ALKYLATION OF TOLUENE WITH 1-HEXENE OVER MACRORETICULAR ION-EXCHANGE RESINS

Madelin Cadenas, Roger Bringué*, Carles Fité, Montserrat Iborra, Eliana Ramírez, Fidel Cunill

Department of Chemical Engineering, University of Barcelona, Martí i Franquès,1, 08028 Barcelona, SPAIN
*rogerbringue@ub.edu

ABSTRACT

The macroreticular acidic ion-exchange resins Amberlyst 35, Amberlyst 46 and Purolite CT 275 were investigated as catalysts for the alkylation of toluene with 1-hexene and simultaneous dimerization and isomerization of the olefin at 373 K. After six hours of reaction, 1-hexene conversion was complete. At low toluene concentration double-bound isomerization of 1-hexene was the main reaction. As toluene concentration increased, double-bond isomerization decreased and toluene alkylation and olefin dimerization reactions increased. By using Purolite CT 275 resin and for an almost equimolar toluene to 1-hexene ratio, the selectivity to dimers was 22%, that of mono- and di-alkylated compounds were 42% and 3.5%, respectively, while that of double-bound isomerization was 32.5%. These reactions catalyzed by macroreticular ion-exchange resins of high acid capacity and degree of crosslinking can be useful to boost naphtha streams in the refining industry by reducing volatile compounds and aromatics of low boiling point.

Keywords: alkylation, dimerization, toluene, 1-hexene, macroreticular ion-exchange resins.

1. INTRODUCTION

The alkylation of aromatic hydrocarbons with olefins is applied on a large scale in chemical and fuel production [1]. The reaction can be catalyzed by mineral acids (such as HF, H_2SO_4, or H_3PO_4), Lewis acids, or solid acids (such as silica-alumina, clays, zeolites, and sulfonic ion-exchange resins) by using as alkylating reagents alkenes, alkyl chlorides and alcohols. Traditionally, alkylates of aromatics were obtained using homogeneous acid catalysts; even today Friedel-Crafts catalysts are employed in the production of alkyl-substituted aromatics. The use of solid acids avoids several drawbacks of mineral acids present in homogeneous catalysis, namely, handling, safety, corrosion and waste disposal. So, in the last decades many commercial processes for the alkylation of benzene and toluene using acid solid catalyst have been introduced, and the catalysts most used are solid phosphoric acid (SPA), zeolite-type materials and fluoride-based catalysts [2,3]. However, the search of more active and selective solid acid catalysts with the purpose of obtaining the most desirable mono-alkylated product is still in progress [4,5].

Despite the fact that alkylation of aromatic hydrocarbons with olefins is applied on a large scale in the chemical and petrochemical industry, there is also interest in using this kind of reaction in the

refining industry due to the increasingly more stringent regulations on benzene and aromatics contents in gasoline and diesel fuels. Usually, in petrochemical industry, aromatic alkylation processes are operated at high aromatic to olefin molar ratio to limit side reactions involving olefins such as olefin oligomerization and multiple alkylations. However, when aromatic alkylation is employed for fuels production, the final product is a complex mixture and the quoted side reactions are not necessarily undesirable [6]. Thus, on one hand, dimerization of C_5 olefins present in naphtha streams coming from FCC processes can contribute to the reduction of evaporative emissions which allows for an increase of the volatile bioethanol to be blended in gasoline pool. Dimers and trimers of C_6 olefins of naphtha could go to the diesel pool in detriment of gasoline production which would be in agreement with the actual market demand of both fuels in Europe. On the other hand, aromatics alkylation offers increases in octane number for gasoline and products of low cetane number for diesel. The catalyst aforementioned for alkylation can also be used to catalyze olefin oligomerization because it is an acid-catalyzed reaction. Therefore, both types of reactions can occur simultaneously if there is no excess of aromatics [7]. In doing so, refiners could achieve the benefits above noted in a single refining step. Care have to be taken into account since excessive amounts of high molecular weight oligomers and poly-alkylated aromatics can adversely affect the gasoline pool blending specifications, particularly the end boiling point of the corresponding fuel and they can also cause catalyst deactivation from pore blockage.

As the knowledge of olefin oligomerization reaction can be useful for understanding what happens when aromatic alkylation and olefin oligomerization are both main reactions some literature on olefin oligomerization will be introduced. Even though the available literature on oligomerization of ethylene and propylene is excessively abundant, many for butylenes, it is scarce for pentenes and heavier olefins [8-10]. However, some papers about oligomerization of biomass-derived C_9 alkenes have recently appeared [11,12]. It is surprising to notice that in the open literature the majority of the work on alkylations with olefins and olefins oligomerizations employ mainly zeolites-based materials and solid phosphoric acid, and only in a much reduced cases use acidic ion-exchange resins, despite they can show an acid strength similar to zeolites mentioned above in non-aqueous conditions [13]. In our previous work [14], some macroreticular ion exchange resins were active for 1-hexene oligomerization with a negligible amount of tetramers and cracking products at temperatures lower than 383 K.

