Journal of Catalysis 261 (2009) 177–187

Contents lists available at ScienceDirect

Journal of Catalysis

www.elsevier.com/locate/jcat

Phenol alkylation with isobutene — influence of heterogeneous Lewis and/or Brønsted acid sites

Elena Modrogan, Michael H. Valkenberg, Wolfgang F. Hoelderich*

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

ARTICLE INFO

Article history:
Received 6 October 2008
Revised 14 November 2008
Accepted 15 November 2008
Available online 19 December 2008

Keywords:
Solid acid catalysts
Immobilized phosphonium ionic liquids
Lewis and Brønsted acidity
Phenol alkylation
Liquid-phase reaction

ABSTRACT

Acidic solid catalysts with different types of acidity were used to study the liquid-phase alkylation of phenol with isobutene. A phosphonium ionic liquid immobilized on silica type carrier exhibiting pure Lewis acidity, Amberlyst 15 with pure Brønsted acidity as well as WO_3/ZrO_2 with both types of acid sites were used for this study. The active sites are postulated based on pyridine-FT-IR and NH_3-TPD studies, BET analyses, MAS NMR and XRD measurements. The different properties of the chosen catalysts are mirrored in the product distribution of the reaction mixture. It was found that WO_3/ZrO_2 is a very active and selective catalyst for the production of 2,4-di-*tert*-butylphenol under mild reaction conditions.

1. Introduction

The alkylation reaction of phenol [1] is of great industrial importance since the alkylated products cresols, xylenols and tertiary butylphenols (450000 tonnes/year) are used in the manufacture of antioxidants, UV absorbers and for the production of phenolic resins. Among the *tert*-butylphenols, the mono-alkylphenols [2,3] and di-alkylphenols are commercially important. The dialkylphenol 2,6-di-*tert*-butylphenol (2,6-DTBP) is used as an antioxidant intermediate and in pharmaceuticals industry, while triphosphate and benzotriazole derivatives of 2,4-di-*tert*-butylphenol (2,4-DTBP) are employed for the production of stabilizers for PVC or UV absorbers in polyolefins. Traditionally, Brønsted and Lewis acids such as H_2SO_4, $AlCl_3$, BF_3 or HF are employed as catalysts for such reactions. But the current trend is to replace them by solid acid catalysts, which have the advantage of recycling and reuse [4,5]. The alkylation reaction of phenol over heterogeneous catalysts has been especially studied in the presence of *tert*-butanol and liquid olefins, respectively, as alkylating agents. Three different reaction systems are generally proposed in literature: liquid-, vapor- and mixed-phase reactions [6].

From an industrial point of view, successful use of heterogeneous acid catalysts is based on the understanding of the influence of Lewis and/or Brønsted acid sites on the reaction path. Generally, the type and strength of acidic sites of solid acid catalysts is proved with the help of FT-IR analyses using pyridine as probe molecule and by NH_3-TPD measurements. Heterogeneous acid catalysts such as microporous and mesoporous materials [7,8], amorphous mixed oxides comprising also sulfated zirconia and titania [9], modified clays [10] and immobilized Al-based ionic liquids [11] have been shown to convert phenol to the corresponding alkylated compounds. For example, the use of molecular sieves MCM-41 and MCM-48 containing extra-framework aluminum or iron demonstrated high para-selectivity [12]. Over H-AlMCM-41, 36% of phenol was converted with a selectivity for para-*tert*-butylphenol of about 84%. As proved by NH_3-TPD profiles, both Brønsted and Lewis acid sites are present in such a catalyst and the high para-selectivity was related to moderate up to strong Brønsted acid sites. The more bulky, thermodynamically favored, di-alkylated phenol compound 2,4-di-*tert*-butylphenol was produced with a selectivity of about 4% at a molar ratio phenol/*tert*-butanol of 1:2.

Over sulfated zirconia with surface area of about 125 $m^2\,g^{-1}$ and weaker strength of Brønsted acid sites than in H-ZSM-5, Selvam and co-workers [13] could find that para-product is formed with a selectivity of about 87% at phenol conversion of 58%. Despite the fact that the used molar ratio phenol/*tert*-butanol was 1:2, the selectivity of 2,4-DTBP was found lower than 10% most probably due to the weak Brønsted acid sites.

In our research group, pure and immobilized imidazolium ionic liquids with $AlCl_3$ as precursor for the anion have been tested as catalysts for phenol alkylation with dodecene at temperatures between 80 and 180 °C [11]. Al-based ionic liquid immobilized by wet impregnation method on SiO_2 T350 type carrier (Degussa AG) was found to convert about 55% dodecene when a molar ratio phenol/dodecene of 10:1 was applied. The amount of C-alkylated products was observed to be about 40%.

---

* Corresponding author. Fax: +49 241 8022291.
E-mail address: hoelderich@rwth-aachen.de (W.F. Hoelderich).

0021-9517/$ – see front matter © 2008 Elsevier Inc. All rights reserved.
doi:10.1016/j.jcat.2008.11.019

In the context of new designed materials, a particularly interesting challenge is represented by the synthesis of purely Lewis and purely Brønsted solid acids. Several methods have been proposed for the immobilization of imidazolium based ionic liquids with $AlCl_3$ as precursor for the anion [14]. The grafting method has been proved to create active and stable catalysts aromatics alkylation with dodecene. However, phosphonium based ionic liquids are more attractive since they posses higher thermal and chemical stability and they are usually much cheaper than imidazolium based ionic liquids. A particular disadvantage of Al-based ionic liquids is that they are air- and moisture-sensitive while In-based ionic liquids have been described as water-tolerant and recyclable catalysts for Friedel–Crafts acylation reactions [15]. In this work, we report the immobilization using a grafting method of a phosphonium ionic liquid with $InCl_3$ as precursor for the anion on silica support. With the help of FT-IR analyses using pyridine as probe molecule we found that the material behaves like pure Lewis solid acids. Its catalytic performance has been studied for liquid-phase *tert*-butylation of phenol with isobutene. For comparison, Amberlyst 15, with pure Brønsted acidity, and WO_3–ZrO_2, with both types of acid sites, were also considered as potential catalysts. More specifically, the aim was to check if such solid catalysts influence the product distribution of the reaction mixture in a different manner, and which considerations are to be taken into account for the design of a very active and selective heterogeneous catalysts in the investigated reaction.

2. Experimental

2.1. Preparation of materials

For this research, most of the chemicals were purchased from Sigma-Aldrich, Fluka and Merck and used without further purification. Samples of WO_3/ZrO_2 sulfated zirconia, Amberlyst 15, Al_2O_3/SiO_2 and Al_2O_3 Puralox were provided by MEL Chemicals, Rohm & Haas, Mitsubishi Chemical Corporation and SI Group-Switzerland GmbH, respectively. The solvents were dried by usual methods and when necessary they have been distilled and kept under argon. Isobutene was supplied by Westfalen Gas.

Immobilized phosphonium ionic liquids by grafting method were obtained in a three-step reaction (see Fig. 1). First step consists of a nucleophilic displacement of 3-chloropropyltriethoxysilane with trioctylphosphine. Toluene (20 mL) was added to a round bottom Schlenk flask flushed with argon. 3-Chloropropyltriethoxysilane (3 g) was then added to the toluene via syringe under argon. Trioctylphosphine (6 g; stoichiometric excess) was added in the same way as 3-chloropropyltriethoxysilane. The reaction mixture was stirred at reflux under argon for 24 h. The immobilization of phosphonium ionic liquid (chloride form) was achieved on commercial silica type support (Davicat 10017 kindly provided by Grace Silica). 3 g of silica support prior calcined for 6 h at 550 °C was added to 150 cm^3 of toluene solution containing 4.5 mmol of prepared grafting agent under a dry argon atmosphere. The reaction mixture was kept at 90 °C for 3 h under stirring. Then, the solid was collected by centrifugation and dried at 110 °C for 2 h under vacuum. The In-based phosphonium ionic liquid was formed by the reaction of grafted silica with $InCl_3$. For this step, 1 g of grafted silica was dispersed in toluene at 80 °C for 2 h. Then, an amount in excess (2.5 fold) of metal salt was added to the reaction mixture under stirring. Soxhlet extraction using boiling CH_2Cl_2 as solvent was performed to remove the excess of metal salt. The final material has been dried at 100 °C for 3 h under vacuum conditions (10^{-2} Torr) and kept under argon.

