



Natural aluminosilicates for catalytic depolymerization of polyethylene to produce liquid fuel-grade hydrocarbons and low olefins



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ABSTRACT

Different chemical modifications were performed to the natural aluminosilicate Montanit300[®] in order to improve its catalytic activity in PE depolymerization. Performance of such prepared catalysts was compared to established solid acid catalysts, such as HZSM-5, sulfonated and fluorinated γ -Al₂O₃ and amorphous silica–alumina. Pyridine TG and DRIFTS characterization revealed mild acid treatment and aluminum grafting as successful in increasing acid site density through impurity removal and specific surface area increase. Mesoporous catalyst structure that allows facile diffusion through its pore network, together with high-density Brønsted acid sites, was found to be crucial to obtain high catalytic activity. The T_{50} value for PE depolymerization was lowered by 162 °C with sulfonated γ -Al₂O₃ solid, compared to non-catalyzed reaction, whereas with aluminum-grafted Montanit300[®] catalyst this value was lowered by 65 °C. PE depolymerization products present in the condensed liquid phase using aluminum-grafted Montanit300[®] catalyst were exclusively alkanes with chain length up to 21 carbon atoms. Liquid, coke and gas yields were found to be 53, 0.4 and 46.6%, respectively, the latter consisting of linear and branched C₂–C₄ alkenes and alkanes.

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1. Introduction

Global production of plastics is increasing exponentially in the last few decades and was estimated at 57 Mt/a in EU27 states in 2012. The share of polyethylene (PE) was equal to about 30% [1]. A substantial part (39.4%) of all European Union member states (EU27)-produced plastics is used for purposes having a short service life, such as bags and packaging, which after improper disposal represent an enormous environmental burden. Landfill disposal (38%) and energy recovery (36%) currently have similar shares in waste plastic re-utilization, with recycling (26%) trailing behind [1]. Natural decomposition pathway of plastic materials usually requires several decades, making landfilling not an acceptable means for disposal, due to serious negative environmental impact and low weight-to-volume ratio. Quality of recycled plastics is often lower compared to virgin ones, which restricts the range of its possible utilization [2]. Due to the size of PE market, its easy availability, high energy density (LHV > 40 MJ/kg) and

defined chemical composition (C and H only, low reactivity and no functionality), thermocatalytic pathways offer attractive means for depolymerization of PE into paraffins and olefins of appropriate chain length, so they can be used directly as liquid fuels/fuel additives [2]. This represents an attractive option when considering recent trends of rising and uncertain liquid-fuel stock prices [3]. Thermocatalytic depolymerization of long hydrocarbon chains is usually performed using solid acid catalysts, such as zeolites, natural or modified natural aluminosilicates, etc. [4–7].

High acid strength/density and porosity of synthetic zeolites that can both be tailored accordingly to requirements enable unmatched catalytic activity and shape selectivity in modern hydrocarbon cracking and petroleum refining industry. By modifying acid strength, pore topology, size (distribution) and type of solid acid sites, selectivity for (C1–C4) hydrocarbons, petroleum (C5–C12), diesel-like (C8–C21), heavy wax fractions and coke can be favored [8]. Nevertheless, in order to prevent over-cracking and coke accumulation, only moderate acidity is usually required [9–11]. From here, parallels that can be applied to polymer cracking can be drawn.

During catalytic depolymerization of PE over microporous ZSM-11 zeolite, Pierella et al. [12] observed lower yields of C9–C16

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products (6 vs. 43 wt%, respectively, at 410 °C), compared to mesoporous MCM-41 counterpart. By changing the Lewis/Brønsted acid site ratio in ZSM-11 through ion exchange with Mo and Zn, both liquid hydrocarbon and coke yields were increased.

Manos et al. [13] showed that over large-pore ultrastable Y (US-Y), Y and β zeolites, alkanes and aromatics were the main products, while over medium-pore mordenite and ZSM-5 zeolites, significantly more olefins were formed. In the medium-pore zeolites, secondary bimolecular reactions were sterically hindered, which in turn resulted in the formation of higher amounts of alkenes as primary products. The following order was found regarding the increasing carbon number distribution in formed products: ZSM-5 < mordenite < β < Y < US-Y.

Gobin and Manos [14] performed PE depolymerization in the presence of HZSM-5, US-Y and commercial cracking catalyst. They obtained increasing liquid product yields with these catalysts, ranging from 39 and 55 to 72%, respectively. Coke yields obtained were between 4 and 6%. By employing montmorillonite, saponite and their pillared clay analogs for the same catalytic reaction, liquid product yields were higher and varied between 62 and 83% at 430 °C, with corresponding coke yields between 1 and 6%. The authors ascribed lower acid strength of clays and their pillared analogs as being responsible for higher liquid product yields (low acid strength did not result in severe over-cracking of primary products to small gaseous molecules) and not catalyzing coke accumulation. Catalyst regeneration by burning of deposited coke was also performed, which resulted only in negligible activity decline in consecutive experiments.

In addition, inherent to Fischer–Tropsch processes (catalytic transformation of syngas, aimed at liquid fuel production) is also the formation of large amounts of long-chain paraffins (Fischer–Tropsch waxes). The latter are not applicable for transport-fuel applications. However, catalytic cracking of these waxes is an appealing way for production of additional amounts of lower olefins, diesel and gasoline fuels. Yields and properties of the obtained liquid products (e.g. amounts of aromatics and lower olefins as well as the extent of isomerization) are strongly influenced by the solid acid catalyst (faujasite- and mordenite-type of zeolites are most often used) and reaction conditions [15].