Comparatively, alkylation with olefins catalyzed by acidic resins is a better documented reaction, but again oligomerization is usually considered as a side-reaction [15] and focused mainly in benzene alkylation, being the 2-phenyl isomer the most preferred product. It is quoted that macroreticular resins showed significantly higher activity than gel-type ones in non-swelling reacting system such for alkylation reaction with olefins, illustrating in these kinds of reactions the importance of opening up the microstructure of gel zone for reactivity. Focusing only on alkylation of toluene catalyzed by ion exchange resins, a study [16] compared three macroreticular resins (Amberlyst 35, Amberlyst 15 and Lewatit SPC112) using 1-octene as alkylating agent under mild reaction conditions (<383 K) and in

toluene excess. Mono- and di-alkylation products were obtained in different proportions depending on the resin. Amberlyst 35 showed the highest activity and selectivity in the formation of mono-alkylated isomers.

With the aim to make up for the absence of knowledge on the aromatic alkylation with excess of olefin catalyzed by acidic macroreticular ion exchange resins, the present paper investigates the alkylation of toluene with 1-hexene in liquid phase with excess of olefin. The results could be interesting for refiners to reduce olefins content in naphtha with high aromatics contents.

2. EXPERIMENTAL

2.1 Chemicals and catalysts.

Toluene (99.5%) and 1-hexene (99%) were obtained from Sigma-Aldrich and used without further purification. Reaction mixtures were prepared with toluene and 1-hexene at four initial toluene/1-hexene weight ratios: 0, 0.125, 0.25 and 0.5.

Catalysts were sulfonic resins Amberlyst 35 (A-35) and Amberlyst 46 (A-46) (Rohm and Haas) and Purolite CT-275 (CT-275) (Purolite). While A-35 and CT-275 are oversulfonated with more than one sulfonic group per phenyl ring, A-46 is only sulfonated on the external surface. Some properties of these resins are listed in Table 1 [17]. Pore volume and surface area in dried state were calculated from nitrogen adsorption-desorption isotherms at 77 K. The adsorption enthalpy of ammonia [18,19, 20] was also included as a relative measure of the acid strength of the ion exchange resins.

TABLE 1

2.2 Analysis and procedure

All samples were analyzed by gas chromatography/mass spectrometry (GC/MS). The gas chromatograph with a mass selective detector (Agilent 6890 + 5973 GC/MS) was equipped with a capillary column (HP 190915-433; 5% phenyl methyl siloxane, 30 m x 250 μm x 0.25 μm nominal). More detailed information can be found elsewhere [21].

The reactions were carried out in a 200 mL jacketed batch reactor at 373 K (Autoclave Engineers). In each experiment, the autoclave was preloaded with 4 g of dry resin of commercial size and the calculated amount of toluene. Previously, the resin was activated by drying at 373 K overnight under vacuum, being the final content of water less than 3% $g_{water} \cdot g_{cat}^{-1}$ (Karl-Fisher titration). After the system was leak tested with nitrogen at 1 MPa, it was heated to the required reaction temperature and the stirring speed was set to 500 rpm to avoid the influence of external mass transfer. To start the experiments, the reactor pressure was lowed to the atmospheric one and the calculated amount of 1-hexene previously placed in a calibrated burette was forced into the system by nitrogen and then the

pressure was readjusted to 2 MPa. After a short while, the temperature was recovered and that moment was taken as the starting point of the experiment. The autoclave was equipped with a sample loop including a sampling valve that injected 0.2 µL of pressurized liquid to the chromatograph. The remaining liquid into the loop was returned to the reactor by nitrogen which was then used to clean the loop.

2.3 Calculations

For each experiment, 1-hexene conversion (X_{1-hex}), selectivity to mono-alkylated toluene (S_{MAT}), selectivity to di-alkylated toluene (S_{DAT}), selectivity to tri-alkylated toluene (S_{TAT}), selectivity to 2-hexene (S_{2-hex}), and selectivity to dimers (S_{Dim}), were calculated using the following expressions:

$$X_{1-hex} = \frac{n^0_{1-hex} - n_{1-hex}}{n^0_{1-hex}} = \left[\frac{n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}}{n_{1-hex} + n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}} \right]_t \quad (1)$$

$$S_{2-hex} = \left[\frac{n_{2-hex}}{n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}} \right]_t \times 100 \quad (2)$$

$$S_{MAT} = \left[\frac{n_{MAT}}{n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}} \right]_t \times 100 \quad (3)$$

$$S_{DAT} = \left[\frac{2n_{DAT}}{n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}} \right]_t \times 100 \quad (4)$$

$$S_{TAT} = \left[\frac{3n_{TAT}}{n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}} \right]_t \times 100 \quad (5)$$

$$S_{Dim} = \left[\frac{2n_{Dim}}{n_{2-hex} + n_{MAT} + 2n_{Dim} + 2n_{DAT} + 3n_{TAT}} \right]_t \times 100 \quad (6)$$

The expression for trimers of 1-hexene was not included because these compounds were only detected in very low amounts. Repeated runs were made for some experiments and the reproducibility of the results was found to be reliable. The standard deviation for 1-hexene conversion was 1% and 3% for selectivity. The error of the mass balances was always less than 7% for all the experiments.

