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Immobilised Ionic Liquids as Lewis Acid Catalysts for the Alkylation of Aromatic Compounds with Dodecene

C. DeCastro, E. Sauvage, M. H. Valkenberg, and W. F. Hölderich[1]

Department of Chemical Technology and Heterogeneous Catalysis, University of Technology-RWTH-Aachen, Worringerweg 1, 52074 Aachen, Germany

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Immobilised ionic liquids were used as acid catalysts for the alkylation of benzene, toluene, naphthalene, and phenol with dodecene. The reactions were carried out in batch, continuous liquid-phase, and continuous gas-phase systems. The influences of the concentration of the reactants, solvents, and temperature, as well as the acid strength of the ionic liquids, were studied. The catalysts proved to be very active for the alkylation of aromatic compounds with dodecene. The alkylation of benzene resulted in 98% selectivity to monoalkylated products at 99% conversion of dodecene at 80°C. Naphthalene and phenol featured lower conversions and high selectivity towards monoalkylated products. These results were compared to those obtained over conventional H-beta zeolite. The activities of the immobilised ionic liquids were found to be higher than those for the zeolite used under the same conditions. Possible leaching of the ionic liquid from the catalyst surface was followed by ICP measurements of the catalyst after the reaction and of the reaction mixture. No leaching was found. Deactivation of the catalyst was detected in the continuous liquid-phase reaction and it leads to a slight loss of conversion with time. © 2000 Academic Press

Key Words: **immobilisation; supported catalysts; Friedel–Crafts alkylation; LAB; ionic liquids; Lewis acids.**

INTRODUCTION

Ionic liquids (ILs), previously known as molten salts, were mainly used in electrochemistry studies due to their ionic nature. The most important step in the chemistry of the ILs occurred when Osteryoung *et al.* (1) described a mixture of 1-(1-butylpyridinium) chloride and aluminum chloride which was liquid at room temperature. Later, Wilkes *et al.* (2) discovered other ionic liquids based on dialkylimidazolium salts (see Scheme 1) that featured even more convenient physical and electrochemical properties than the butylpyridinium salts. Therefore, dialkylimidazolium and butylpyridinium salts are the most used and studied classes of ILs so far (3–5).

Ionic liquids show Lewis acidity when a Lewis acid (e.g., aluminum trichloride, $AlCl_3$), which forms the counteranion, is used in excess. The acidity of the resulting IL can be controlled by varying the amount of the Lewis acid in the final ionic liquid. The possibility of modifying the acidity of the ILs through a wide range of values is very interesting from the catalytic point of view, since the selectivity in some reactions depends on the acid strength of the catalyst (6). A clear example is the alkylation of phenol, where higher acid strength of the catalyst favours C-alkylation rather than O-alkylation (7, 8).

Friedel–Crafts reactions are of considerable importance in the production of fine chemicals. Many industrial processes for the production of fine chemicals and pharmaceutical products have an intermediate step that is a Friedel–Crafts-type reaction (9, 10). In this work we focus on the alkylation of aromatic compounds with olefins, especially benzene with dodecene, since it leads to the production of linear alkyl benzene compounds (LABs), which are the first intermediates in the synthesis of biodegradable detergents (11, 12). Conventional methods for alkylation reactions use HF or $AlCl_3$ as acid catalysts. These processes feature serious drawbacks: HF is highly toxic, volatile, and corrosive; $AlCl_3$ is also toxic and corrosive, and is consumed in large amounts. This generates a large amount of contaminated wastes, mainly salts, that require treatment before their final disposal (13). Data recently published by UOP discloses DETAL technology as a new alkylation process for the alkylation of benzene with heavy olefins, using solid acids as catalysts in the liquid-phase reaction (12, 14).

The use of ILs as catalysts would result in the easy separation of the catalyst from the reaction mixture, allowing its fast reuse and avoiding the generation of contaminated waste and its subsequent treatment. Ionic liquids have already been proposed as catalysts for Friedel–Crafts alkylation of benzene with olefins in order to produce LABs (15). Nevertheless, the use of ILs in their liquid form presents some inconveniences in an industrial continuous system. The supporting of reagents and catalysts is being widely studied as a way of generating clean technology (16). The immobilisation of ILs on an inert support brings many advantages for the system, such as the easier separation

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[1] To whom correspondence should be addressed. Fax: 00-49-241-8888291. E-mail: HOELDERICH@rwth-aachen.de.

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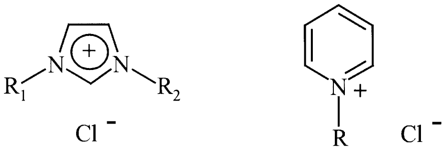

SCHEME 1. 1,3-Dialkyl-imidazolium chloride and 1-alkyl-pyridinium chloride.

of the catalyst from the reaction media and the possible utilisation of the catalyst in a continuous system.

