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Study of the oligomerization of 1-octene catalyzed by macroreticular ion-exchange resins

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HIGHLIGHTS

- Ion-exchange resins can dimerize 1-octene at 373 K without producing cracking products.
- The accessible acidity of the catalysts is the most important structural parameter.
- Selectivity to C_{16} and branched C_8 isomers increased with increasing temperature.
- Equations derived from the proposed kinetic model fit well the experimental results.

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ABSTRACT

Oligomerization of 1-octene is a feasible alternative to improve the properties and the quality of fuels and lubricants oils. The performance of macroreticular ion-exchange resins as catalysts for such reaction has been evaluated. The experimental setup consisted of a batch stirred-tank reactor that operated at 353–393 K and 2 MPa. 1-Octene conversion was practically complete and the selectivity to double-bond isomerization and dimers after 6 h at 373 K was up to 95% and 12%, respectively. The accessible acidity of the catalysts was the most important structural parameter for these reactions. Selectivity to dimers and branched isomers increased with increasing temperature. Cracking compounds were not detected at all. The theoretical equations derived from the proposed kinetic model fit well the experimental results.

1. Introduction

Gasoline composition is in a continuous evolution due to technical and ecological issues. Major efforts in oil industry are dedicated to improve fuel properties and quality and, at the same time, to fulfill environmental regulations. Oligomerization of linear olefins is an alternative for obtaining heavy olefins with great flexibility in its composition. The obtained products can be added to gasoline, diesel and lubricating oils.

The available literature on oligomerization of olefins is in reverse order to the number of carbon atoms. A great deal of references can be found for ethylene and propylene, many for butylenes and very scarce for pentenes and heavier ones. The number of existing commercial plants follows the same tendency. Oligomerization of light olefins (C_3–C_5) [1–4] is widely found in the literature. Some works have recently appeared concerning C_6 olefins oligomerization [5–9] over different solid catalysts. As for 1-octene oligomerization only a few works are available in the open literature. De Klerk [10] evaluated the liquid-phase oligomerization of 1-octene in the temperature range 373–573 K over some solid acid catalysts, such as solid phosphoric acid, amorphous silica, sulfated zirconia, MCM-41 and some zeolites. He found that between 373 K and 473 K the main products were C_{16} dimers but deactivation occurred rapid. When temperature exceeded 473 K cracking increased considerably and, conversely, the catalyst stability also increased. In another work, De Klerk [11] studied the reactivity differences between 1-octene and 2,4,4-trimethylpentene over solid phosphoric acid in the temperature range of 348–493 K. The observed higher oligomerization, skeletal isomerization and cracking reactivity of the branched olefin compared to 1-octene is explained by the classic carbocation mechanism. De Klerk compared these results with the ion-exchange resin Amberlyst 15, concluding that the latter was more active in the temperature range studied. Grigor'eva et al. [12] studied the oligomerization of 1-octene over several zeolites in the temperature range 423–523 K. They found high activity at temperatures higher than 453 K, being C_{16} dimers the main product. The concentration and strength of the Brönsted acid sites of the zeolites, and the size of their cavities and channels were the most important structural parameters for the oligomerization reaction.

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Since linear olefins, and in particular 1-octene, are an important feedstock for chemical industry, such as production of Linear Low Density Polyethylene (LLDPE), its production is widely studied [13].

The use of ion-exchange resins as catalysts offers some advantages in the petrochemical industry, such as reduction of equipment corrosion, and ease of product separation and catalyst recovering. Ion exchange resins are known to catalyze the oligomerization of olefins, e.g. oligomerization of C_4 alkenes over Amberlyst type resins and oligomerization of higher olefins over Nafion resin [14]. Furthermore, ion-exchange resins show acid strengths similar to zeolites [15] but higher acid capacity, so they could be used at lower temperatures, limiting side reactions. But surprisingly, there is a lack of works concerning heavy olefins oligomerization using these catalysts.

The aim of this work is to study the liquid-phase conversion of 1-octene over several acidic resins to check the potential of these solids as catalysts in the formation of heavier compounds such as dimers and oligomers. Only macroreticular acidic resins were considered to ensure enough accessibility to acidic centers in the non-polar media due to their permanent porosity. The effect of the temperature on products distribution was also studied. Finally a kinetic model was proposed.

2. Materials and methods

2.1. Chemicals

1-Octene of commercial grade (97%, Fluka) was used as received in the oligomerization reaction. 1-Octene (99.9%) and 1-hexadecene (97%) from Acros, and 2-octene (cis + trans, 98.5%) from TCI-Europe were used for calibration purposes.