3. RESULTS and DISCUSSION

3.1 Product distribution and reaction types

   Blank experiments with toluene (without 1-hexene) in presence of A-35 showed that there was no reaction. Gas chromatography of reaction products of a standard experiment with toluene and 1-hexene at 373 K and 2 MPa showed many peaks arranged in clusters and GC/MS indicated that those clusters represent products such as double-bound isomers (*cis*-2-hexene, *trans*-2-hexene and 3-hexene in low amounts), dimers of 1-hexene, and mono-alkylation products, in different proportions depending on the resin and the experimental conditions. GC/MS also showed the presence of trimers of 1-hexene, three di-alkylates and some tri-alkylates, in less amount. Neither branched isomers of alkylates, which would be a result of skeletal isomerization of the olefin, nor cracking compounds were detected.

   2-hexene presence was identified easily but formed dimers identification was difficult because many of these compounds are not commercially available as reference compounds and there exist no mass spectrum for them. The isomer composition of the mono-alkylation products of toluene showed 5 hexyltoluene isomers but not the corresponding *ortho*, *meta* and *para* isomers. The only hexyltoluene that was identified with high probability was 1-(2-hexyl)-2-methylbenzene or 2-(*o*-tolyl)hexane. If for hexylbenzene one can expect 17 isomers [5], for toluene the number of potential hexyltoluenes (*o*-, *m*- and *p*-) could be 51. As only linear mono-hexyl alkylates were found because there was no branched hexenes that huge number of isomers was reduced to 9. These facts are in good agreement with literature data, e.g. in the reaction of 1-hexene with excess of toluene in the presence of aluminium chloride [22] four hexyl chains per aromatic ring were reported. 2-tolylhexane, 3-tolylhexane, di-hexyltoluene and tri-hexyltoluene were identified and that poly-alkylated compounds proportion increased on decreasing the temperature.

   Figure 1 shows the progress of the reaction in the alkylation of toluene with 1-hexene at 373 K in olefin excess over A-35. The quick depletion of 1-hexene and the subsequent formation of linear 2-hexene is clearly observed. The fact that the 2-hexene curve went through a maximum at around 1 hour of reaction and then it decreased slowly indicates the sequential nature of the dimers formation.

FIGURE 1

   After the sharp decrease for 1-hexene, it seemed the curve levelled off indicating a possible equilibrium position at the initial instants of the reactions. As time went by, the pseudo-equilibrium position shifts and in some cases complete conversion of 1-hexene was achieved. Toluene consumption was less accused than for 1-hexene and mono-hexyl toluene amount increased more or less linearly. Di- and tri-hexyl toluene were also formed but in a very low extension. It is clear that, in

this example, 1-hexene had a higher selectivity for double bond isomerization than for dimerization and alkylation, i.e. the reaction rate of the former reaction was higher than the latter one.

In the alkylation of toluene with 1-heptene over large pore zeolites [23] (HFAU and HBEA) at 363 K, similar products profiles were found except after alkene double bound shift the main reaction was toluene alkylation instead of 1-heptene dimerization. This fact can be explained considering that they used a toluene to alkene molar ratio of 3. Same picture was found in alkylation of toluene with amylenes catalyzed by SiO_2-Al_2O_3 and zeolites Y and β in the range 373-473 K with toluene to 1-pentene molar ratio of 3:1 and 10:1 [24]. At those conditions, alkylation was the main reaction and amyltoluenes the main products with selectivity higher than 81%. Oligomerization and di-alkylation decreased at high aromatic to olefin ratio. At higher temperature (453 K) they also noted, as expected, that skeletal isomerization was significant and, consequently, besides linear alkylates, branched ones were also formed. Changes in selectivity with temperature are also noted in the alkylation of benzene over solid phosphoric acid (SPA) catalyst at 493 K with benzene and 1-hexene in equimolar amounts [5]. At this rather high temperature linear hexenes were readily skeletally isomerized to branched hexenes. Skeletal isomerization became the main reaction followed by alkylation and dimerization.

Based on the products profiles, a reaction scheme is proposed in Figure 2. Double bond isomerization, oligomerization and alkylation reactions were observed at 373 K over macroreticular ion exchange resins. These are all acid-catalyzed reactions and were expected from literature data at rather low temperature. Double bond isomerization of 1-hexene to 2-hexene was fast and then dimerization and alkylation took place in parallel. In a previous work [14], 3-hexene and skeletal isomers were detected in very small amounts (less than 2 wt%) at the same temperature and catalyst but using only pure 1-hexene as feed. However, significant amounts of 3-hexene were found in the alkylation of benzene with 1-hexene added in equimolar quantity at 493 K, 3.8 MPa and using SPA (solid phosphoric acid) as catalyst [5]. Higher temperature and different catalyst could explain such difference. They also noted that cracking was noticeable only in the reactions with branched hexenes. These facts are supported by the work of De Klerk [25], who suggested that skeletal isomers formation needed higher temperatures. Also, he noted that conversion of 1-hexene over various acid catalysts showed that cracking only become significant at temperatures above 548-573 K. It is to be observed that the presence of the double bond isomerization reaction could be positive when the final product was sent to gasoline pool because 2-hexene has an octane number higher than 1-hexene [6]. Something else to bear in mind is that part of the mono-alkyltoluene formed initially could come from 1-hexene [23]. Unfortunately, the shapes of the mole-time plots in Figure 1 did not allow confirming this fact.