In this work we have studied the catalytic behaviour of immobilised chloroaluminate ILs in the alkylation of aromatic compounds with olefins in order to improve the reaction conditions and to be able to recuperate and reuse the catalyst. Following these targets, ionic liquids possessing different Lewis acidity were tested in order to study the influence of the acid strength on the distribution of the reaction products. In the case of the alkylation of benzene with dodecene, the products include the dodecene isomers, alkylated products, isomers of the monoalkylated products and the heavier products, i.e., di- and trialkylated products as well as dimers and trimers of dodecene.

Benzene, toluene, naphthalene, and phenol were used as aromatic substrates and as solvents at the same time. Nevertheless, some reactions using solvents such as cyclohexane (C_6H_{12}), dichloromethane (CH_2Cl_2), tetrahydrofurane (THF), and carbon tetrachloride (CCl_4) have also been carried out in order to study the influence of different solvents. The influence of the temperature and the behaviour in a continuous flow system were also studied for this catalyst.

EXPERIMENTAL

The IL used throughout the experiments consisted of 1-butyl-3-methyl-imidazolium chloride ([bmim]Cl) and $AlCl_3$, and this compound will be referred to as Al-IL in this work.

The imidazolium salts used for the preparation of the ionic liquids were kindly provided by Elementis Specialties. Aluminum chloride was supplied by Merck. The silica supports FK700, SP18, and T-350, as well as the titanium oxide P-25 (TiO_2), were kindly provided by Degussa. Alumina oxide (Al_2O_3 Pural SB) was kindly provided by CONDEA Chemie GmbH, and zirconium oxide 99% pure (ZrO_2) was provided by Aldrich.

Table 1 shows a list of the supports used as well as their surface area values (BET, in m^2/g) and pore size (Å).

The aromatic compounds, dodecene, dichloromethane, and the internal standard undecane, were supplied by Fluka with 99% purity grade.

Analytics

Solid-state MAS-NMR measurements were carried out on a Bruker Avanza 500. X-ray diffractometry (XRD) was done on a D 5000 from Siemens, using a copper tube FL Cu 4KE. FT-IR was performed on a Nicolet Protégé 460. For adsorption and desorption measurements an ASAP 2000 machine from Micromeritics was used. The concentrations of Si and Al in the samples were determined by ICP-AES, using a Spectro-Flame D machine from Spectro. CHN analysis was performed on a Elementar Vario EL. The GC analyses were carried out on a Carlo Erba 4200 gas chromatograph equipped with a 60-m-long FS-SE54 capillary column. The temperature program used was a ramp beginning at 100°C going to 270°C at 10°C/min and making an isotherm at 270°C for 40 min.

Catalyst Preparation

The AL-ILs were prepared by the slow addition of the desired amount of aluminum chloride to the imidazolium salt. The reaction was left stirring overnight at 0°C, in order to allow a perfect homogenisation of the resulting AL-IL. The whole process was kept under an argon atmosphere to avoid the hydrolysis of $AlCl_3$. The AL-ILs, once prepared, could be stored for a long time in an inert atmosphere before the impregnation was carried out. The amount of aluminum present in the resulting AL-IL was analysed by ICP in order to control the amount of AL-IL impregnated.

TABLE 1

Textural Properties of the Supports Used and the Supported AL-ILs*

Materials	Description	Surface area (m^2/g)	Average pore diameter (Å)
T-350	SiO_2	168	156
T-350/AL-IL ($N = 0.60$)*	SiO_2/AL-IL ($N = 0.60$)	150	147
Pural SB	Al_2O_3	201	75
Pural SB ($N = 0.60$)	Al_2O_3/AL-IL ($N = 0.60$)	167	73.2
FK700	SiO_2	391	59.6
FK700/AL-IL ($N = 0.60$)*	SiO_2/AL-IL ($N = 0.60$)	306	58.7
SP18	SiO_2	254	234
SP18/AL-IL ($N = 0.60$)	SiO_2 AL-IL ($N = 0.60$)	203	222
H-beta (Si/Al = 13.8)	SiO_2/Al_2O_3	328	—[a]
H-beta/AL-IL ($N = 0.60$)*	SiO_2/Al_2O_3 AL-IL ($N = 0.60$)	306	—[a]
TiO_2	TiO_2	29.3	214
TiO_2/AL-IL ($N = 0.60$)*	TiO_2/AL-IL ($N = 0.60$)*	25.2	214
ZrO_2	ZrO_2	31.3	222
ZrO_2/AL-IL ($N = 0.60$)	ZrO_2/AL-IL ($N = 0.60$)	31.5	202

[a] H-beta is a microporous material. Adsorption isotherms only allow calculation of the size of mesopores.

