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Preparation of an active and regenerable catalyst for liquid-phase alkylation of toluene with 1-decene

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ABSTRACT

Zeolite Y was tested as an alternative solid acid catalyst for the production of linear alkyl aromatics with the emphasis on its activity and stability towards regeneration. Liquid-phase alkylation of toluene with 1-decene at 100 °C was used as the model reaction. Deactivated catalyst samples were regenerated by the temperature programmed calcination (TPC) in air flow at 550 °C. The activity of the unmodified HY zeolite during alkylation was significant but decreased to a minimum after regeneration, as a result of a partial structure collapse during regeneration using TPC. To avoid the structure collapse hydrothermal stabilization of zeolite Y at 560, 670 and 780 °C was performed. Subsequent chemical dealumination using 0.5 M HCl or ion-exchange with the 2 M NH_4NO_3 solution, in order to improve the catalyst activity, were carried out. All the samples were then tested in alkylation. The main monitored parameters were the conversion of 1-decene, selectivity to 2-phenyldecane isomer and the amount of side-products. The sample stabilized at 560 °C and ion-exchanged subsequently showed the highest activity with the lowest amount of by-products. This sample was also regenerated and reused four times in the cycle alkylation–regeneration with no loss of structure or activity. In fact there was a slight activity increase of this sample after regeneration.

1. Introduction

The discovery of synthetic alkylbenzene sulfonates has formed the basis for the detergent industry. The first alkylbenzene sulfonates were obtained by the Friedel–Crafts alkylation of benzene with a mixture of C_{12} olefins. As a result, the corresponding alkylbenzene sulfonate was highly branched [1]. Due to the lower biodegradability and the imminent possibility of pollution, the dodecylbenzene sulfonates have been replaced by their linear forms using 1-alkenes as feed.

Valuable intermediates in the linear alkylbenzene sulfonates production are linear alkylbenzenes (LAB) with long-chains (usually C_{10}—C_{14}). These have some conceivable positional isomers, i.e. 2-, 3-, 4-phenyl isomers, etc. A higher percentage of 2-phenyl isomer is desired because it has the highest biodegradability, solubility and detergent properties among the related isomers [2].

Homogeneous catalysts for LAB production are used industrially in the first place, such as HF and $AlCl_3$ [3–5]. As these are very corrosive and polluting, a great effort has been directed towards their substitution by solid catalysts such as zeolites that do not present this inconvenience. Large pore zeolites such as HFAU, HMOR and HBEA have furthermore been demonstrated as active and selective catalysts for the monoalkylation of benzene or toluene by linear alkenes [6].

Though zeolites possess very high activity and selectivity for the production of 2-phenyl isomers, their main drawback is their deactivation after a certain period of time-on-stream. It has been proposed that the deactivation occurs due to the formation and trapping of dimers and heavy alkylates (known as liquid coke [7]) mainly in the pores and cavities of zeolites [8]. Industrial applications of zeolite catalysts require the possibility of catalyst regeneration with minimum changes in activity or stability. Many articles dealing with the zeolite-catalysed alkylation of aromatics with long-chain alkenes have been published so far, though many of them do not include the regeneration process in their research at all [6,9,10]. Some of them deal with other routes for the zeolite catalyst regeneration; Liang et al. [7] studied the deactivation of the HY zeolite during alkylation of benzene with dodecene proposing the coke removal via extractive regeneration in the presence of benzene. This route proved as effective but only recovering the initial catalyst activity up to 80% maximum. Guisnet and Magnoux [11] investigated the regeneration of HY zeolite via oxidative

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treatment taking into account the major influence of the regeneration temperature which in case of HY zeolite can be responsible for a massive dealumination and structure alteration. As a result they proposed an oxidative regeneration process in two steps, the first one at low temperature and the second one at high temperature. The proposed route extends the severity of the regeneration process though. Zhao et al. [12] studied the effect of HY ion-exchange with lanthanum and cerium cations without any form of hydrothermal stabilization. Zeolite stability towards oxidative regeneration was maintained although considering its application on the industrial scale, the availability of rare earth metals is questionable. An important consideration is that the zeolite catalyst regeneration comprises the removal of coke through oxidative treatment at the temperature of ca. 500 °C. For standard HY zeolite such treatment could result in a strong hydrothermal dealumination and even in the degradation of the zeolite structure [13]. Based on the latter there is a certain need for the regeneration of the Y zeolite to be as simple as possible, preferably in one step, avoiding the structure degradation and providing the maintenance of its activity.

Thermal stability of zeolite Y can be upgraded by increasing the Si/Al molar framework ratio. Hydrothermal treatment in presence of steam is the most frequently used method for adjusting the framework Si/Al ratio as it leads to replacement of a part of the framework aluminium (Al^{IV}) by silicon [14]. Steam at high temperature (500–800 °C) dealuminates zeolitic framework via framework aluminium hydrolysis, relocating it into extra-framework positions (EFAL). The presence of large amounts of EFAL has a detrimental effect on catalytic and transport properties so there is a certain need for the extra-framework aluminium extraction [14]. Acid treatment (with HCl, HNO_3, $(COOH)_2$) is one way to lower the non-framework aluminium fraction in the zeolite. Among several methods another way would be repeated ion-exchange with NH_4NO_3 to exchange extra-framework aluminium ions for ammonium ones.

In this paper we tried to improve catalytic properties of a zeolite-Y-based-type of catalyst for alkylation of aromatics with long-chain olefins. Using hydrothermal stabilization and following chemical treatment, we believe that we have obtained a highly active and fully regenerable catalyst.