FIGURE 2

Isomerization and oligomerization of olefins and alkylation by olefins reactions take place via a carbocation intermediate. It is well known that the carbocation acts as electrophile and may rearrange

to look for the most stable one. The stability of a carbocation decreases from a tertiary to a primary carbon. The carbocation needs not to be a free ion but may exist as a tight ion pair, which is almost certainly the case for catalysis by ion exchange resins in non-polar medium. The reactions occur by concerted mechanism with proton transfer directly to olefin from the sulfonic groups of the resin. Protonation of 1-hexene forming the 2-hexyl carbenium and its subsequent deprotonation explains the formation of 2-hexene, a more stable olefin. The same carbocation can attack the aromatic ring of toluene forming an arenium ion (σ complex) which eliminates the hydrogen bonded to the attacked aromatic carbon with the formation of the alkylated product. Further attacks on alkylated products by others hexyl carbenium can explain the formation of di- and tri-alkylates. The exact nature of the intermediate species on ion exchange resins is not yet precisely known but it could take place by participation of several sulfonic groups of the resin. In parallel, 2-hexyl carbenium attacks another molecule of hexene to give branched dimers after eliminating a proton. As dimerization is also a bimolecular reaction several sulfonic groups could be needed to participate in the concerted mechanism to stabilize such big intermediate of reaction. Trimers formation can be explained in a similar way.

3.2 Effect of resin and aromatic to olefin weight ratio on 1-hexene conversion

Figure 3 shows that conversion of 1-hexene was almost complete within 1 h in the presence of toluene for A-35 and CT-275. The last one was something more active because it took less time to get 100% conversion, but the difference was small. A sharp curve towards total conversion means high reaction rate and very active catalyst.

FIGURE 3

It can be also observed that there was no effect of the initial aromatic to olefin weight ratio in the range explored for the three assayed resins because the curves for the same resin overlapped. The range 0-1 of aromatic to olefin weight ratio was used in present paper to cover the range used to produce fuels and double-bound isomerization of olefin and toluene alkylation in important amounts. As already noticed, commercial alkylation is typically done with an aromatic to olefin molar ratio of 6-8 to reduce isomerization and oligomerization reactions of olefin and poly-alkylation.

A-46 took 3 h to reach complete conversion and the reaction rate was lower than the two other resins. The lower activity of A-46 can be explained due to it has an acid capacity six-fold lower than the other two catalyst and because their active centers have a lower relative acid strength compared with A-35 and CT-275 (see Table 1). However, A-46 was capable of making the same catalytic work in terms of olefin conversion, but with a period of time three fold longer. This fact could mean that only a part of the active sites for A-35 and CT-175, mainly located at the more external zone of the gel-phase, took part in the reactions because A-46 is surface-sulfonated, and practically all its acid

centers are accessible and participated in the reactions. This is clearly noticed on calculating 1-hexene conversion divided by the acid capacity of the catalyst after 0.5 h of reaction (at higher time it was most difficult to notice such differences because complete conversion was reached). Values of 55 %/meq/g were obtained for A-46 while values of 16 and 18 %/meq/g were obtained for A-35 and CT-275, respectively. That fact was even more highlighted, if it is considered that A-35 and CT-275 are oversulfonated, which not only provides a greater acid density, but a higher acid strength as well [19].

Finally, after considering that operation temperature for the batch reactor was lower than the temperature for possible thermal deactivation (see Table 1) and that runs lasted only 6 hours, deactivation of the catalyst was not considered of importance. Besides, no discoloration or deposits were observed on the used catalyst.

3.3 Effect of resin and aromatic to olefin weight ratio on selectivity

As can be seen in Figure 4 for the three resins, selectivity towards mono-alkylates increased with higher toluene content in the initial reaction mixture, while the selectivity towards dimers and double-bound isomerization decreased. Selectivity to double bond isomerization products is not showed in Figure 4, but it can be easily calculated by subtracting from 100 the sum of alkylate and oligomers selectivities. In toluene presence, the concentration of trimers was very low with selectivities lower than 1%. By using A-46 the main reaction was double bond isomerization reaching a selectivity of around 75% for all the different aromatic to olefin weight ratios. On increasing the aromatic to olefin weight ratio from 0 to 1, selectivity to dimers decreased from 22% to 10% whereas that of mono-alkylated toluene increased from 0 to 14%.

A-35 and CT-275 showed similar values of dimers selectivity for all the essayed toluene to 1-hexene ratios. This fact can be also observed for the selectivity to mono-alkylated toluene at low toluene to 1-hexene ratio but at almost equimolar ratio (weight ratio of 1) mono-alkylated selectivity for CT-275 was higher (42%) than that for A-35 (27%).

Table 2 shows that on CT-275 the highest selectivity towards tri-alkylates was obtained at an initial toluene/1-hexene weight ratio of 0.5. Tri-alkylates were not formed at all on A-46.

FIGURE 4, TABLE 2

As mentioned, despite its lower acid capacity, A-46 is capable of producing mainly double-bond isomerization, while dimerization and alkylation in less extension. Of course, A-35 and CT-275, with a higher acid capacity, can also catalyze 1-hexene double-bound isomerization. But in contrast to A-46, both resins produce more dimerization and alkylation because they have a convenient spatial distribution and density of acid centers in the gel phase to catalyze bimolecular reactions for which a bigger reaction intermediate needs to be stabilized, as already mentioned. On the other hand, the highest selectivity towards alkylation and dimerization products by CT-275 with respect to A-35 can be explained by its higher porosity, which facilitates reactant more accessibility to a greater number of

acid centers. The lower selectivity values of A-46 towards toluene alkylation and 1-hexene oligomerization reactions products, and consequently, the higher one towards double-bond isomerization to 2-hexene, can be illustrated by the reaction mechanism. As double-bond isomerization involves only a unique molecule, with only one sulfonic group it is possible to stabilize the intermediate of the reaction. In this way, low acid density provided by A-46 would be enough to produce double-bond isomerization.