The immobilisation of the ionic liquids consisted of the addition of the AL-IL to the previously dried and calcined support (500°C during 3 h and stored under argon) until its appearance changed from a dry to a wet powder. This supported ionic liquid was stirred overnight and the excess of AL-IL was extracted for 24 h with boiling dichloromethane in a Soxhlet extraction system. Conductivity measurements of the dichloromethane showed the extraction to be complete after 12 h at most, depending on the support used. The extracted catalyst was then dried under vacuum and stored in argon for its further use in the reaction.

Reaction Conditions

The reactions were carried out under an inert atmosphere due to the sensitivity of the catalyst towards moisture. All reactions were carried out according to standard Schlenck procedures. The solvents were dried according to the literature.

The batch reactor system consisted of a dry round-bottomed flask (slurry reactor) equipped with a reflux cooler, gas-inlet valve, and sampling exit. The temperature was kept stable by a silicon oil bath equipped with a thermostat and a magnetic stirrer; the temperature was measured in the oil bath. The stirring speed was 700 rpm in all of the experiments. The catalyst was weighed in the reactor under reflux of inert gas and then the aromatic compound was added according to the proportion desired (6 or 1 wt% of catalyst over the total mass of reactants). Undecane was added as an internal standard to follow the reaction kinetics and to calculate the mass balance. Finally the olefin was added in order to obtain the desired molar ratio of the aromatic compound to the olefin (10 : 1; 5 : 1; 2 : 1; 1 : 1). Samples were taken periodically and analysed by gas chromatography in order to quantify the conversion and yields of the reaction.

The continuous liquid-phase reactor system consisted of a stainless steel tube of 100 mm length and 6 mm width. The catalyst was transferred to the reactor and the endings were closed with a metallic net to prevent the loss of catalyst. A peristaltic pump pushed the solution containing the aromatic compound, the olefin, and the internal standard through the reactor with an adjusted space velocity (WHSV). The reaction temperature was controlled by a thermostatic silicon oil bath. Samples were taken periodically and analysed by GC in order to follow the reaction course.

The continuous gas-phase reactor system consisted of a 1-m-long tube in the form of a coil. The catalyst would stay at the lower part of the tube and the upper coiled part would be used to vaporise the reaction mixture. The reactor was introduced into an electrically heated oven, and the temperature was measured in the middle of the coil. The reaction mixture was also pumped by a peristaltic pump and a flow of dry nitrogen was used to carry the vaporised reaction mixture through the reactor. The products were collected in a cooling trap from which samples were periodically withdrawn to follow the reaction course by GC.

RESULTS AND DISCUSSION

Catalyst Characterisation

The ionic liquid used to test the supports contained a ratio of 1.5 mol of $AlCl_3$ to 1 mol of 1-butyl-3-methyl-imidazolium chloride ([bmim]Cl). This ratio (N) is defined as

$$N = [AlCl_3/(AlCl_3 + [bmim]Cl)]. \qquad [1]$$

According to this expression, the AL-IL used possessed $N = 0.6$.

The amount of aluminum present in the sample was determined by ICP-AES, and from this value the amount of AL-IL remaining on the catalyst was calculated. The results were confirmed by CHN analysis of the samples, using the nitrogen content to calculate the amount of ionic liquid. In the case of alumina carriers, CHN analysis was the only basis for the calculation. Table 1 shows the BET surface area and pore size of the supports used. The pore sizes of the mesoporous materials were derived from gas adsorption isotherms. The amount of AL-IL adsorbed depends mainly on the nature of the carrier. Carriers based on SiO_2 and Al_2O_3 retain higher amounts of AL-IL after the extraction; for different silica carriers, the coverage (mmol/m^2) is almost constant (Fig. 1). The immobilisation of the AL-IL on the surface of the support is believed to be due to covalent bonding between the aluminum atoms and the M–OH groups, where M stands for the metal atom of the support. Such groups are present on the surface of the oxide. The low surface area and lack of these M-OH groups in ZrO_2 and TiO_2 led to a low amount of AL-IL retained on these carriers after the extraction. The main change observed on the support after impregnation with AL-IL was the decrease of the surface area, which can be explained by the obstruction of the pores of the carriers by the AL-IL molecules. This can be well noticed in Table 1 where the values of BET area and pore volume of the supports before and after the impregnation are listed.

During immobilisation the formation of HCl could be observed. Should the mechanism assumed for the immobilisation be correct, this is unavoidable. It has to be assumed that a certain amount of HCl remains on the surface of the catalyst even after extraction and drying under vacuum. So far we have no data allowing a discussion of the influence the HCl might have on the behaviour of the catalyst in alkylation reactions. In view of the fact that protons are generally considered to be necessary for Friedel–Crafts-type reactions, we assume that the effect is beneficial.

