of hexane for 5 cm^3 samples. The flow rate of the solvent and sample through the column was maintained at $2\text{--}3 \text{ cm}^3 \cdot \text{min}^{-1}$ under vacuum. The columns were then washed with 2 cm^3 of hexane. Analysis was carried out in an Agilent Technologies 6890N Network GC coupled to 5973 Network Mass Selective Detector, used in 70 eV electron impact (EI) mode. Analytes were separated using an Agilent HP-5MS capillary column of $30 \text{ m} \times 0.25 \text{ mm}$ with a phase thickness of $0.25 \mu\text{m}$. The quadrupole temperature was 280°C . Qualitative analysis was carried out in a full-scan acquisition mode in the $50\text{--}500 \text{ a.m.u.}$ range.

RESULTS AND DISCUSSION

TG-DTA-MS measurements of pure PE-LD alone and for PE-LD/c clinoptilolite mixtures are presented in Figure 1 (the mass of catalyst, which did not change during the experiment has been deducted from the mass of the polymer). The decomposition processes, taking place in temperature range $410\text{--}510^\circ\text{C}$ for thermal and $340\text{--}460^\circ\text{C}$ for catalytic degradation, are illustrated by TG, DTG and DTA curves. The selected gaseous products evolved during PE-LD decomposition are represented by MS profiles with appropriate m/z ratios: 2, 15, 29, 43, 57 characterising respectively the formation of fragmental ions of hydrogen, methane, ethane, propane and butane evolved in both thermal and catalytic processes. The evolution of hydrogen at temperatures of about 500°C can be attributed to the formation of highly dehydrogenated unsaturated hydrocarbons appearing finally as graphite like carbon residues.

The activity tests of thermal and catalytic degradation of PE-LD indicate that the apparent cracking rate over a catalyst is higher than the corresponding rate in the absence of the catalyst at the same temperature. The