4. CONCLUSIONS

Experimental data clearly show that oversulfonated macroreticular acidic ion-exchange resins have enough acid strength at 373 K to catalyze the double-bond isomerization and oligomerization of 1-hexene, and the alkylation of toluene with such olefin. Complete 1-hexene conversion was rapidly achieved over resins Amberlyst 35 and Purolite CT-275 for initial toluene to 1-hexene weight ratio ranging 0 to 1. With an excess of olefin, the main reaction was double-bond isomerization followed by olefin dimerization and alkylation reactions. As toluene concentration increased, double-bond isomerization decreased and toluene alkylation and olefin dimerization reactions increased. Thus, for an initial toluene to 1-hexene ratio of 1, the selectivity to dimers was 22%, that of mono- and di-alkylated compounds 42% and 3.5%, respectively, while that of double-bound isomerization 32.5%. The best catalyst for double-bond isomerization was A-46 and CT-275 for toluene alkylation. This behavior can be related to the catalytic working zone. While for A-46 the zone is located on the particle surface, for CT-275 it is inside the outer gel-phase zones.

Nomenclature

A-35   Macroreticular ion-exchange resin Amberlyst 35

A-46   Macroreticular ion-exchange resin Amberlyst 46

CT-275   Macroreticular ion-exchange resin Purolite CT 275

GC/MS   Gas chromatograph with mass detector

n^o_{1-hex} Initial mole of 1-hexene (mol)

n_j Mole of component j (mol)

S_j Selectivity to product j (%)

t   Time (min)

X_{1-hex} Conversion of 1-hexene (%)

Subscripts

DAT   Di-alkyl toluene

Dim   Dimers

1-hex   1-Hexene

2-hex   2-Hexene

j   Component j

MAT   Mono-alkyl toluene

TAT   Tri-alkyl toluene

REFERENCES

1. Kirk-Othmer, *Encyclopedia of Chemical Technology*, fifth ed., vol.2, 2004, pp.177-196.

2. J.A. Kocal, B.V Vora, T. Imai, Appl. Catal: A. 221 (2001) 295-301

3. C. Perego, P. Ingallina, Catal. Today. 73 (2002) 3-22.

4. I. Cracium, M-F. Reyniers, G.B. Marin, J. Mol. Catal. A: Chem. 277 (2007) 1-14.

5. R.J.J. Nel, A. De Klerk Ind. Eng. Chem. Res. 46 (2007) 2902-2906.

6. A. De Klerk Green Chem. 10 (2008) 1249-1279.

7. G.C. Laredo, J.J. Castillo, J. Navarrete-Bolaños, P. Perez-Romo, F.A. Lagos, Appl. Catal. A. 413-414 (2012) 140-148.

8. R. Schmidt, M.B. Welch, B.B. Randolph, Energy Fuels 22 (2008) 1148-1155

9. R. Van Grieken, J.M. Escola, J. Moreno, R. Rodríguez, Chem. Eng. J. 155 (2009) 442-450.

10. A. De Klerk, Ind. Eng. Chem. Res. 45 (2006) 578-584.

11. D. Martin-Alonso, J.Q. Bond, J.C. Serrano-Ruíz, J.A. Dumesic, Green Chem. 12 (2010) 992-999.

12. J.C. Serrano-Ruíz, J.A. Dumesic, Energy Environ. Sci. 4 (2011) 83-99.

13. E.G. Lundquist, K. Beshah, 213th ACS National Meeting, San Francisco, CA, April, (1997) 13-17.

14. M. Cadenas, R. Bringué, C. Fité, E. Ramírez, F. Cunill, Top. Catal. 54 (2011) 998-1008.

15. M.A. Harmer, Q. Sun, Appl. Catal. 221 (2001) 45-62.

16. R.M. Fernandes, E.R. Lachter, Catal. Commun. 6 (2005) 550-554.

17. R. Bringué, M. Cadenas, C. Fité, M. Iborra, F. Cunill, Chem. Eng. J. 207-208 (2012) 226-234.

18. M. Hart, G. Fuller, D.R. Brown, J.A. Dale, S. Plant, J. Mol. Catal. A: Chem. 182-183 (2002) 439-445.

19. P.F. Ciril, H.E. Cross, D.R. Brown, J. Mol. Catal. A. 279 (2008) 63-68.

20. M. Granollers, Doctoral Thesis, (2012), University of Barcelona, Spain, p.90

21. V. Cruz, J.F. Izquierdo, F. Cunill, J. Tejero, M. Iborra, C. Fité, React. Funct. Polym. 65 (2005) 149-160.

22. K.D. Black, F.D. Gunstone, Chem. Phys. Lipids. 79 (1996) 79-86.

23. Z. Da, Z. Han, P. Magnoux, M. Guisnet, Appl. Catal. A, 219 (2001) 45-52.

24. M. Cowley, A. De Klerk, R.J.J. Nel. Ind. Eng. Chem. Res. 44 (2005) 5535-5541.

25. A. De Klerk, Ind. Eng. Chem. Res. 44 (2005) 3887-3893.

Table 1. Properties of sulfonic macroreticular resins

Resin	A-35	A-46	CT-275
Acid capacity (meq $\cdot$ g_{dry}^{-1})	5.32	0.87	5.20
Specific surface area (m$^2 \cdot$ g_{dry}^{-1})	29	57	22
Mean pore diameter (nm)	23.6	19.2	32.9
Mean particle diameter (mm)	0.51	-	0.72
Maximum temperature (K)	423	393	418
Ammonia adsorption enthalpy -$\triangle H_{ads}$ (kJ/mol)	117	108	119
Porosity (%)	24	23	39