FT-IR was done with SiO_2 FK700 self-supported wafers, prepared with weighed amounts of sample. The spectra showed that after supporting the ionic liquid on the silica carrier, the band around 3745 cm^{-1}, assigned to the stretching vibration of the OH bond of terminal Si–OH group,

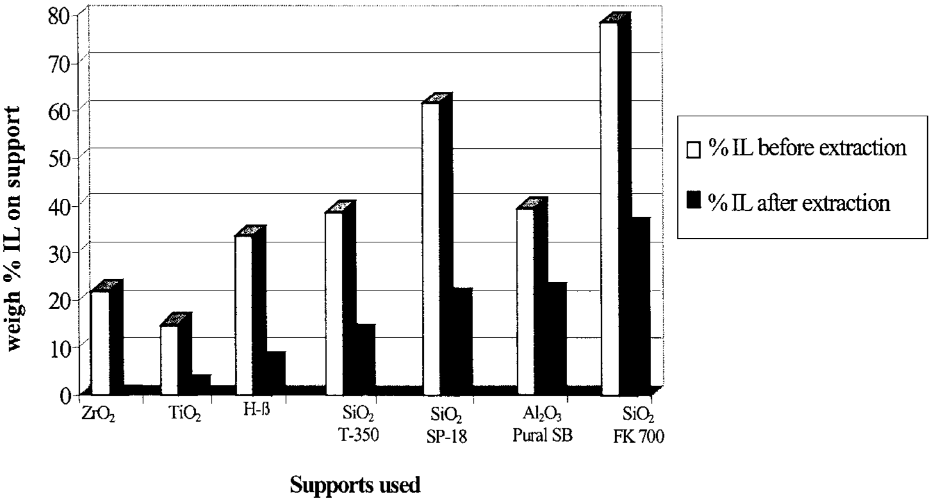

FIG. 1. Immobilisation of AL-IL ($N = 0.60$) on different supports.

disappears. When the catalyst is heated to 450°C in dry air flow, the Al-IL is removed from the surface of the carrier and the band corresponding to the SiOH stretching band reappears. ^{29}Si and ^{27}Al NMR analytical data also confirm the nature of the bonding between ionic liquid and SiOH species (17). In the case of ZrO_2 and TiO_2, a correspondent M–OH band is not observed. That would explain the low amounts of Al-IL kept on the support after the Soxhlet extraction. In the case of Al_2O_3, the band corresponding to the Al–OH is assigned to water molecules adsorbed on the surface.

The X-ray diffraction analyses were especially useful in the case of the crystalline material used, such as beta zeolite. These results led to the conclusion that the crystalline structure of the zeolite is partially destroyed during the impregnation process. The bonding of the Al-IL to the support surface leads to the formation of hydrochloric acid in the interior of the zeolite. Since protons are reported to have superacidic properties in ionic liquids; this explains the damage to the structure.

Batch Reactions

Alkylation of benzene and toluene. The alkylation of benzene with dodecene was used as a test reaction in order to evaluate the catalyst activity. The standard conditions used were 80°C reaction temperature, catalyst amount corresponding to 0.078 wt% of aluminum of the total weight of the reaction mixture (6 wt% of the catalyst T-350/Al-IL ($N = 0.60$)), and the reactants molar ratio 10 : 1. The

TABLE 2

Dodecene Conversion and Selectivity to Products for the Alkylation of Benzene

Catalyst	T (°C)	Benz./$C_{12}^{=}$ ratio	$C_{12}^{=}$ conversion	$C_{12}^{=}$ isomers	Sel. monoalkylated	Sel. heavier prod.
Al-IL, pure	80	10 : 1	4.5	86.7	13.3	0.0
MCM 41, pure	80	10 : 1	0.1	100.0	0.0	0.0
FK700/$AlCl_3$	80	10 : 1	15.7	80.2	19.8	0.0
FK700/AL-IL	80	10 : 1	99.4	0	99.7	0.3
T350/AL-IL	80	10 : 1	99.9	0.1	99.8	0.1
T350/AL-IL	40	10 : 1	81.0	0.0	100.0	0.0
T350/AL-IL	80	5 : 1	62.4	13.1	86.0	1.0
T350/AL-IL	80	1 : 1	82.7	16.1	82.5	1.4
FK700/AL-IL, filtered, 2nd run	80	10 : 1	2.2	100.0	0.0	0.0
FK700/AL-IL, washed, 2nd run	80	10 : 1	79.9	0	99.5	0.5
T350/AL-IL, washed, 2nd run	80	10 : 1	47.2	6.9	92.7	0.4
H-BETA, pure	80	10 : 1	56.8	58.9	39.0	2.1

Conditions: batch reactor, reaction time 30 min, 6 wt% catalyst.