All the other catalysts applied in this work were used after a special thermal treatment. Prior to the reaction, each catalyst was dried for 2 h at 150 °C and then calcined under air for 8 h at 550 °C (1 °C min^{-1}). No further treatments have been performed. The modification of WO_3/ZrO_2 with silica has been achieved in two steps. First step was consistent with the treatment of WO_3/ZrO_2 with H_2O_2 in toluene at 40 °C. The second step was the addition of silica source (TEOS). The reaction mixture was kept at 90 °C for 12 h. After filtration and drying, the material was calcined following the same procedure as for WO_3/ZrO_2.

2.2. Characterization

The liquid NMR measurements for synthesized grafting agent triethoxysilane-propyltrioctylphosphonium chloride were analyzed on a Mercury-300BB instrument with a pulse of 45 degrees and a relaxation delay of 0.1 s. MAS-NMR spectra of immobilized ionic liquids were recorded on a Brucker DSX 500 spectrometer equipped with a wide-bore superconducting magnet operating in a field-strength of 11.744 T.

Nitrogen adsorption was carried out at 77 K on an ASAP 2010 sorption system (Micromeritics). The samples were degassed at 120 °C (heating rate 5 °C min^{-1}). The pore diameter and specific pore volume were calculated according to the Barrett–Joyner–Halenda (BJH) theory. The specific surface area was obtained with the Brunauer–Emmett–Teller (BET) equation.

TG/DTA/DSC analyses were acquired using a Netzsch 209/2/E instrument equipped with a STA 409 thermal analysis data processing system. The measurements were run under air with a temperature ramp of 2 °C min^{-1} between 50 and 1000 °C and α-Al_2O_3 was used as a reference material.

FT-IR spectra were recorded on a Nicolet 510P spectrometer equipped with an MCT detector. For FT-IR analyses using pyridine as probe molecule, the in-situ cell was equipped with KBr windows and a thermocouple. Prior to analysis, all samples of solid catalysts were degassed at 150 °C for 20 h, under high vacuum conditions (10^{-4} Torr). The background spectra were collected at 50, 100 and 150 °C. Pyridine was adsorbed in successive doses at 50 °C onto thin plates in a thickness of 10 mg cm^{-2}. Simultaneous heating of the apparatus prevented adsorption of pyridine on the apparatus walls. The FT-IR spectra of our samples using pyridine as probe molecule were measured at 50, 100 and 150 °C and difference spectra were obtained by subtracting the original spectrum of the solid from the spectrum of the solid with pyridine entities.

Temperature programmed desorption of ammonia was measured on a TPDRO 1100 apparatus from CE Instruments. First, the materials were calcined for 2 h at 500 °C under argon, followed by ammonia loading at 100 °C (3% NH_3 in argon, 2 h). Subsequently, the system was purged with argon for 2 h, then NH_3 was desorbed by heating the sample with 25 °C min^{-1} to 900 °C under flowing argon.

XRD powder diffraction patterns were collected on a Siemens Diffractometer D5000 equipped with a secondary monochromator, a variable diaphragm V 20 and a nickel filter using Cu Kα radiation (wavelength 1.5406 Å), the angle speed was 0.02° min^{-1}. Bulk elemental chemical analyses were done with inductive couple plasma atomic emission spectroscopy (ICP-AES) on a Spectroflame D (Spectro Analytic Instrument).

2.3. Catalytic tests

Alkylation reactions of phenol with isobutene have been carried out in batch reactors: normal glass vessel and stainless steel autoclave (75 mL). When working at atmospheric pressure, the three-neck flask was equipped with a condenser, a magnetic bar, a temperature controller and a frit for dosing isobutene in the liquid phenol.

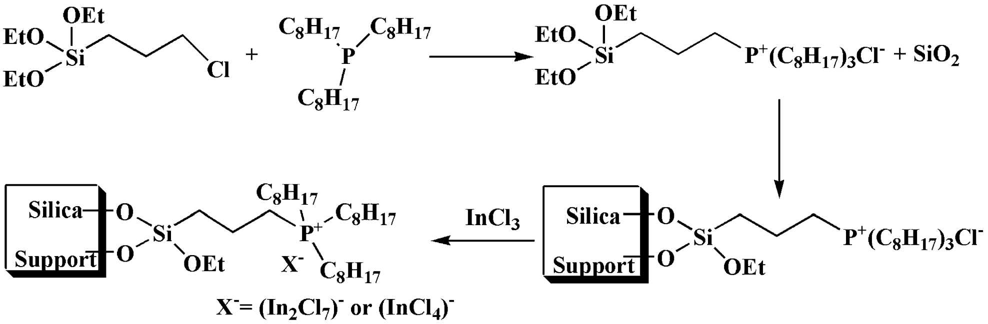


Fig. 1. Scheme for the synthesis procedure of In-based phosphonium ionic liquid (In-IL(Phos)/SiO_2) immobilized by grafting method on silica carrier.

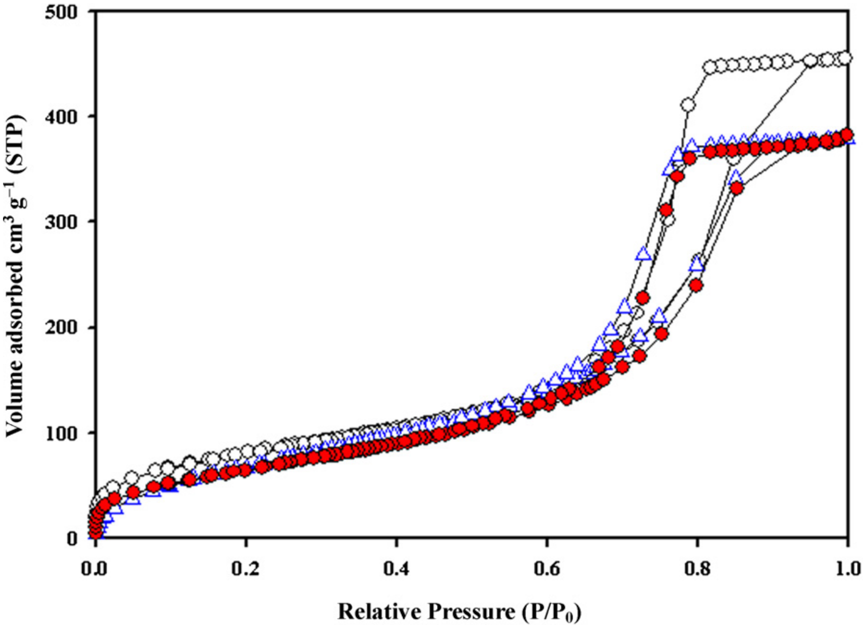


Fig. 2. Nitrogen adsorption–desorption isotherms of (a) In-IL(Phos)/SiO_2, (b) Cl-IL(Phos)/SiO_2 and (c) SiO_2 type support.

Additionally, for a precise control of isobutene flow, a Brooks flow meter was used. The catalyst (1 g) was placed together with the substrate (1 mol) and the mixture was allowed to reach the reaction temperature (90 °C) under stirring. No solvent was used for these experiments. Aliquots were taken from reaction mixture at regularly intervals. When working under pressure, the stainless steel autoclave was equipped with a temperature controller and a magnetic stirring bar. Usually, phenol and the catalyst were placed in a glass reactor, which was well fitting to the internal part of the autoclave. The isobutene pressure was kept constant at 3 bar during the reaction. The reaction temperature was 90 °C. The substrate (20 mmol) was used together with 1% by weight catalyst. The reacted isobutene has been calculated by measuring the mass of autoclave without pressure prior and after the reaction. To avoid possible errors of weighing, the measurements were done by rapid cooling of the autoclave to room temperature. The evolution of the reaction mixture was analyzed on a HP 6890 gas chromatograph with temperature programming equipped with a 54 m FS-SE-54 column, a FID detector and N_2 as gas carrier. For precision, the aliquots were analyzed also on a Siemens RGC gas chromatograph with temperature programming equipped with a 50 m column Cyclodex β, a FID detector and N_2 as gas carrier. Both temperature programs were established in collaboration with SI Group-Switzerland GmbH.

3. Results and discussion

3.1. *Effect of Lewis acidity*

Ionic liquids are a particular attractive class of materials due to their special properties [16]. Lewis acidic ionic liquids with anions based on $AlCl_3$ or $FeCl_3$ have been shown to be active catalysts for alkylation reactions in both homogeneous [17] and heterogeneous forms [18]. Although the immobilization on solid supports of imidazolium based ionic liquids with $AlCl_3$ as precursor for the anion was successfully achieved, there is no published evidence for the immobilization of phosphonium ionic liquids despite their higher chemical and thermal stability. Al-based ionic liquids are very sensitive to moisture. Therefore, we oriented our studies on the use of $InCl_3$ as precursor for the anion.