Table 2. Selectivity to tri-alkylates after 6h at 373 K on increasing the toluene to 1-hexene initial weight ratio on Amberlyst 35 and Purolite CT-275.

Toluene (wt%)	12.5	25	50
Selectivity to tri-alkylates (wt%)			
Amberlyst 35	1.9	2.1	2.1
Purolite CT275	0.00	0.97	3.5

Figure captions

Figure 1. Typical time-dependent products distribution for a 0.125 toluene to 1-hexene weight ratio over Amberlyst 35 at 373 K (A) ♦1-hexene; ■2-hexene; ● dimers; ＊ trimers; (B) ▲toluene; ×

mono-alkyltoluene; ＊di-alkyltoluene ; ０ tri-alkyltoluene .

Figure 2. Scheme of toluene alkylation with 1-hexene and 1-hexene oligomerization over cation exchange resins

Figure 3 Catalyst activity comparisons in alkylation reaction of toluene with 1-hexene over 4 g of dry resin for different initial weight ratio of aromatic to olefin at 373 K and 2 MPa (♦ 12.5%; ■ 25%; ▲ 50.0%).

Figure 4. Effect of the resin type (♦A-35; ■ A-46; ▲ CT-275) and of initial toluene/1-hexene weight ratios on selectivity to toluene mono-alkylated products and 1-hexene dimers at 373 K after 6 hours.
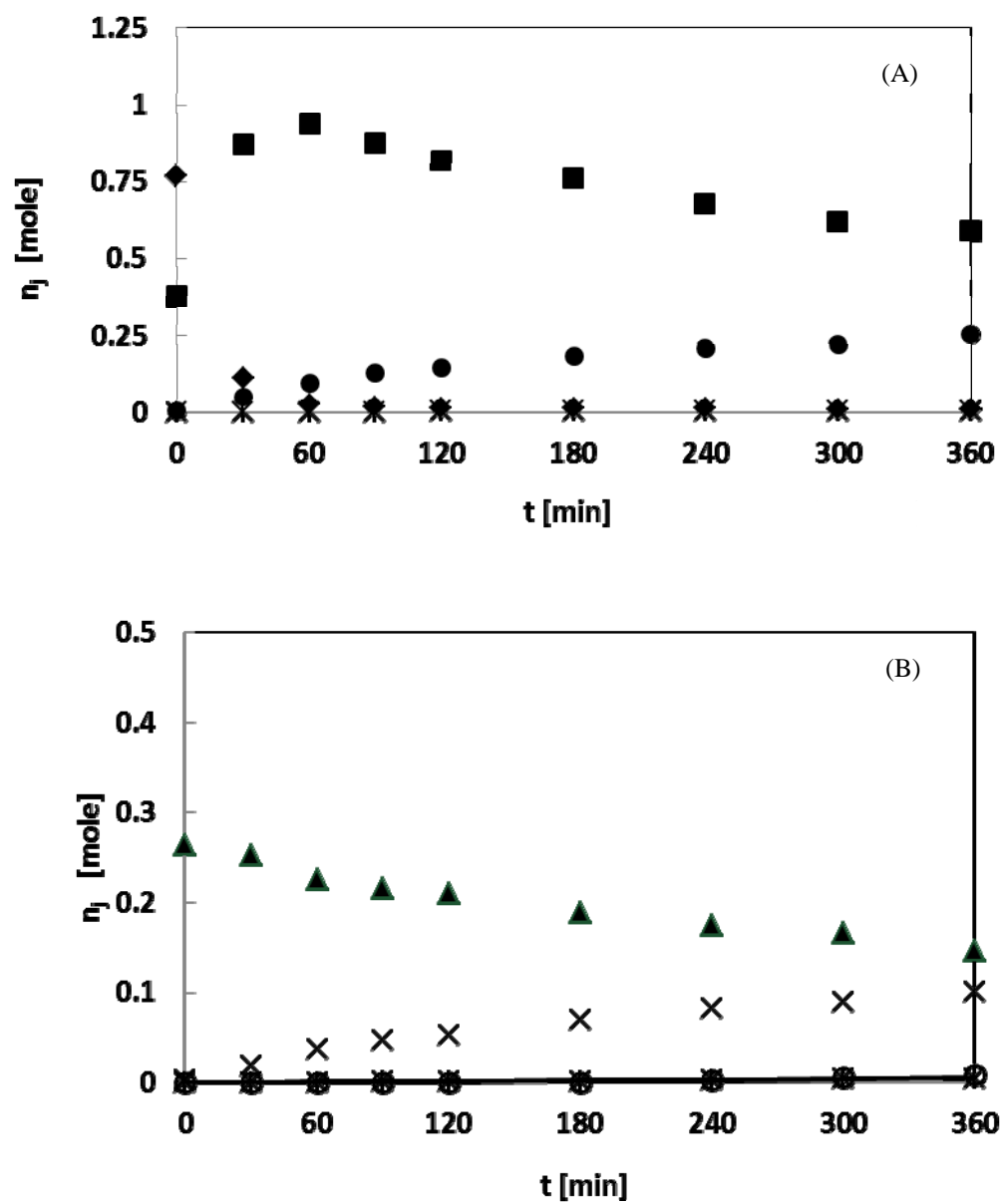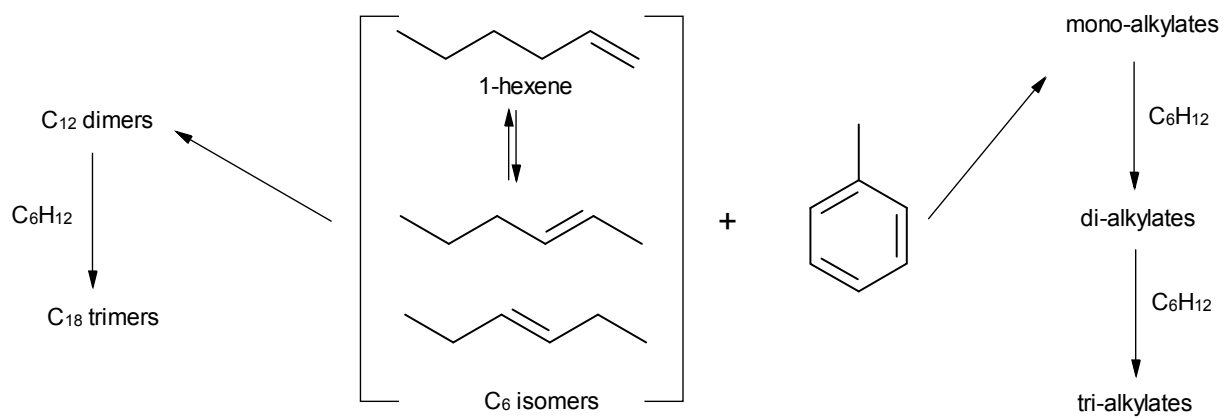
Figure 1. Typical time-dependent products distribution for a 0.125 toluene to 1-hexene weight ratio over Amberlyst 35 at 373 K (A) ◆1-hexene; ■2-hexene; ● dimers; ✳ trimmers; (B)▲ toluene; ×mono-alkyltoluene; ✳di-alkyltoluene ; o tri-alkyltoluene .