TABLE 3

Product Distribution Dependency on the Catalyst Used

Catalyst	2-Phen. dodecane	3-Phen. dodecane	4-Phen. dodecane	5-Phen. dodecane	6-Phen. dodecane
$AlCl_3$	46.4	19.4	12.7	12.1	9.5
Al-IL ($N = 0.6$)	36.7	19.0	15.0	15.5	13.8
T350/Al-IL	42.9	22.8	13.0	11.8	9.4
H-beta	75.7	19.0	3.8	1.1	0.4
H-beta/Al-IL	43.9	21.2	12.4	12.0	10.5

Conditions: batch reactor, $T = 80°C$, reaction time 30 min, 6 wt% catalyst, molar ratio benzene/dodecene = 10 : 1.

catalysts prepared with different supports were tested using these conditions.

The selectivity towards the products of the double bond migration ($C_{12}^{=}$ isomers) is displayed because the isomerisation is a parallel reaction to the alkylation, and can be catalysed by weak acidic sites as well. As shown in Table 2, the weak Brønsted acidity of an all-silica MCM 41 catalyses the isomerisation, but not the alkylation reaction.

A comparison of different supports showed that only the silica-based supports were active in the alkylation reaction of benzene with dodecene.

Although zeolites are also silica-based compounds, they were not chosen as supports for the experiments because, as shown in the characterisation part, the crystalline structure is significantly damaged by the adsorption of the AL-IL. Experiments showed that while pure beta zeolite displayed shape-selective effects towards the 2-phenyl-dodecane, this effect is lost after immobilisation of an ionic liquid on the zeolite (see Table 3). This can easily be explained by the destruction of the crystalline structure and a filling of the remaining micropores with ionic liquid, allowing only surface reactions. Furthermore, the H-beta tested displayed poorer conversion and selectivity to the monoalkylated product. Since they gave essentially the same product distribution, the cheaper silica-based supports FK700 and T-350 were chosen to be studied in more detail. Generally, the distribution of the monoalkylated products is close to that of reactions catalysed with pure $AlCl_3$ or pure chloroaluminate ionic liquids (see Table 3).

The supported catalyst shows improved activity and selectivity compared to the free ionic liquid (see Table 2). This is probably due to the better dispersion of the solid catalyst in the reaction media. The ionic liquid used in this experiment is essentially not soluble in benzene. Better results can be achieved by using optimised reaction conditions, most importantly a higher stirring speed and improved stirrer design. Nevertheless, we chose to compare the conversions at fixed conditions to display the advantages heterogeneous catalysts have in this reaction.

Further experiments were carried out with these catalysts in order to study the influence of different parameters on the reaction system. Temperature, acid strength, and solvents have been varied and different aromatic compounds have also been used in order to test and compare the catalytic activity of the immobilised AL-IL in different systems.

Benzene was alkylated with dodecene at 80°C using 6 wt% of the T-350/AL-IL ($N = 0.60$) catalyst over the total amount of reactants. Dodecene conversion reached close to 100 mol% with a selectivity of over 99% towards monoalkylated products in the first 30 min of the reaction. In this case, benzene was used as solvent (molar ratio of benzene to dodecene = 10 : 1). The influence of temperature was studied and the results can be seen in Table 2. As expected the dodecene conversion increases with temperature. The selectivity was not influenced. The catalyst already presented good results under the conditions first tested; a decrease of temperature could only lead to lower conversion values. Experiments using FK700/AL-IL ($N = 0.60$) as catalyst showed similar results. The amount of catalyst used for FK700/AL-IL ($N = 0.60$) was proportional to the aluminum content of T-350/AL-IL ($N = 0.60$) in order to make a valid comparison between the two catalysts.

Experiments with different ratios of the aromatic substrate to the alkylating agent were carried out in order to study the effect of the reactant concentration on the selectivity. The results of the alkylation of benzene with different reactants ratios (Table 2) shows that an increase of dodecene led to a decrease in its conversion as well as in the selectivity towards monoalkylated products, favouring the formation of isomers, di- and trialkylated products (heavy products).

The reaction has also been carried out in different solvents in order to study their influence on the reaction. The use of solvents showed no beneficial effects to conversion or selectivity of the reaction.

Leaching of the AL-IL from the surface of the support was studied by ICP-AES and found to be negligible (see Table 4). A filtration study of the catalyst showed no further reaction after filtration but since experiments regarding the recyclability of the catalysts showed a strong deactivation due to residual moisture in the filters, this result was not considered to be of value.