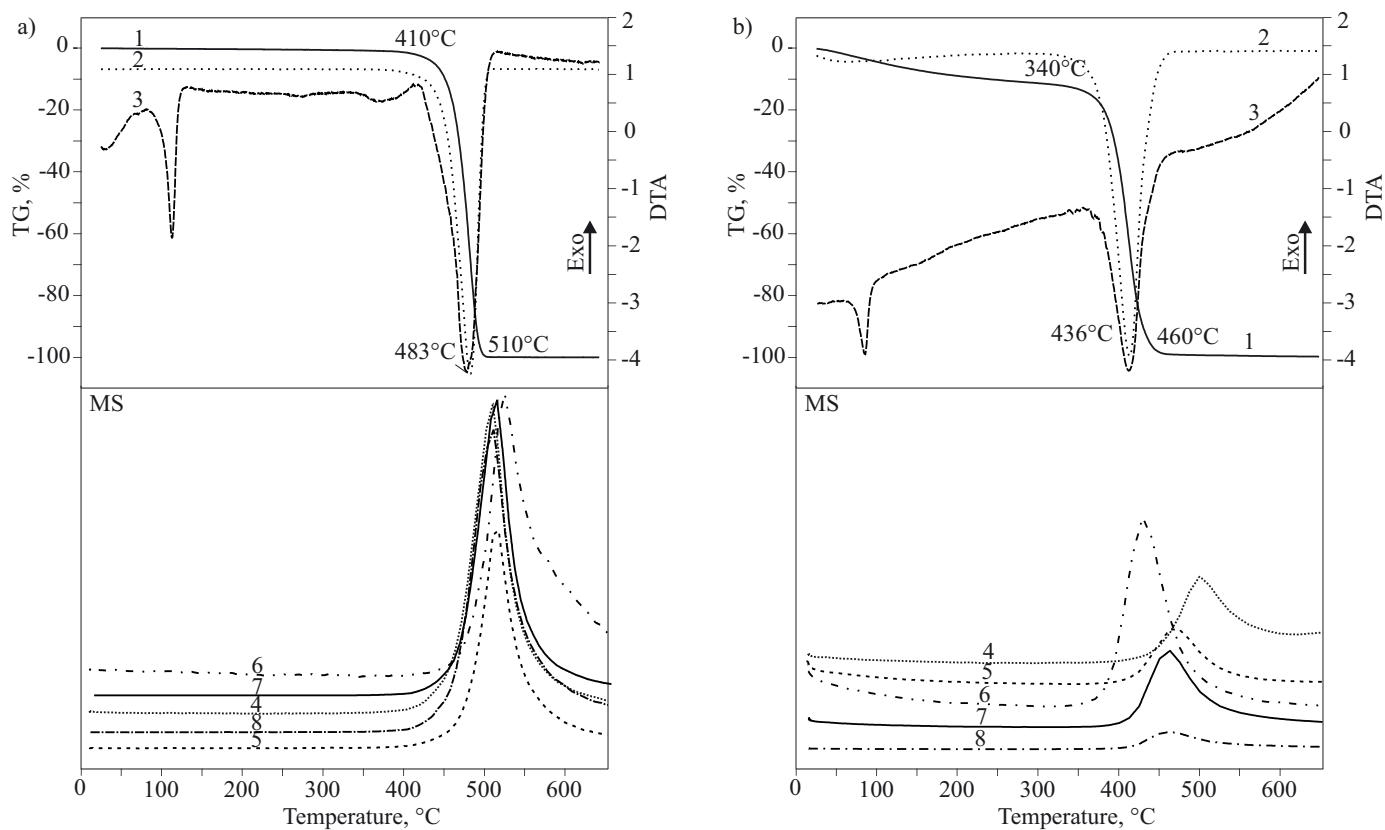


Fig. 1. TG-DTA curves and MS profiles of gaseous products of PE-LD degradation with heating rate $10\text{ }^{\circ}\text{C} \cdot \text{min}^{-1}$: a) thermal, b) catalytic degradation with clinoptilolite (CL); description of curves: 1 — TG, 2 — DTG, 3 — DTA, 4 — $m/z = 2(\text{H}_2^+)$, 5 — $m/z = 15(\text{CH}_3^+)$, 6 — $m/z = 29(\text{C}_2\text{H}_5^+)$, 7 — $m/z = 43(\text{C}_3\text{H}_7^+)$, 8 — $m/z = 57(\text{C}_4\text{H}_9^+)$