As method for immobilization, it is known that at least three possibilities were proposed in literature. The most appropriate for catalytic purposes is the so-called *grafting method*. We obtained immobilized phosphonium ionic liquid in the chloride form by grafting of synthesized chloropropyltrioctylphosphonium tetraethoxysilane onto silica as shown in Fig. 1.

To prove the successful grafting, nitrogen adsorption–desorption isotherms were measured after each step of the synthesis procedure. Fig. 2 shows the results obtained for chloride and metal chloride form of grafted phosphonium ionic liquid. The fact that

Table 1
Textural characteristics of In-IL(Phos)/SiO_2 and Cl-IL(Phos)/SiO_2.

Sample	S_{BET} ($m^2\,g^{-1}$)	S_{BJH} ($m^2\,g^{-1}$)	V_{macro} ($cm^3\,g^{-1}$)	Pore diam. (Å)
SiO_2	377	454	1.03	90.9
Cl-IL(Phos)/SiO_2	232	315	0.58	65.8
In-IL(Phos)/SiO_2	228	306	0.57	65.5

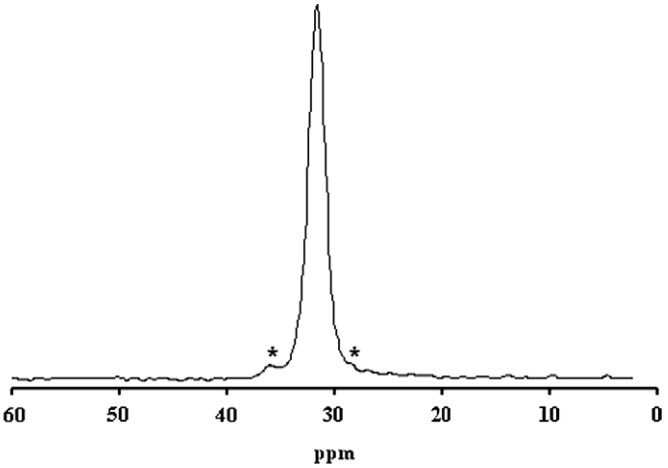


Fig. 3. ^{31}P MAS NMR spectrum of In-IL(Phos)/SiO_2 (side bands are marked with asterisk).

the isotherms of the studied samples are similar to that of non-modified silica is an evidence for the preservation of structure after each step of grafting procedure. The retained meso–macro structure of support (with pore diameter of $\geqslant$65 Å as revealed by N_2 adsorption–desorption measurements after immobilization procedure) suggests that the grafting agent is located mostly on the external –OH groups situated on the surface and macro-cavities of SiO_2 type carrier. This assumption is in good agreement with the FT-IR analysis (not shown) of silica support which revealed only one peak at 3745 cm^{-1} corresponding to external silanol groups as reported by Laforge et al. [19].

Table 1 shows the textural characteristics corresponding to each immobilization step. By grafting the bulky phosphonium containing units, a change of the textural properties as compared to pure silica support was observed, while the addition of metal salt to form the final catalyst was proved to give only a slight modification of textural parameters. The immobilization of phosphonium groups was found to decrease the specific surface of carrier from 377 $m^2\,g^{-1}$ to 232 $m^2\,g^{-1}$. The same tendency was observed in the case of pore diameter (from 90 to 65 Å) and volume of mesopores (from 1.032 to 0.58 $m^3\,g^{-1}$).

^{31}P MAS NMR spectrum of the as-synthesized sample of In-IL(Phos)/SiO_2 has revealed basically one phosphorous environment with a band at 31.6 ppm (Fig. 3). The two slightly visible side bands that appear in the spectrum might be due to the presence of some impurities.

The cross-polarized ^{29}Si MAS NMR spectrum of prepared catalyst is shown in Fig. 4. The major peak at −111 ppm has been proved to be due to $Si(OSi)_4$ (Q^4) atoms. By comparison with the ^{29}Si MAS NMR spectrum of silica support, the peak at −102 ppm corresponding to vicinal silanols is greatly reduced after immobilization. The fact that successful grafting of triethoxysilanepropyltrioctylphosphonium chloride was achieved is proved by the peak at −52.2 ppm corresponding to T^2 $[-CH_2-Si(OR)(OSi\equiv)_2]$ atoms. Based on observations of Yamamoto and Tatsumi [20], smaller in intensity bands observed at −60.1 and −49.6 ppm are attributed to T^3 $[-CH_2-Si(OSi\equiv)_3]$ and T^1 $[-CH_2-Si(OR)_2(OSi\equiv)]$ atoms, respectively.

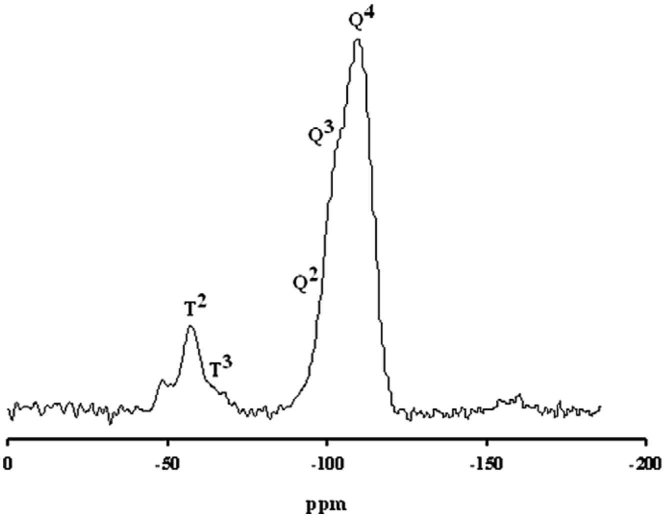


Fig. 4. ^{29}Si CP MAS NMR spectrum of In-IL(Phos)/SiO_2.

The results are sustained by thermogravimetric (not shown) and ICP-AES analyses. Mainly two decomposition steps take place on In-IL(Phos)/SiO_2. The first exothermic peak was observed at 215 °C while the second step of decomposition was accompanied by a much broader exothermic peak with the maximum at 319 °C. Choi et al. [21] have assigned the peak occurring between 227 and 500 °C to the decomposition of alkylsilyl groups. Taking into account these findings, it can be considered that the main part of the mass loss is due to decomposition of organic groups from the grafting agent. For nonporous silica, Corma and Garcia [22] reporting on earlier work of Sunseri et al. [23] have assigned the peaks which occur at high temperatures (up to 900 °C) to the condensation of neighboring silanol groups to form a silanoxy bridge (Si–O–Si). In our case, no evidence for the existence of free silanol groups after the immobilization was found. If the influence of physisorbed solvent molecules is neglected (very small mass loss) it can be concluded that the catalyst In-IL(Phos)/SiO_2 is stable up to 160–180 °C. The total mass loss was about 45% corresponding to about 0.55 mmol of grafting agent per g catalyst. The observation is consistent with the ICP-AES analyses, which have proved a molar ratio P/In of 1:1.8 suggesting the formation of polymetallic species with increased Lewis acidity. However, this ratio is showing that the formation of monometallic species corresponding to a neutral ionic liquid with ratio of P/In of 1:1 is possible, too. Such species have been shown by Corma and Garcia [24] to exhibit latent acidity, which is particularly to be exploited. The form of an ionic liquid with latent acidity can be in contrast to the highly acidic form of the pair, much more stable to moisture with the possibility of reuse and easy storage of such catalysts as shown by Corma and Garcia [24].

The acidity of In-IL(Phos)/SiO_2 as a function of temperature for evacuation of pyridine is illustrated in Fig. 5. At 50 °C, pyridine was found to be mostly physisorbed (1597.8 cm^{-1}) on the sample. At 100 and 150 °C, the ring stretching frequency characteristics of pyridine chemisorbed on Lewis acid sites considered to be the anionic species from immobilized ionic liquid (1447.3 and 1608.4 cm^{-1}) were observed. It is assumed that Lewis acid centers with the highest strength are revealed with the increase of time for sample evacuation at 150 °C. Although a clear attribution of the peak at 1487.8 cm^{-1} has not been yet reported, In-IL(Phos)/SiO_2 can be considered a pure Lewis acid solid. This consideration is also based on the lack of peak at about 1545 cm^{-1} corresponding to pure Brønsted acid sites. The silica support has shown no acidity at all.