Figure 2 Scheme of toluene alkylation with 1-hexene and 1-hexene oligomerization over cation exchange resins
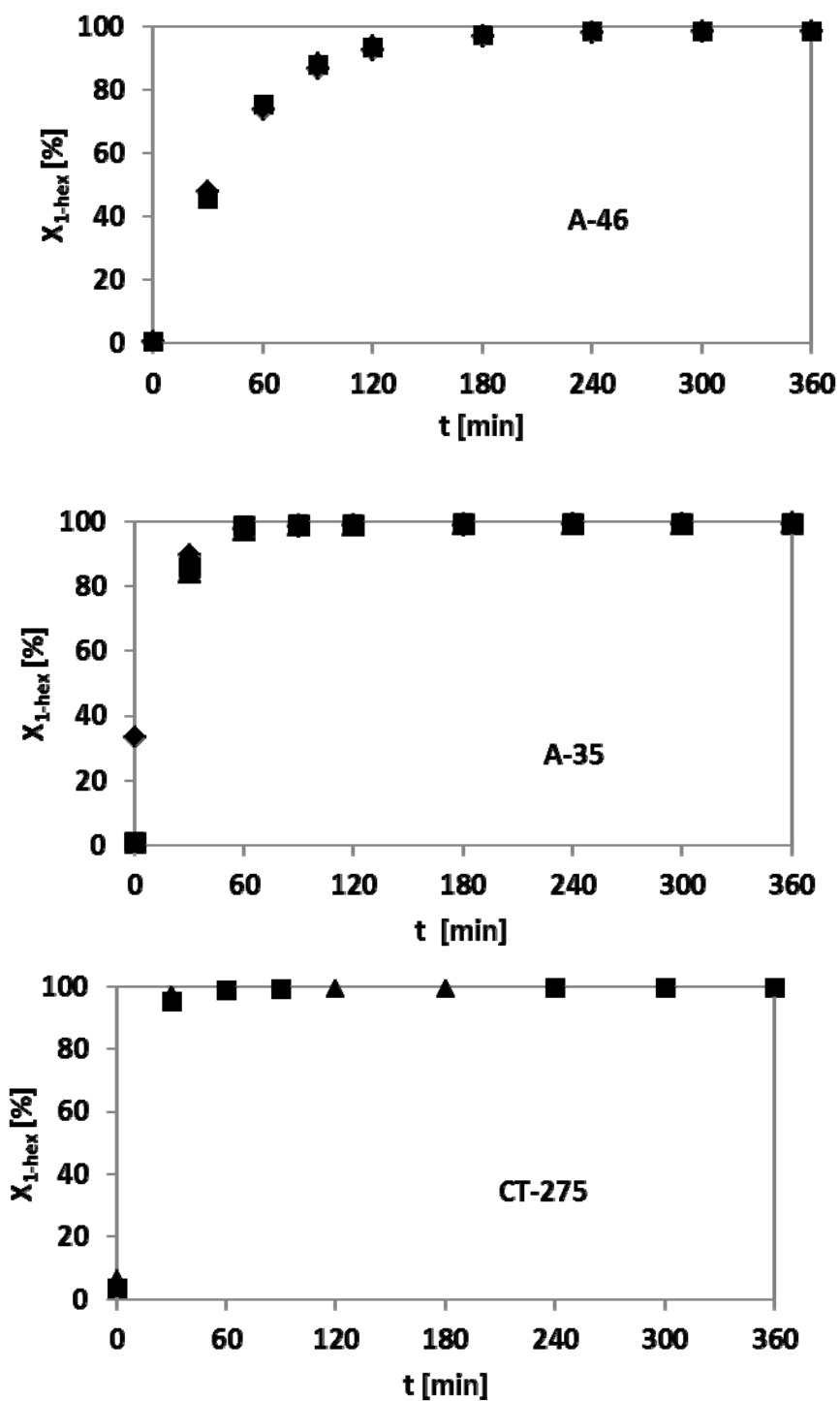
Figure 3 Catalyst activity comparisons in alkylation reaction of toluene with 1-hexene over 4 g of dry resin (A-46, A-35 and CT-275) for different initial weight ratio of aromatic to