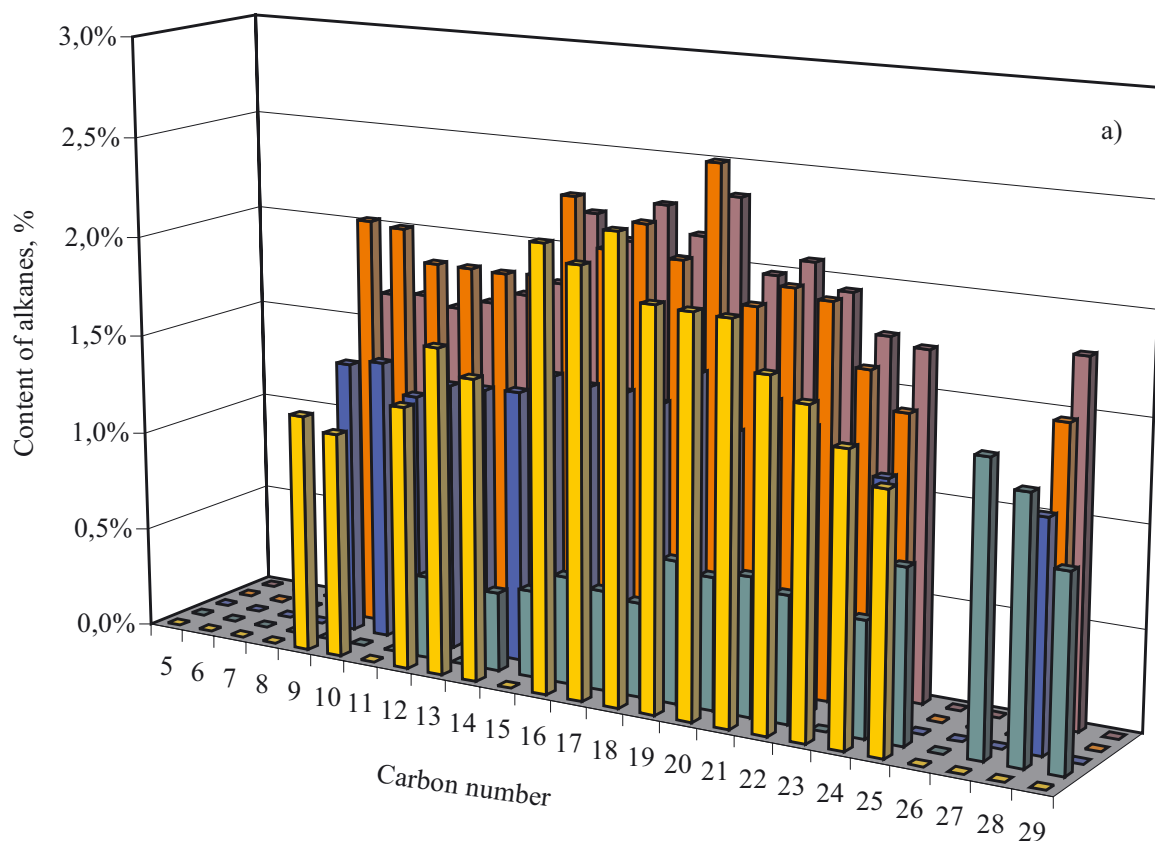
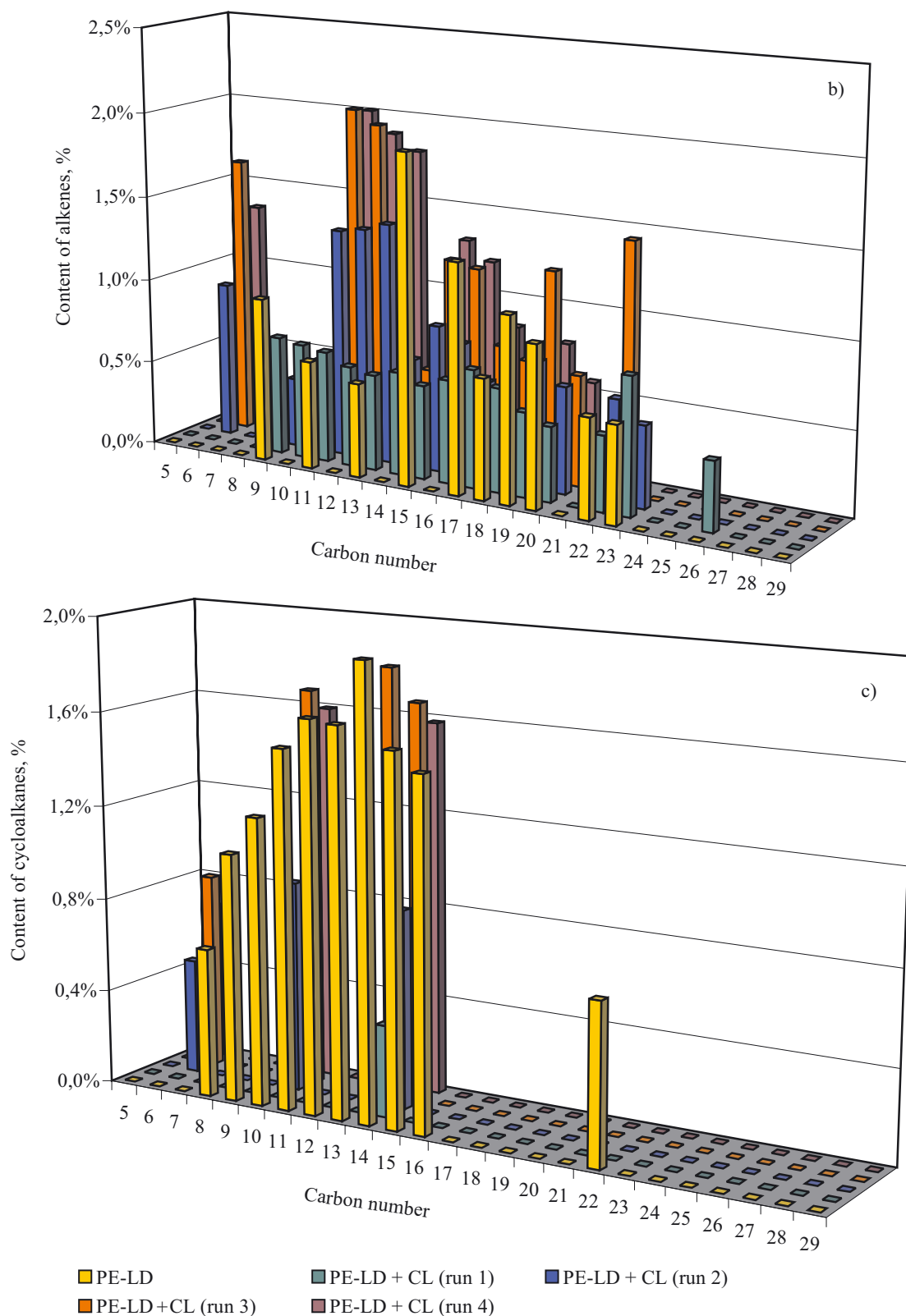