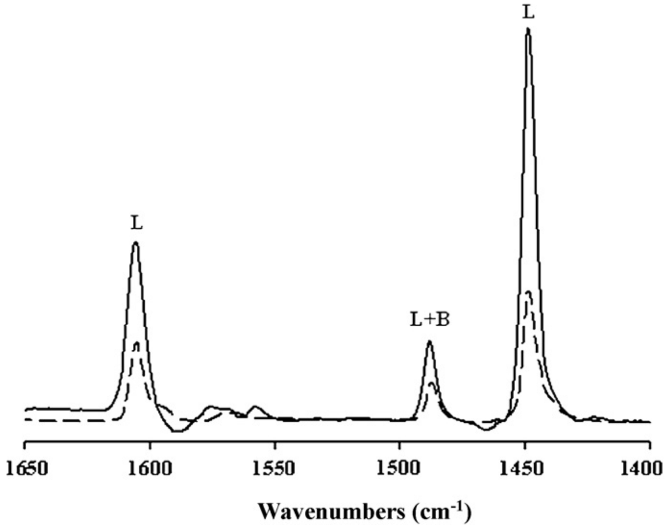


Fig. 5. Py-FT-IR spectra of In-IL(Phos)/SiO_2 as a function of temperature of desorption at 100 °C (straight line) and 150 °C (dashed line).

The catalytic performance of In-IL(Phos)/SiO_2 as Lewis acid solid catalyst has been checked for the production of alkylphenols. The conversion of phenol as a function of reaction time is given in Fig. 6. After 150 min at 90 °C, the phenol conversion was about 80% with a selectivity for 2,4-DTBP of 60%. At short reaction time, the catalyst was found to produce mainly mono-alkylphenols (2-TBP and 4-TBP), while the selectivity to di-alkylated product was found to increase with time. This observation is consistent with the fact that the formation of 2,4-DTBP from phenol is mainly taking place in two steps, each step being in fact a monoalkylation reaction. However, the initial increase of selectivity for di-alkylated product might be due to a direct di-alkylation reaction of phenol over the strong acid sites.

The effect of molar ratio isobutene/phenol on the catalyst performance is presented in Fig. 7. At very low ratios, the selectivity to mono-alkylphenols was found to have a small increase. However, at high ratios, the consumption of mono-alkylphenols for the production of 2,4-DTBP is taking place. The selectivity to di-alkylated product was found the highest at a molar ratio isobutene/phenol of 2:1.

Studies regarding the stability of the catalyst In-IL(Phos)/SiO_2 have been considered, too. Cross-polarized ^{29}Si MAS NMR and ^{31}P MAS NMR spectra (not shown here) recorded before and after reaction have revealed the preservation of catalyst structure. Besides these results, the use of In-IL(Phos)/SiO_2 for a second reaction cycle was providing almost similar rates of products accumulation in the reaction mixture as for the first cycle, demonstrating the recyclability of the catalyst.

3.2. Effect of Brønsted acidity

The ion-exchange resins (Amberlyst type) have been reported [25] as pure Brønsted acid solid catalysts, while Arata [26] has characterized sulfated zirconia as very strong Brønsted acidic catalysts. Sulfated zirconia (SZ) or metal-doped SZ have been proved to be active catalysts for isomerization reactions [27]. For example, Sakthivel et al. [28] have proved sulfated zirconia as efficient catalyst for phenol alkylation with *tert*-butanol at 448 K. The conversion of phenol was found to reach 49.5% while the major product corresponding to a molar ratio phenol/alkylating agent = 1:2 was found to be para-isomer (76%). Over a homogeneous imidazolium based ionic liquid with Brønsted acidity, Gui et al. [29] have obtained a maximum selectivity for 2,4-di-*tert*-butylphenol of 60.2% at 80.4% conversion of phenol.

The results in terms of conversion and selectivity over Amberlyst 15 dry with an exchange capacity of 4.9 meq g^{-1} and SO_4/ZrO_2 with a specific surface of about 164 $m^2\,g^{-1}$ and pore diameter of 58.7 Å are presented in Table 2. For an equimolar ratio isobutene/phenol, Amberlyst 15 was showing comparable conversion (80%) as our prepared immobilized phosphonium ionic liquid. For the same ratio, the conversion observed over SO_4/ZrO_2 catalyst was twofold lower. This observation is consistent with the findings of Sakthivel et al. [28]. Over such a catalyst, a conversion of phenol of almost 37% corresponding to a molar ratio *tert*-butanol/phenol = 1 was found.

In our case, two assumptions can be made for the low catalytic performance of sulfated zirconia. On one hand, the apparent low

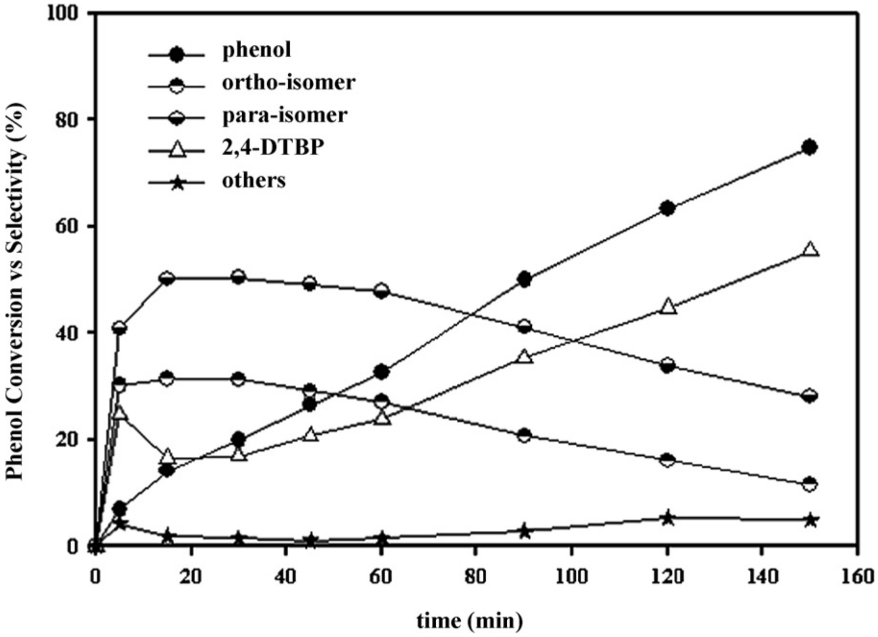


Fig. 6. Influence of reaction time on phenol alkylation with isobutene over In-IL(Phos)/SiO_2. Conditions: phenol 1 mol, catalyst 1 g, isobutene flow 145 mL/min, $T = 90$ °C, no solvent.

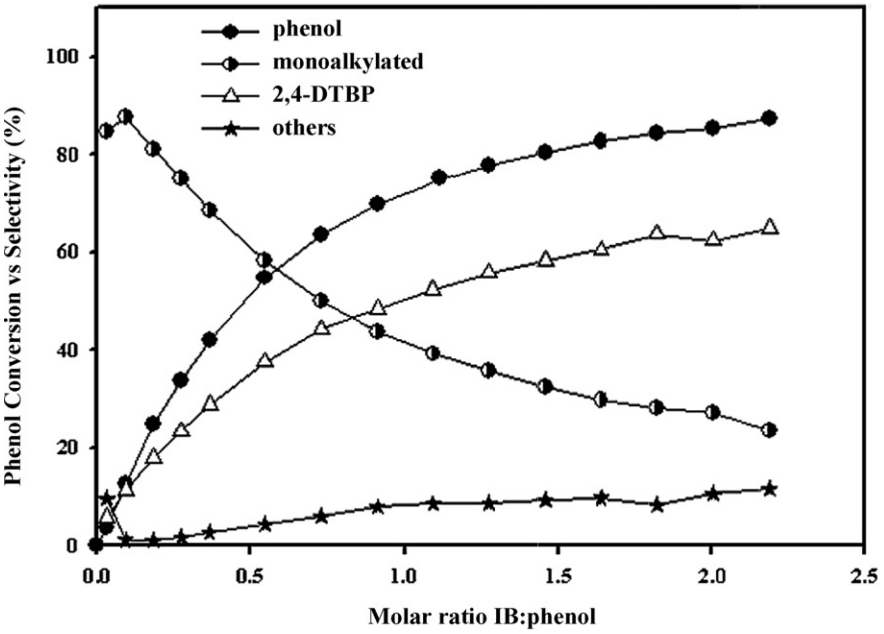


Fig. 7. Influence of molar ratio alkylating agent/phenol on the product distribution over In-IL(Phos)/SiO_2.

Table 2
Catalytic performance of solid acid catalysts with Brønsted acidity.