2.2. Catalysts

The catalytic behavior of the following acidic macroreticular resins Amberlyst^{TM} 15-wet (A15), 35-wet (A35), 36 (A36), 46 (A46) and 48 (A48) (Rohm and Haas), and Purolite CT175, CT252, CT275 and CT276 (Purolite) were tested. Their physical properties are summarized in Table 1.

The adsorption enthalpy of ammonia [16] is included as a relative measure of the acid strength of the ion exchange resins. Amberlyst 15 is conventional sulfonated with a high crosslinking degree. Amberlyst 35 and 36 are oversulfonated with high and medium crosslinking degree, respectively. Both properties have a clear effect on the physical properties of the resins. A decrease of the crosslinking degree leads to a diminution of the surface area, pore volume and porosity, whereas the oversulfonation involves an increase of the acid capacity and acid strength but also of the stiffness of the structure. Consequently, the surface area, pore volume and porosity of oversulfonated resins are lower than the analog conventional sulfonated resins (see Amberlyst 15 and 35). Similarly, CT175 and CT275 differ on the sulfonation degree and acid strength, being both high crosslinked macroreticular resins. CT252 and CT276 are both medium crosslinked and oversulfonated with a wide pore diameter. Amberlyst 46 should be highlighted. It has a very low acidity but it is only surface-sulfonated, which means that all acid centers are fully accessible.

The acidic ion-exchange resins were delivered saturated with water. They were activated by drying at 383 K, first at atmospheric pressure and then overnight under vacuum at the same temperature. Final water content after drying was less than 3% w/w (Karl-Fisher titration). Commercial particles sizes were used in all the experiments.

2.3. Analysis

All samples were analyzed by gas chromatography. Liquid samples were obtained through a sampling valve (Valco A2CI4WE.2) that injected 0.2 μL of pressurized liquid into a Hewlett–Packard 6890 gas chromatograph equipped with a capillary column (HP 190915-433; 5% phenyl methyl siloxane, 30 m × 250 μm × 0.25 μm nominal). A mass selective detector (HP 5973) was used in the gas chromatography (GC) analysis. The injector temperature was set to 523 K, the electron source of the mass detector was set to 503 K, and the quadrupole was set to 423 K. A temperature ramp was programmed: from 308 K (isotherm during 1.5 min) to 473 K at a 50 K min^{-1} ramp rate, with the final temperature maintained for 10 min. Helium (Air Liquide, Barcelona, Spain) with a minimum purity of 99.998% was used as a carrier gas.

2.4. Apparatus and procedure

Experiments were carried out in a 200-cm^3 stainless steel jacketed batch reactor (Autoclave Engineers). The stirring speed was set to 500 rpm, in order to avoid external mass transfer effects [17] and the temperature range was set to 353–393 K, which was controlled by a thermostated 1,2-propanediol–water mixture within ±0.1 K. The reaction pressure was maintained with nitrogen at 2 MPa to ensure the liquid phase for the reacting system.

The reactor was loaded with 4 g of fresh dried resin and, after the desired temperature was reached, pure 1-octene was shifted to it by means of nitrogen from a calibrated burette. No solvents were used. Then, agitation was switched on and this moment was considered as the starting point of the reaction. Periodically,

Table 1
Physicochemical properties of the resins.

Catalyst	Crosslinking	Sulfonation[a]	Acidity ($eqH^+ kg^{-1}$)	S_{BET} ($m^2 g^{-1}$)	V_g [b] ($cm^3 g^{-1}$)	d_{pore} [c] (Å)	ρ_s [d] (g/cm^3)	θ [e] (%)	$-\Delta H_{ad}^{NH_3}$ (kJ/mol)
A15	High	C	4.81	42	0.33	314	1.4164	32	111
A35	High	O	5.32	29	0.21	290	1.5417	24	117
A36	Medium	O	5.40	21	0.14	270	1.5671	18	117
A46	High	SS	0.43	57	0.26	182	1.1369	23	–
A48	High	O	5.62	34	0.25	294	1.5378	28	–
CT175	High	C	4.98	29	0.48	662	1.4984	42	114
CT252	Medium	O	5.40	22	0.22	400	1.4929	25	–
CT275	High	O	5.20	28	0.42	600	1.5056	39	119
CT276	Medium	O	5.20	24	0.21	350	1.4890	24	–

[a] C: conventionally sulfonated; O: oversulfonated; SS: surface-sulfonated.

[b] Pore volume estimated from adsorption/desorption of N_2 at 77 K.

[c] Assuming pore cylindrical model.

[d] Skeletal density, measured by helium displacement.

[e] Porosity was estimated as $100V_g/(V_g + (1/\rho_s))$.