Fig. 2. Composition of the liquid products of thermal and catalytic degradation of low density polyethylene at $410\text{ }^{\circ}\text{C}$

cd. Rys. 2



polymer degradation on the catalyst surface appears more efficient at lower temperature.

The product composition obtained for PE-LD, PE-LD with fresh or several times re-used clinoptilolite at 410 °C is presented in Table 1. The liquid phase selectivity about 87 % is highest for PE-LD with fresh clinoptilolite in comparison with the values about of 65 % for only PE-LD. The increase in carbon deposit did

not affect on reaction time or products composition significantly.

The results of GC/MS analysis shown in Figure 2 indicate that the liquid products of both thermal and catalytic degradation of PE-LD were broadly distributed in the carbon fractions from C₅ to C₂₉. The liquid products obtained in the catalytic degradation over fresh clinoptilolite were much lighter than the corresponding

non catalytic products formed at the same temperature. The application of the catalyst in thermal degradation of PE-LD led to a lower ratio of saturated to unsaturated hydrocarbons and inhibits the formation of cyclohydrocarbons. An increase in carbon deposit on clinoptilolite surface led to a higher ratio of alkanes to alkenes, but neither did it change the time and temperature of the reaction nor the phase composition of the products significantly.

Table 1. Reaction time and composition of products of PE-LD degradation at 410 °C obtained without the catalyst, "fresh" and several times re-used clinoptilolite

Catalyst	Reaction time, min	Yield of products, wt. %		
		gaseous	liquid	solid
—	270	35	65	0
Clinoptilolite (1-st run)	105	10	87	3
Clinoptilolite (2-nd run)	110	10	84	6
Clinoptilolite (3-rd run)	120	11	82	7
Clinoptilolite (4-th run)	125	10	81	9

CONCLUSIONS

Clinoptilolite is a very effective catalyst both in lowering the degradation temperature and the melting point of PE-LD. It is also assumed to be very efficient in shorting the time of this reaction and improving its selectivity to liquid products.

Hydrocarbons with carbon number from C₅ to C₂₉ were obtained in both thermal and catalytic degradation

of PE-LD. Liquid products obtained in catalytic degradation process over "fresh" clinoptilolite are much lighter than the corresponding non catalytic products obtained at the same temperature. The application of clinoptilolite in the thermal degradation of PE-LD leads to production of lighter hydrocarbons with a lower alkanes to alkenes ratio in comparison to degradation without catalyst. An increase in carbon deposit on the clinoptilolite surface does not affect significantly on time and temperature of the reaction neither phase composition of the products, but it leads to higher ratio of saturated to unsaturated hydrocarbons in liquid products. The re-use of clinoptilolite up to four times confirms its high resistance to catalyst deactivation.

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