TABLE 4

ICP Analysis of Catalysts before and after Reactions (Leaching Test)

Catalyst	Al (mg/g)	Si (mg/g)	Al/Si	Procedure
T-350/AL-IL ($N = 0.60$)	12.9	378	0.034	Before reaction
T-350/AL-IL ($N = 0.60$)	13.0	380	0.034	After 2nd run[a]
T-350/AL-IL ($N = 0.60$)	13.9	394	0.035	Before reaction
T-350/AL-IL ($N = 0.60$)	11.3	314	0.036	After 2nd run[b]

[a] Batch reaction toluene/$C_{12}^{=}$.

[b] Continuous liquid-phase benzene/$C_{12}^{=}$(TOS > 10 h).

Catalyst recycling is an important subject, especially when dealing with supported catalyst. Heterogeneous catalysts tend to lose activity when used in consecutive reactions. The reason can be either leaching of the active phase, deposits on the surface (adsorption on the acid sites), or deterioration of the catalyst due to water adsorption.

Because the catalysts were not very active in a second run when filtered from the product solution, it was thought that the method for recovering the catalyst could be influencing the results. The main reason for the deactivation was thought to be residues of moisture in the filter. Therefore, a different method was tested in order to recover the catalyst. It consists of washing the catalyst with dichloromethane in the same flask in which the first reaction was carried out in order to avoid exposure of the catalyst to moisture. The catalyst was then dried under vacuum and used in a second reaction run. The results (Table 2) show that the catalysts are active in a second run, but extreme care must be taken to ensure completely dry conditions.

Apart from deactivation of the catalyst by water, the adsorption of reactants on the catalyst surface has also been found to be a factor of deactivation. In order to assess the influence of the different reactants, two experiments were conducted. In two different flasks the catalyst was weighed and the reactants were added one at a time keeping the same standard conditions (6 wt% catalyst, 10 : 1 molar reactants ratio). In one experiment, dodecene was first added to the catalyst and stirred for 30 min before addition of the toluene. In a second experiment, the order of addition was reversed, with toluene being added first, followed by dodecene. Both reactors were stirred at room temperature for 1 h. The first experiment showed no conversion while the second experiment featured 30% of dodecene conversion with 100% selectivity towards monoalkylated products. The experiments prove the strong adsorption of dodecene on the surface of the catalyst, possibly followed by its oligomerisation. This causes blocking of the active sites of the catalyst, preventing the alkylation reaction.

The alkylation of toluene with immobilised AL-IL ($N =$ 0.60) also featured high selectivity at high conversions. After 1 h of reaction more than 80% of the dodecene had been consumed and the selectivity towards monoalkylated products was 96% (*para* plus *ortho* products). It is interesting to notice that the initial rate of the alkylation of toluene is lower than that for the alkylation of benzene (see Fig. 2). This is explained by the fact that benzene possesses six equivalent positions for the electrophilic attack and toluene only five, where two of them are hindered (*ortho* positions) and two are electronically deactivated towards electrophilic substitutions (*meta* positions). Alkylation with pure Al-ILs, on the other hand, proceeds faster for toluene than for benzene. This can be explained by the better solubility of toluene in the ionic liquid.

By increasing the temperature and changing the molar ratio of the reactants, the reaction showed an increase in the conversion of dodecene with temperature and a decrease in selectivity towards monoalkylated compounds. Polyalkylated compounds were formed when the molar ratio of the reactants was increased.

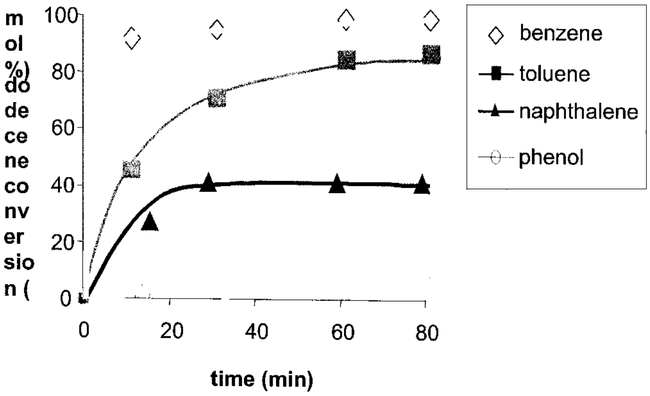

FIG. 2. Dodecene conversion in the alkylation of different aromatic compounds.

When the alkylation of toluene was carried out in the presence of solvents, the conversion dropped due to the dilution effect of the reactants. When tetrahydrofuran (THF) was used, the selectivity towards monoalkylated products also decreased. Instead, products from the ring opening and alkylation of THF were found. THF is an oxygenated polar compound; its affinity for the catalyst is higher than that of dodecene, resulting in low conversion, low selectivity, and formation of undesirable products.