Catalyst	Molar ratio IB:phenol	Conversion (%)	Selectivity			
			2-TBP[a]	4-TBP[b]	2,4-DTBP[c]	2,6-DTBP[d]
Amberlyst 15	1:1	80.7	4.7	59.8	29.4	0
Amberlyst 15	2.1	89.6	2.3	47.4	45.6	0
SO_4/ZrO_2	1:1	32.9	25.2	53.1	15.0	0
SO_4/ZrO_2	2.1	61.9	16.1	49.5	27.0	0

[a] 2-*tert*-butylphenol.
[b] 4-*tert*-butylphenol.
[c] 2,4-di-*tert*-butylphenol.
[d] 2,6-di-*tert*-butylphenol.

catalytic activity can be explained by the presence of dealkylation reactions, which can take place on the very acidic centers of such a catalyst. On the other hand, the chemical stability of sulfated zirconia can be affected even at mild reaction temperatures as shown by the work of López et al. [30]. Therefore, studies regarding acidity were considered in our experiments. For a sample calcined at 550 °C for 6 h, the profile (not shown) of NH_3-TPD has proved a peak (with a maximum visible at 660 °C) which is usually attributed to strong acidic centers. These observations are in direct correlation with the assumption of dealkylation reactions responsible for the low catalytic conversion of phenol in the presence of sulfated zirconia.

3.3. *Effect of mixed acidity — Lewis and Brønsted*

The catalyst WO_3/ZrO_2 has been first reported for strong acid catalyzed reactions such as light alkane isomerization [31]. We have proved the high catalytic performance for the alkylation reaction of ortho-*tert*-butylphenol with isobutene. We found that the substrate is completely consumed at a molar ratio ortho-*tert*-butylphenol/isobutene of 1:1.5 with a selectivity for 2,4-DTBP of 95% at 50 °C. When alkylating phenol with isobutene over such a catalyst, the mixed-phase reaction was found to take place at 90 °C (Fig. 8). The complete conversion of phenol was achieved within 3 h at a GHSV of 9000 h^{-1} for isobutene. Over the first hour, a slow increase of the selectivity for para-isomer was observed while at longer time of reaction a decrease of its concentration in the reaction mixture was found. The maximum selectivity for 2,4-DTBP of about 80% was achieved after 4 h. As observed in the case of immobilized In-based ionic liquid, the initial increase of selectivity for 2,4-DTBP is attributed to the existence of strong acid sites able to convert phenol to the di-alkylated product.

Fig. 9 shows the catalytic performance of modified with silica of WO_3/ZrO_2. By comparison, the catalyst $WO_3/ZrO_2–SiO_2$ was giving about 60% conversion for phenol at isobutene/phenol = 1:1. 4-*tert*-butylphenol was found as major product while a very slow increase of 2,4-DTBP could be detected as a function of molar ratio isobutene/phenol. The lower catalytic activity observed for $WO_3/ZrO_2–SiO_2$ is believed to be due to the lower acidity of the catalyst. Moreover, no initial increase of selectivity for 2,4-DTBP has been observed suggesting also that the catalyst modification was accompanied by a modification of acid strength of the catalyst.

Moreover, the reuse of catalyst WO_3/ZrO_2 demonstrated its catalytic effectiveness since no modification of catalytic activity was observed over at least four runs (Fig. 10). Tanabe and Nishizaki [32] as well as Klemm et al. [33] have suggested a vertical orientation in the adsorption of phenol molecules at Lewis acid sites. In this case, the formation of ortho-isomer is preferred. The Brønsted acid sites are interacting strongly with the aromatic ring, thus permitting the alkylation in the ortho and para positions. In our work, the production of 2,4-DTBP was shown to be possible over all studied solid acid catalysts. However, the catalyst WO_3/ZrO_2 has provided the highest conversion and selectivity for this product. The catalytic results are sustained by the N_2 sorption experiments for WO_3/ZrO_2. Although the products are usually less tightly adsorbed than reactants on the catalytically active sites, our previous observation might be also consistent with the fact that both types of acid sites are located more on the outer surface of the catalyst WO_3/ZrO_2.

The excellent catalytic properties of WO_3/ZrO_2 were tentatively assigned to a very good dispersion of WO_3 particles on the surface of zirconia. This assumption is demonstrated in this work with help of XRD and N_2 sorption experiments. In addition, the high acidity of the catalyst anticipated by the high selectivity of 2,4-di-*tert*-butylphenol, can be proved by NH_3-TPD, while a clear differentiation of acidic centers can be made with the help of Py-FT-IR analyses.

Since no catalytic activity was observed for WO_3/ZrO_2 in the absence of activation by calcination, a more detailed study regard-

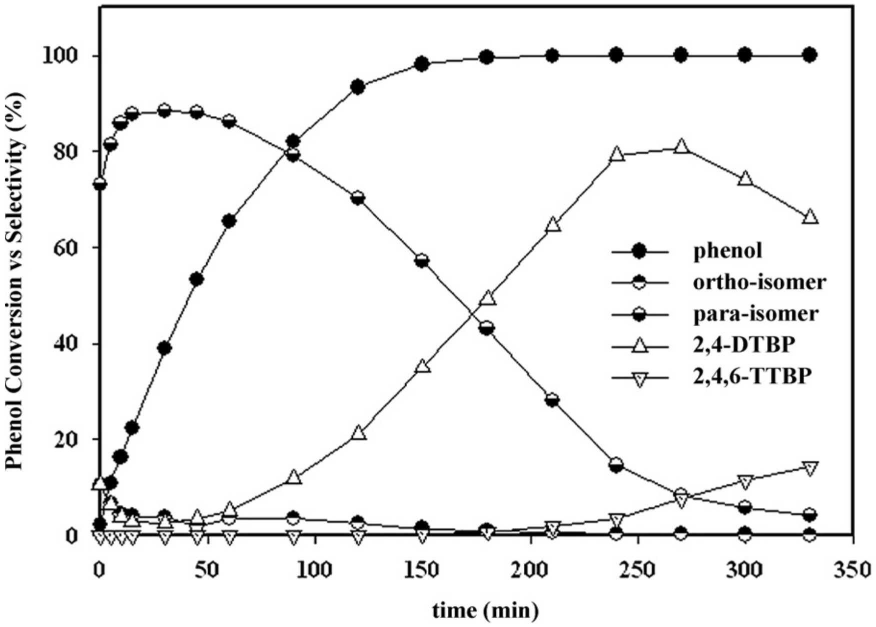


Fig. 8. Influence of reaction time for phenol alkylation with isobutene over WO_3/ZrO_2. Conditions: phenol 1 mol, catalyst 1 g, isobutene flow 145 mL/min, $T = 90\,^{\circ}C$, no solvent.