olefin at 373K and 2 MPa (♦ 12.5%; ■ 25%; ▲ 50.0%).
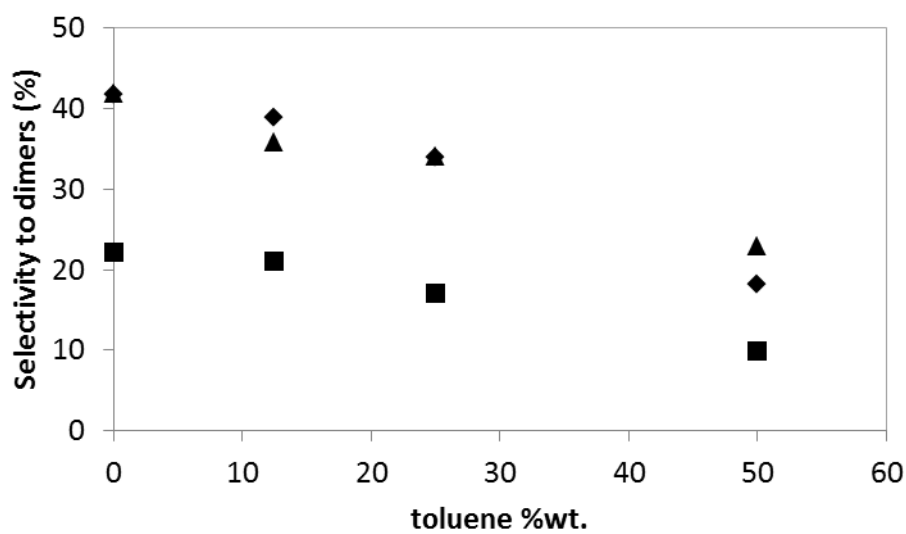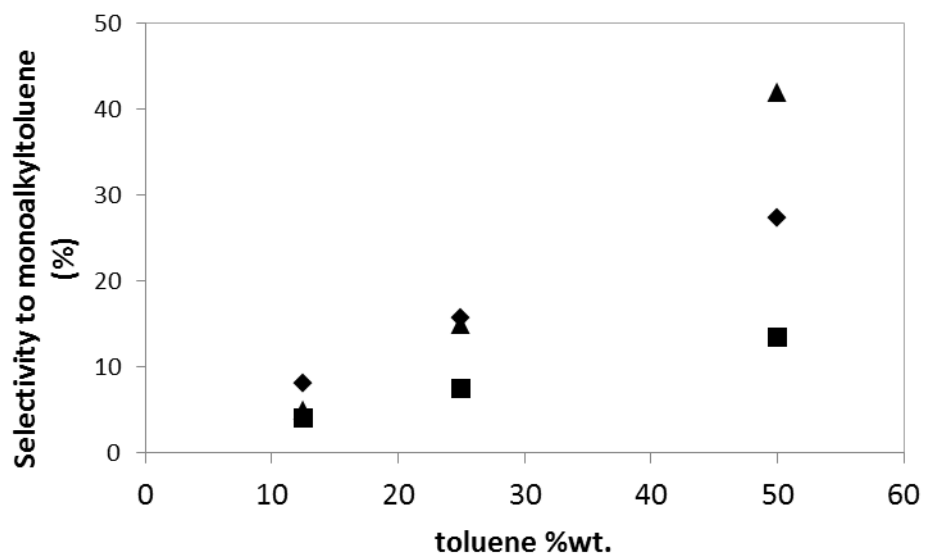
Figure 4. Effect of the resin type (♦A-35; ■A-46; ▲ CT-275) and of initial toluene/1-hexene weight ratios on selectivity to toluene mono-alkylated products and 1-hexene dimers at 373 K after 6 hours.