Alkylation of naphthalene. The aromatic system in naphthalene is different from the ones studied so far in this work. The condensed aromatic nucleus decreases the reactivity of the ring from the electronic as well as from the sterical point of view (18). Thus, it is not surprising that the results for the alkylation of naphthalene with dodecene show poorer conversion compared to those of benzene and toluene. The alkylation of naphthalene featured after 1 h reaction time a dodecene conversion of 67% and the selectivity to monoalkylated products was of 71% (see Table 5). In addition to the higher stability of the condensed aromatic

TABLE 5

Dodecene Conversion and Selectivity to Products for the Alkylation of Naphthalene

Ratio naphth./$C_{12}^{=}$	$C_{12}^{=}$ conversion	Isomers	Monoalkylated	Heavy products
1 : 1	30.9	16.6	49.6	33.8
2 : 1	31.2	21.6	72.6	5.8
5 : 1	43.6	27.9	70.2	1.8
10 : 1	66.9	27.0	71.7	1.3

Conditions: catalyst T350/Al-IL ($N = 0.6$), 6 wt% catalyst, batch reactor, reaction time 60 min, $T = 80°C$.

TABLE 6

Dodecene Conversion and Selectivity to Products for the Alkylation of Phenol

Catalyst	Time (min)	Temperature (°C)	Ratio phenol/$C_{12}^{=}$	$C_{12}^{=}$ conversion	$C_{12}^{=}$ isomers	O-alkylated	C-alkylated	Heavy products
T350/AL-IL ($N = 0.6$)	120	80	10 : 1	7.2	41.0	35.0	24.0	0.0
T350/AL-IL ($N = 0.6$)	120	150	10 : 1	42.7	33.5	32.5	33.9	0.0
T350/AL-IL ($N = 0.6$)	60	180	10 : 1	54.8	32.3	29.2	38.3	0.2
T350/AL-IL ($N = 0.6$)	150	180	10 : 1	54.8	32.3	29.2	38.3	0.2
T350/AL-IL ($N = 0.6$)	150	180	5 : 1	52.4	33.7	24.4	41.9	0.0
T350/AL-IL ($N = 0.6$)	150	180	1 : 1	21.8	61.7	16.9	21.1	0.2
T350/AL-IL ($N = 0.67$)	90	180	10 : 1	56.6	25.8	26.1	46.2	1.9
AL-IL ($N = 0.6$)	60	180	10 : 1	57.8	19.0	29.0	52.0	0.0
AL-IL ($N = 0.67$)	60	180	10 : 1	77.5	15.6	17.1	66.8	0.6

Conditions: batch reactor, 6 wt% of catalyst.

ring, the adsorption of the bulky naphthalene molecules might be a reason for the lower conversion.

In the case of naphthalene, the use of a solvent did not influence the conversion or the selectivity of the reaction. Nevertheless, the use of solvents facilitates the handling of the reactants since naphthalene is a solid at lower temperatures and it also sublimes very easily. Table 5 depicts the reaction of naphthalene with dodecene at naphthalene : dodecene molar ratios of 10 : 1 and 5 : 1. When the molar reactants concentration (R) was varied, it was found that at higher concentrations of dodecene the conversion increased, but leading to the increase of polyalkylated products (Table 5). The best ratio observed was 10 : 1, just as for the other aromatic compounds. At a 30% conversion of dodecene, it can be observed that a ratio of 5 : 1 naphthalene : dodecene gives better selectivity to monoalkylated products. However, as the reaction continues, the experiment with reactants at a 10 : 1 molar ratio features the best selectivity towards monoalkylated products, showing that the dodecene polymerisation reaction competes with the alkylation at higher dodecene concentrations.

Alkylation of phenol. As shown in Fig. 2, the rate of the alkylation of phenol is very low under the same conditions as those used for the alkylation of benzene (80°C, 6 wt% catalyst, $N = 0.6$, reactants ratio = 10 : 1). One of the reasons for this effect is that the hydroxyl group of phenol readily reacts with $AlCl_3$ to form a highly stable complex. This complex diminishes the availability of acid centres on the catalyst as well as increasing the electron-withdrawing effect of the hydroxyl group in the ring. Both factors have a negative influence on the reactivity of phenol towards electrophilic substitution on the aromatic ring. In order to overcome these problems, new experiments at higher temperatures and with catalysts possessing a higher N ($AlCl_3$/bmim) have been carried out.

When the alkylation of phenol with dodecene was carried out at different temperatures, the results were as expected. The conversion increases with the increase of temperature (Table 6). It is also interesting to notice that the selectivity towards C-alkylated products increases with the temperature, which is in accordance with results reported by other authors (19).