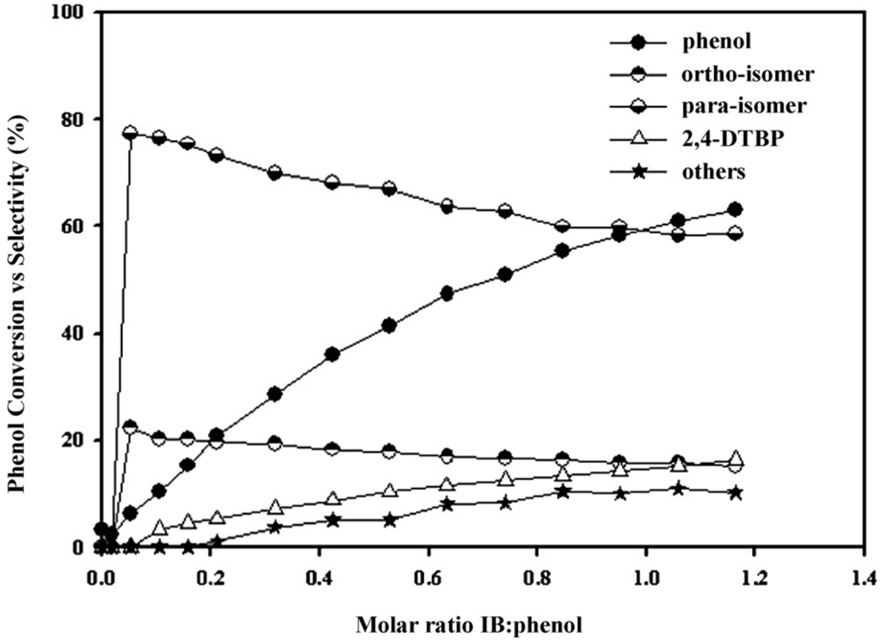
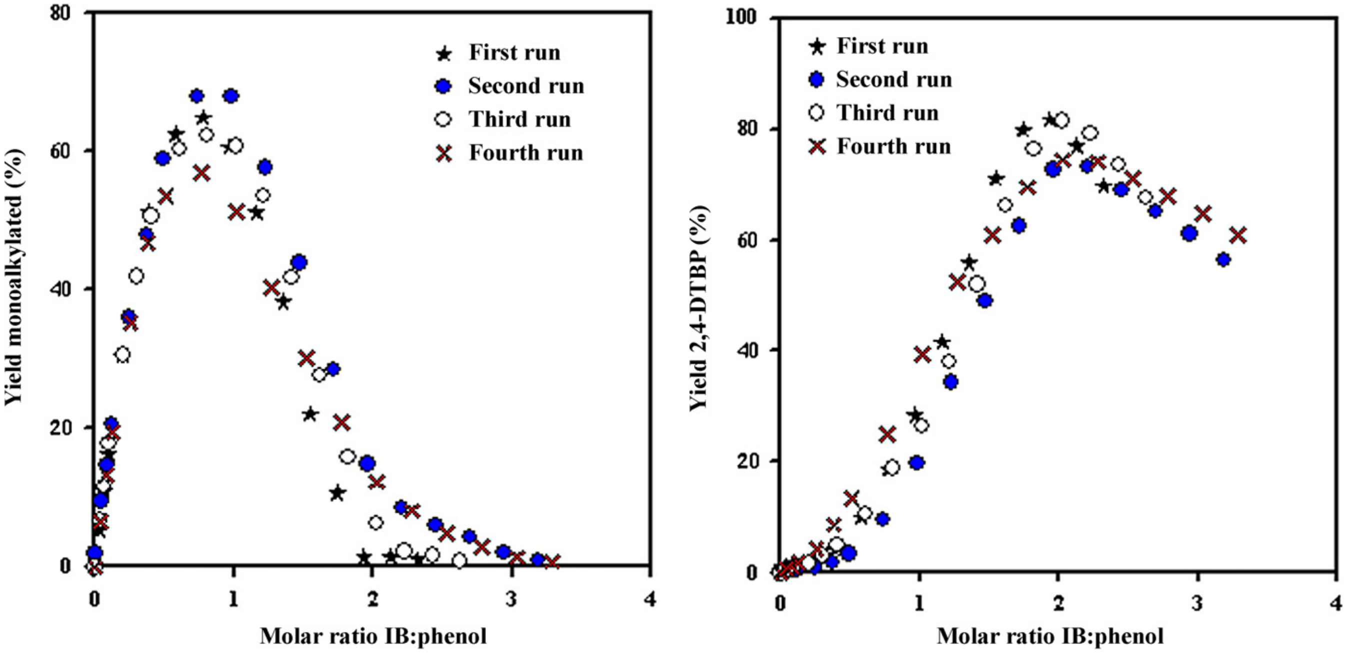


Fig. 9. Conversion of phenol and product selectivity over WO_3/ZrO_2–SiO_2 as a function of molar ratio alkylating agent/substrate.

ing the structure of this catalyst by X-ray analyses has been performed. The WO_3/ZrO_2 structure changes by calcination at 550 °C from amorphous to a crystalline structure as shown in Fig. 11. The pattern exhibits no peak corresponding to a wolfram oxide phase after calcination at 550 °C. López et al. [34] have shown by X-ray analyses that at temperatures higher than 800 °C the formation of detectable bulk WO_3-like species with characteristic 2θ diffraction peaks at 23.12°, 23.59° and 24.38° is possible. In fact, the crystalline structure is attributed to ZrO_2 as major phase. After calcination, the intense line appearing at $2\theta = 30.2°$ is characteristic for the tetragonal phase of zirconia.

This is in agreement with the findings of Matta et al. [35]. The authors have shown that up to 300 °C the amorphous structure of ZrO_2 is retained while after calcination at higher temperatures than 700 °C the lines appearing at low 2θ (28.2° and 31.5°) are characteristic for a monoclinic phase of zirconia. Moreover, Sun et al. [36] have demonstrated by XRD measurements that a molar ratio Zr/W lower than 8 is stabilizing the tetragonal phase of zirconia which is much more important for the formation of acidic centers [37]. For our experiments, the ICP-AES analyses performed on the catalyst resulted after calcination at 550 °C have revealed a molar ratio $Zr/W = 4.5$ which suggests the presence of tetragonal phase of zirconia believed to be responsible for the catalytic activity.

Fig. 12 shows the adsorption–desorption isotherms of N_2 over samples such as WO_3/ZrO_2, WO_3/ZrO_2–SiO_2 and Al_2O_3 Puralox. The textural characteristics of these solid acid catalysts are presented in Table 3.



(A) (B)

Fig. 10. Effect of catalytic run of WO_3/ZrO_2 on the yield of mono-alkylated and 2,4-di-*tert*-butylphenol.

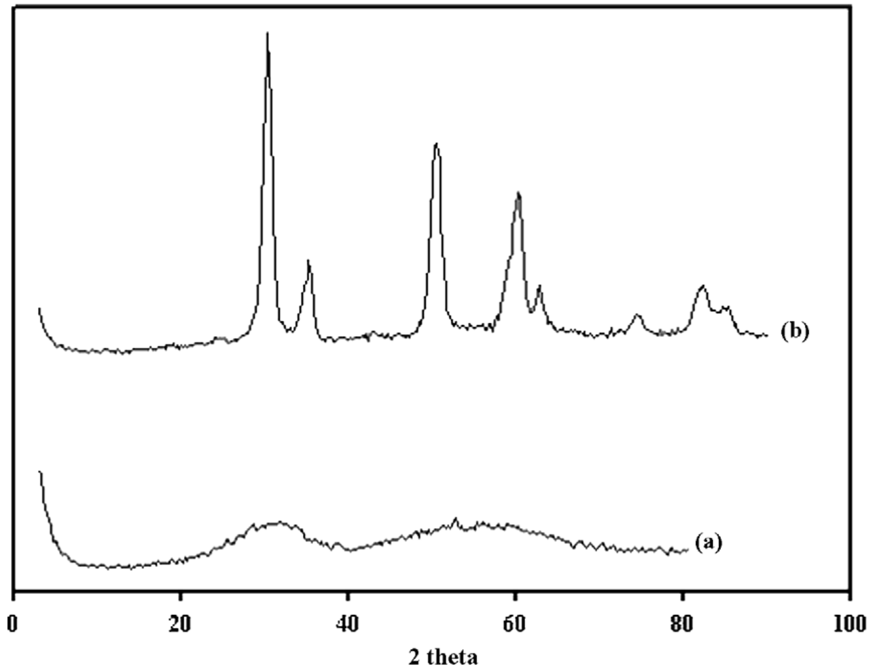


Fig. 11. X-ray diffractogram patterns of WO_3/ZrO_2: (a) before calcination and (b) after calcination.

The porous structure of WO_3/ZrO_2 is believed to be responsible for a facile transport of the reactants and products with the minimization of eventual undesired side reactions favored by diffusional restrictions.

The samples WO_3/ZrO_2 and WO_3/ZrO_2–SiO_2 were investigated in temperature programmed desorption of NH_3 (Fig. 13). The peak that usually occurs between 120 and 450 °C is attributed to surface hydroxyl groups responsible for the weak acidity of a catalyst. The studied samples were showing a peak corresponding to weak acidity with a maximum at 240 °C for WO_3/ZrO_2 (Fig. 13a) and 230 °C for WO_3/ZrO_2–SiO_2 (Fig. 13b) after deconvolution. In the case of WO_3/ZrO_2 modified with silica a second peak with a maximum at 271 °C was found after deconvolution suggesting the presence of silica and its influence on the acidity of the catalyst. The moderate acidity of a solid catalyst is usually proved by the peaks situated between 350 and 450 °C while a strong acidity is responsible for the peaks situated between 450 and 600 °C. WO_3/ZrO_2 was showing a broad peak with a maximum at 394 °C corresponding to a moderate acidity while a much more narrow peak with a maximum at 407 °C was observed for WO_3/ZrO_2–SiO_2. Based on these results we conclude that both samples possess low-to-moderate acidity and the total acidity of the modified WO_3/ZrO_2 was found four fold lower than for pure WO_3/ZrO_2, confirming the better catalytic performance of this catalyst.