2. Experimental

Zeolite Y in its sodium form as NaY (SiO_2 to Al_2O_3 molar framework ratio = 5.76, Na_2O content = 13.54 wt.%) was supplied by the Research Institute of Petroleum and Hydrocarbon Gases, Bratislava, Slovak Republic. The ammonium form of the NaY zeolite, NH_4Y (Na_2O content = 1.13 wt.%) was obtained by repeated ion-exchange with a 2 M solution of ammonium nitrate at 85 °C. Before the alkylation reaction the ammonium form was converted to the H-form (HY) by calcination at 450 °C for 3 h.

Ultra stable forms (USY) were prepared from NH_4Y by hydrothermal stabilization in a deep-bed at three temperatures, 560, 670 and 780 °C for 4 h at the heating rate of 2.5 °C/min. The procedure was carried out in a non-hermetically closed fused silica tube with the overall height of 26 cm, a bed-height of 9.8 cm and the diameter of 2.2 cm, under static conditions. Further extraction of the extra-framework aluminium (EFAL) was performed using two methods obtaining two series of zeolite samples. Samples EY were obtained through acid treatment of USY zeolite samples using 0.5 M HCl at room temperature, the procedure was carried out via selective extra-framework aluminium extraction, by which the dehydrated USY zeolite was mixed with a NH_4NO_3 solution using 4 ml of the solution per 1 g of USY zeolite and stirred at 25 °C for 0.5 h. The second step was the actual acid extraction with HCl [15]. Another series of catalyst samples NY was obtained by repeated ion exchange of the USY zeolite with 2 M NH_4NO_3 at 85 °C.

Physicochemical properties of all prepared samples were determined as follows. Surface characteristics were measured by physical adsorption of nitrogen at −196 °C using ASAP-2400 (Micromeritics). Overnight evacuation of the samples at 350 °C preceded the adsorption analysis. Specific surface area S_{BET} was obtained using the conventional BET isotherm ($p/p_0 = 0.05–0.3$). The external surface area comprising also the surface of mesopores S_t and the volume of micropores V_{micro} were calculated from the *t*-plot using Harkins–Jura master isotherm. The value of the total pore volume V_p was determined from adsorption data at relative pressure $p/p_0 = 0.99$ [16]. Structural characteristics comprising crystallinity of the fresh and regenerated samples were gained from XRD analysis using a Philips 1730/1050 diffractometer, with CoKα radiation and scan range of 2.98°–51° 2Θ, with the step size of 0.02°. XRD diffractograms were used to calculate the relative crystallinity (% XRD intensity/NaY) of the samples [17]. The SiO_2 to Al_2O_3 molar framework ratio was obtained from FTIR spectra of skeletal vibrations using a KBr technique [18]. The procedure consisted of homogenizing a mixture of 0.0003 g of the zeolite with 0.3 g of KBr powder in a vibratory mill and pressing it into a pellet (diameter of 1.3 cm and thickness of 0.09 cm) under vacuum. Prior to homogenization the KBr powder was dried at 140 °C for 8 h. The IR spectra of the pellet were recorded in the wavenumber region of 400–4000 cm^{-1}. The total acidity of zeolite samples was determined by temperature programmed desorption of ammonia (TPD) in the temperature range of 220–650 °C with a heating rate of 12 °C/min. Analysis of Brønsted and Lewis acidity was performed by room-temperature infrared spectroscopy of adsorbed pyridine at 150 °C using a FTIR Genesis (Mattson-Unicam) spectrometer. Self-supported wafers (surface density ca. 8 mg/cm^2) were activated at 450 °C under vacuum of 10^{-4} Pa for 3 h. The ratio of Brønsted and Lewis acid sites (B/L) was determined based on the integrated area absorbances at 1550 and 1450 cm^{-1} respectively, in correlation with their extinction coefficients.

Alkylation was carried out in a 100 cm^3 stirred batch reactor at 100 °C under a nitrogen atmosphere to maintain an autogenous pressure of 0.5 MPa. 80 g of a reaction mixture with the molar ratio of toluene:1-decene = 8.6:1 was used for the alkylation. Together with the reactants 2 g of the calcinated zeolite was placed in the reactor. Reaction products were taken from the bottom of the reactor through the sampling valve, starting after reaching the reaction temperature (30 min reaction time). Next samples were taken every 30 min up to the reaction time of 240 min.

The reaction feed and reaction products were analyzed on a gas chromatograph Hewlett Packard 5890 A, with a FID detector and a capillary column HP-1 (25 m × 0.22 mm × 0.33 μm). The structure verification of olefins and alkyltoluenes was carried out by GC–MS using an MS 25RFA Kratos, Manchester equipment. Regarding the GC–MS analysis it can be stated that the chemical transformations taking place involve several simultaneous and subsequent reactions. The double bond shift along the 1-decene chain occurs, resulting in the formation of positional isomers of linear tolyldecanes in products. The presence of iso-tolyldecanes in the product stream proves the ongoing 1-decene skeletal isomerization with subsequent alkylation. The oligomerization of 1-decene occurs resulting mostly in 1-decene dimers in the product stream and there is also a toluene polyalkylation(di-alkyltoluenes) taking place but only to a small extent, which is due to the excess of toluene in the feed.

Conversion of 1-decene was evaluated as a percentage of all alkylation products, i.e. linear and iso-alkyltoluenes and alternatively also alkene dimers and di-alkyltoluenes, in the sum of unconverted alkenes (1-decene, its positional and skeletal isomers) and alkylation products. The selectivity to the most desired 2-tolyldecane was calculated as the percentage of 2-tolyldecane in the sum of all alkylation products. To ascertain the repeatability we