The influence of the molar ratio of the reactants has also been tested for the reaction of phenol and dodecene. The results are depicted in Table 6. The tendencies observed for the other aromatic compounds are observed in the case of phenol as well. The increase of the dodecene concentration leads to a decrease in selectivity to the monoalkylated compounds.

As was said in the beginning of this work, the acid strength of an ionic liquid can be controlled by changing the ratio $AlCl_3/[AlCl_3 + [bmim]Cl]$ (N). It is also known that higher acid strength (higher N) should lead to an increase of selectivity towards the C-alkylated product. Table 6 shows the results obtained for the alkylation of phenol with dodecene using the pure and supported AL-IL with different N values. The results show that indeed the increase of $AlCl_3$ content in the AL-IL led to an increase of the dodecene conversion and the selectivity towards the C-alkylated product.

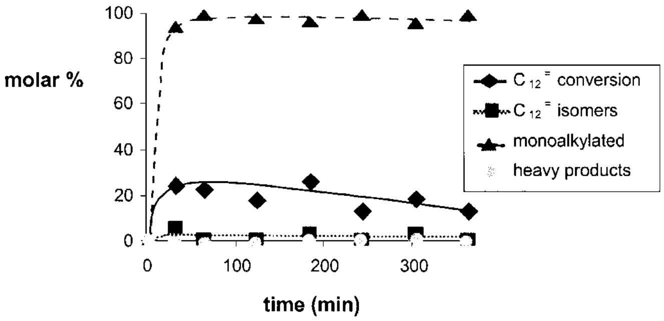

FIG. 3. Dodecene conversion and selectivity towards alkylation products obtained in the continuous liquid-phase reaction of benzene and dodecene.

TABLE 7

Elemental Analyses of Catalysts before and after Alkylation Reaction—Adsorption of Organic Compounds

Sample	C (%)	H (%)	N (%)
FK700/AL-IL ($N = 0.60$)	2.3	2.3	0.4
FK700/AL-IL ($N = 0.60$) after batch reaction (1 h, 80°C)	6.5	2.4	0.4
FK700/AL-IL ($N = 0.60$) after continuous phase reaction (6 h, 40°C)	9.4	3.0	0.4

This difference is not as distinctive for the supported catalysts, but it can still be seen that the conversion and the selectivity towards C-alkylated products increase with N. The most probable explanation for the lower selectivity towards the C-alkylated product is that impregnation of the AL-IL on the surface decreases the total acidity of the ionic liquid.

Continuous Reactions

Liquid phase. The aim of this process is clear: to allow a continuous production of LAB. Figure 3 shows the results for a reaction carried out at 20°C using a molar ratio of benzene : dodecene of 10 : 1 and a WHSV of 7 h^{-1}. A slow deactivation of the catalyst with time on stream (TOS) can be observed. This deactivation is mainly due to the adsorption of dodecene and heavy products on the catalyst which block its active sites from further reaction. Elementary analyses of the catalyst after the reaction have been carried out and a significant increase of the carbon content was found (Table 7), confirming that the deactivation of the catalyst is due to strong adsorption of organic materials on the surface of the catalyst.

Gas phase. The alkylations of benzene and toluene with dodecene have been performed over the catalysts T-350/AL-IL ($N = 0.60$) and FK700/AL-IL ($N = 0.60$) in the continuous gas phase. Temperatures varying from 200°C to 300°C were used, and in the best case, only 3% of dodecene conversion was observed. A strong adsorption of dodecene on the surface of the catalyst might be the responsible for the lack of activity of the catalyst in these conditions. Due to these preliminary results, further experiments with this reaction system have not been carried out.

Batch alkylation reactions of benzene with dodecene using the catalyst after gas-phase and liquid-phase continuous reaction were carried out. The conversions in these cases were smaller than 1 mol% of dodecene converted, showing that the acid sites of the catalysts suffer deactivation during the continuous-phase reaction.

CONCLUSION

Supported ionic liquids proved to be active as catalysts for the alkylation of aromatic compounds with dodecene. Results feature good conversion and high selectivity to alkylated compounds.

Increase of temperature and concentration of dodecene have the expected effect on the reaction results, i.e., the increase of total conversion and decrease of selectivity towards monoalkylated compounds.

Although liquid continuous-phase reactions show good selectivity after a long time on stream, the reaction conditions for this system still have to be optimised. Deactivation of the catalyst can be attributed to two different causes. The first cause, the deactivation by water, can be avoided by careful drying of the starting materials. As a second cause of deactivation, the oligomerisation of dodecene was found. Because of this, the order of addition of the reactants is very important since dodecene should not be adsorbed by the catalyst before the aromatic compound. Experiments showed the possibility of washing the catalyst and removing at least a part of the oligomers, allowing for a longer lifetime of the catalyst.

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