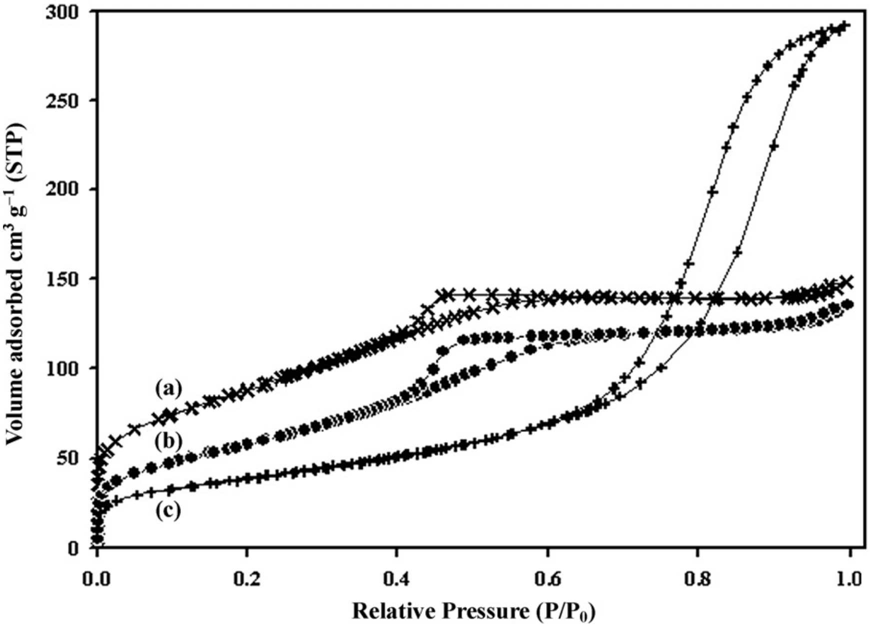
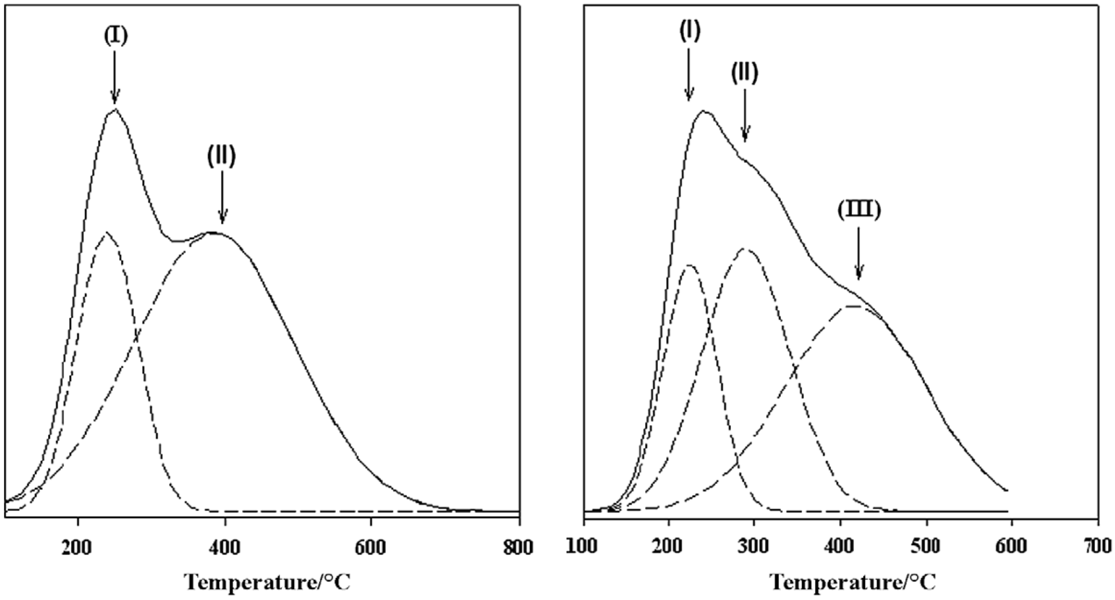


Fig. 12. N_2 adsorption–desorption isotherms of (a) WO_3/ZrO_2, (b) WO_3/ZrO_2–SiO_2 and (c) Al_2O_3 Puralox.



(a)

(b)

Fig. 13. NH_3-TPD profiles and deconvolutions of (a) WO_3/ZrO_2 and (b) WO_3/ZrO_2 modified with SiO_2, calcined samples.

Table 3
Textural characteristics of some samples of solid acid catalysts.

Catalyst	S_{BET} ($m^2\,g^{-1}$)	S_{BJH} ($m^2\,g^{-1}$)	V_{micro} ($cm^3\,g^{-1}$)	V_{macro} ($cm^3\,g^{-1}$)	Pore diam. (Å)
WO_3/ZrO_2	318	325	0.003	0.24	29.2
WO_3/ZrO_2–SiO_2	215	227	0.000	0.21	36.4
Al_2O_3 Puralox	142	178	0.000	0.45	102

A much more valuable observation is provided by FT-IR analyses in the range 1700–1400 cm^{-1} using pyridine as probe molecule. Fig. 14 shows Py-FT-IR analysis for WO_3/ZrO_2 catalyst as a function of temperature for pyridine desorption. The Lewis acidity is proved by the peaks at 1444.4 and 1608.4 cm^{-1} assigned to pyridine associated with Lewis acid sites [38]. The existence of Brønsted acid sites is usually proved by the bands at 1545 and 1636 cm^{-1} due to ring vibrations of pyridine bound to Brønsted acid sites [39]. For our studies, these peaks were observed at 1577.5 and 1641.2 cm^{-1}. While a clear attribution for the peak occurring at 1493 cm^{-1} (for our experiments at 1488.8 cm^{-1}) is not given in the literature [40], we can conclude that WO_3/ZrO_2 is a solid acid catalyst with Lewis and Brønsted acid sites.

The obtained results were confirmed by the work of Triwahyono et al. [41]. Moreover, the Py-FT-IR studies (not shown) performed at higher temperature (400 °C) have confirmed the versatility of the catalyst WO_3/ZrO_2. At this temperature, the peaks corresponding for Lewis acidity were predominantly observed, suggesting the fact that at high temperatures WO_3/ZrO_2 can act mostly as Lewis catalyst.

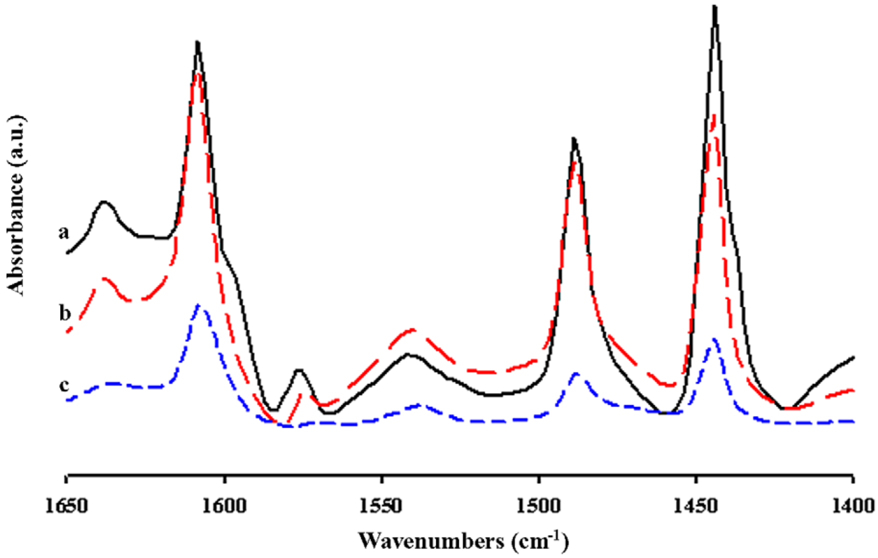


Fig. 14. Py-FT-IR spectra of WO_3/ZrO_2 as a function of temperature of desorption: (a) at 50 °C, (b) at 100 °C and (c) at 300 °C.

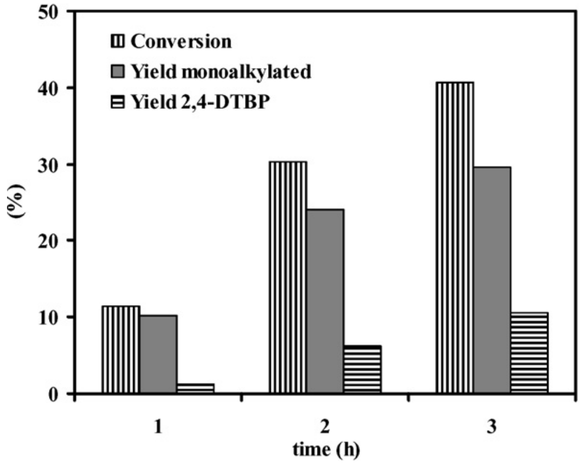


Fig. 15. Catalytic performance of In-IL(Phos)/SiO_2 as a function of time. Conditions: autoclave 75 mL, phenol 20 mmol, catalyst 1 wt%, $T = 90\,^{\circ}C$, $p = 3$ atm, no solvent.