Naturally occurring aluminosilicates are widely abundant and cheap, exhibit moderate to low acidity and have been extensively used before the discovery of synthetic zeolites as catalytic cracking catalysts for hydrocarbons [16]. For these reasons, chemical and morphological modifications to improve their catalytic activity and selectivity provide an attractive approach to liquid hydrocarbon production from PE depolymerization [6].

The purpose of this work was to chemically modify the commercially available Montanit300® natural aluminosilicate comprising primarily heulandite and clinoptilolite, in order to improve its catalytic performance in the process of PE depolymerization into liquid-fuel-range hydrocarbons. Synthesized catalysts were characterized using relevant techniques and these properties were correlated to their catalytic performance. Comparison of the activity to several established synthetic solid acid catalysts was also performed.

2. Experimental

2.1. Preparation of catalyst samples

The natural aluminosilicate Montanit300® was purchased from Montana Žalec. The chemical modifications of this solid were performed to remove impurities, increase specific surface area and generate porosity. For this purpose, treatment with 5, 10, 20, 50 and 80 wt% H₂SO₄ for 6 h under reflux was carried out, followed

by filtration, washing and drying overnight at 105 °C. The weight ratio m(Montanit300®):m(H₂SO₄ solution) was in all cases equal to 1:10. These catalyst samples are in the following text noted as xMS, where x represents acid concentration, M stands for Montanit300® as the starting material and S for sulfuric acid.

The same m(Montanit300®):m(HCl solution) = 1:10 weight ratio was used for treatment with either diluted HCl (0.1, 0.5 and 1 M HCl until boiling) or 5 M HCl, which was performed until boiling or with additional reflux for 5, 10, 20 and 45 min. After acid treatment, filtration, washing with deionized water and drying overnight at 60 °C were performed. The HCl-treated samples are in the following text noted as xMHy, where x represents acid concentration, M Montanit300® as the starting material, H hydrochloric acid and y time under reflux.

Ion exchange was performed by suspending 1 g of Montanit300® in 400 mL of 0.02 M aqueous solution of NH₄NO₃. The temperature of suspension was kept constant at 50 °C under stirring on a magnetic stirrer overnight, followed by filtration. The whole process was repeated twice, the ion-exchanged Montanit300® was filtered, dried overnight at 60 °C and calcined for 4 h at 400 °C to decompose the ammonium ion. This catalyst is in the following text denoted as MI.

Zeolitization of Montanit300® was performed by grafting of aluminum over the previously acid-leached 5MH45 sample. Before aluminum grafting, the sample was dried overnight at 105 °C. The 5MH45 sample was suspended in toluene containing dissolved aluminum isopropoxide. Mass of Al isopropoxide was adjusted to enable 10 wt% aluminum grafting on the 5MH45 support. The suspension (containing 2 g of 5MH45 and 40 ml of toluene) was boiled under reflux for 5 h. After the elapsed deposition time, the suspension was filtered, washed and calcined overnight at 350 °C. This sample is in the following text denoted as MAI. Additional details on this synthesis can be found in the work of Caillot et al. [17].

Amorphous silica alumina (ASA) was synthesized from silica gel ($S_{\text{BET}} = 313 \text{ m}^2/\text{g}$, pore diameter = 9.4 nm, pore volume = 0.74 cm³/g, manufactured by Kemika Zagreb) using the deposition precipitation method. A nominal loading of 15 wt% Al³⁺ from aluminum nitrate precursor was deposited at 90 °C under reflux for 22 h. Urea was used to induce slow precipitation followed by filtration, washing, drying overnight and calcination for 12 h at 800 °C. More details on the synthesis of ASA can be found in the work of Hensen et al. [18].

Gamma Al₂O₃ was purchased from Nikki-Universal Company. Sulfonated γ -Al₂O₃ was prepared by suspending 2 g of γ -Al₂O₃ in a surplus of 0.25 M H₂SO₄ for 3 h, while being stirred on a magnetic stirrer. This was followed by filtration, washing, drying and calcination at 500 °C for 3 h. Elemental analysis revealed that 2.1 wt% S was deposited using this protocol. Fluorinated γ -Al₂O₃ was synthesized by impregnation of γ -Al₂O₃ with aqueous solution of NH₄F, followed by drying and calcination at 400 °C for 4 h. The weight ratio m(Al₂O₃):m(NH₄F) was equal to 9:1. SEM-EDX analysis showed 2.7 wt% content of fluorine in the prepared catalyst.

HZSM-5 zeolite sample with a Si/Al ratio of 14.3 was kindly provided by Süd Chemie.

2.2. Catalyst characterization

Surface morphology of the catalysts was analyzed using Supra 35 VP field emission scanning electron microscope (Carl Zeiss). The energy-dispersive X-ray analysis (EDX) Inca 400 hardware (Oxford Instruments) was used to analyze the elemental composition of these materials. CHNS elemental analyzer (Perkin Elmer, model 2400 Series II) was used as a complementary technique. N₂ sorption (Micromeritics, Tristar II 3020) was used for the determination of BET specific surface area, average pore diameter and total pore volume. Prior to measurements, samples were degassed

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