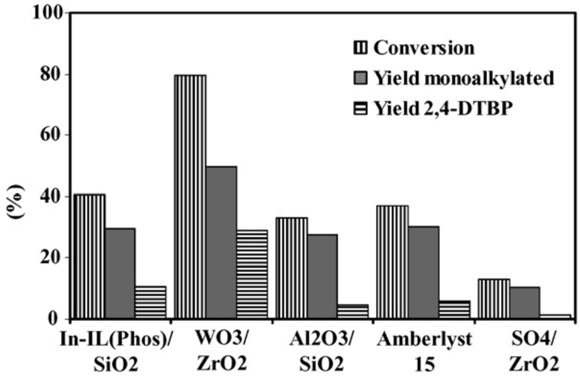


Fig. 16. Catalytic activity of different solid acid catalysts for phenol alkylation with isobutene in autoclave type reactor. Conditions: autoclave 75 mL, phenol 20 mmol, catalyst 1 wt%, $T = 90\,^{\circ}C$, $p = 3$ atm, no solvent.

3.4. *Effect of autoclave reactor*

The catalytic performance of In-IL(Phos)/SiO_2 for phenol alkylation with isobutene, tested in autoclave type reactor at a pressure of isobutene of 3 atm, is plotted as a function of time of reaction in Fig. 15.

The experiments have revealed an increase of phenol conversion with time of reaction. After 1 h, the conversion of phenol was found to be 11.5% while after 3 h about 40.6% of phenol was converted. The same observation was possible when considering the yields of monoalkylated and 2,4-DTBP. It is worth to note that the yield of monoalkylated products was found higher than that of 2,4-DTBP at all considered reaction intervals (1 h, 2 h and 3 h). For the production of di-alkylated isomer 2,6-DTBP, Küpper [42] has proposed the work at low isobutene pressures. In our case, 2,6-DTBP has been not observed at all. To gain more information about the catalyst performance in autoclave type reactor different solid acid catalysts such as In-IL(Phos)/SiO_2, WO_3/ZrO_2, Al_2O_3/SiO_2, Amberlyst 15 and SO_4/ZrO_2 have been tested. Fig. 16 presents the results obtained for alkylation reaction of phenol at 90 °C and a pressure of isobutene of 3 atm. The superior catalytic performance of WO_3/ZrO_2 is in agreement with the results obtained in normal glass reactor. The catalyst was able to convert about 80% and 2-TBP, 4-TBP and 2,4-DTBP were the main products while 2,4,6-tri-*tert*-butylphenol was produced only in a very low amount ($S < 1\%$). Monoalkylated products were produced with a selectivity of 62.5% and 2,4-DTBP was formed in a lower amount ($S = 36.1\%$). Despite the fact that the presence of alkylating agent under pressure was thought to be beneficial for the production of di-alkylated compounds including 2,6-di-*tert*-butylphenol, the yield of monoalkylated products 2-*tert*-butylphenol and 4-*tert*-butylphenol was found higher than the yield of 2,4-di-*tert*-butylphenol over all checked catalysts. In this context, it appeared that phenol alkylation with isobutene in autoclave type reactor is more sensitive toward reaction time over all studied catalysts, both phenol conversion and yields of products being found to increase with reaction time. No traces of 2,6-di-*tert*-butylphenol have been observed at all.

In short, when comparing the effect of acidity type for different solid acid catalysts for alkylation of phenol with gaseous isobutene under mild reaction conditions, the product distribution was found to be strongly influenced by the presence of Lewis and/or Brønsted acid sites of the catalyst. The fact that the formation of the bulky product 2,4-DTBP is more favored over a solid acid catalyst with both Lewis and Brønsted acid sites is sustained by the superior catalytic performance of WO_3/ZrO_2 in both studied batch reactors. Although a common method for the determination of the amount of acid sites for all studied catalysts (In-IL(Phos)/SiO_2, Amberlyst 15 and WO_3/ZrO_2) has been not used, the strong signals for Py-FT-IR and NH_3-TPD in the case of WO_3/ZrO_2 suggest a larger amount of acidic sites available for catalysis. Therefore, the better catalytic results observed for WO_3/ZrO_2 for the production of 2,4-di-*tert*-butylphenol are believed to be due not only to the presence of both types of acid centers but also to the higher acidity of the catalyst.

4. Conclusion

Phenol alkylation with isobutene is among the organic reactions that are requiring a certain control of type and strength of acidity of the solid acid catalyst if high reaction selectivity is to be achieved. In this respect, we developed a pure Lewis acidic solid catalyst by covalent immobilization of a phosphonium based ionic liquid on silica type carrier. The best choice when considering such a reaction was to design an In-based immobilized phosphonium ionic liquid, since Al-based ionic liquids are very sensitive to moisture. The liquid-phase *tert*-butylation of phenol with isobutene to produce di-alkylphenols was successfully shown to be dependent on the type and strength of acid sites of the catalyst. The catalyst WO_3/ZrO_2 was able to produce 2,4-di-*tert*-butylphenol with a selectivity of about 80% at complete conversion of phenol. Moreover, studies regarding the recycling and reuse of such catalyst have showed the maintenance of catalytic performance over at least 4 cycles. The high selectivity of 2,4-di-*tert*-butylphenol is considered satisfactory for the implementation of such a catalyst in an industrial process due to the fact that no other di-alkylated isomer was observed. Right now, WO_3/ZrO_2 catalyst is considered the best catalyst for the formation of 2,4-di-*tert*-butylphenol because no better results could be found in the literature.

Acknowledgments

The authors are grateful to SI Group-Switzerland GmbH and to Dr. Tobias Lotz for financially supporting the work with immobilized ionic liquids. A patent application for catalyst WO_3/ZrO_2 has been filed.

References

[1] H. Fiege, Ullmann's Encyclopedia of Industrial Chemistry, sixth ed., Wiley–VCH, Weinheim, 2002.
[2] G.W. Hearne, T.W. Evans, V.W. Buls, C.G. Schwarzer, Ind. Eng. Chem. 47 (11) (1995) 2311.
[3] N. Kusano, T. Kobayashi, H. Miyajima, JP 61145130 (1986), to Goi Kasei KK.
[4] S.H. Patinuin, B.S. Friedman, in: G.A. Olah (Ed.), Alkylation of Aromatics with Alkenes and Alkanes in Friedel–Crafts and Related Reactions, vol. 3, Interscience, New York, 1964, p. 75.
[5] R.T. Parton, J.M. Jacobs, D.R. Huybrechts, P.A. Jacobs, Stud. Surf. Sci. Catal. 46 (1998) 163.
[6] R. Anand, R. Maheswari, U. Hanefeld, J. Catal. 242 (2006) 82.
[7] D. Mravec, P. Zavadan, A. Kaszonyi, J. Joffre, P. Moreau, Appl. Catal. A 257 (2004) 49.
[8] A. Vinu, T. Krithiga, V.V. Balasubramanian, A. Asthana, P. Srinivasu, T. Mori, K. Ariga, G. Ramanath, P.G. Ganesan, J. Phys. Chem. B 110 (2006) 11924.
[9] T. Mathew, B.S. Rao, C.S. Gopinath, J. Catal. 222 (2004) 107.
[10] A.B. Shinde, N.B. Shrigadi, S.D. Samant, Appl. Catal. A 276 (2004) 5.
[11] C. DeCastro, E. Sauvage, M.H. Valkenberg, W.F. Hoelderich, J. Catal. 196 (2000) 86.
[12] (a) A. Sakthivel, S.K. Badamali, P. Selvam, Micropor. Mesopor. Mater. 39 (2000) 457;
(b) S.K. Badamali, A. Sakthivel, P. Selvam, Catal. Lett. 65 (2000) 153.
[13] A. Sakthivel, N. Saritha, P. Selvam, Catal. Lett. 72 (3–4) (2001) 225.
[14] M.H. Valkenberg, C. deCastro, W.F. Hölderich, Top. Catal. 14 (1–4) (2001) 139.
[15] M.J. Earle, U. Hakala, C. Hardacre, J. Karkkainen, B.J. McAuley, D.W. Rooney, K.R. Seddon, J.M. Thompson, K. Wähälä, Chem. Commun. (2005) 903.
[16] T. Welton, Chem. Rev. 99 (1999) 2071.
[17] (a) J.D. Holbrey, K.R. Seddon, Clean Prod. Process 1 (1999) 223;
(b) Y. Chauvin, A. Hirschauer, H. Olivier, J. Mol. Catal. 92 (1994) 155.
[18] M.H. Valkenberg, C. DeCastro, W.F. Hoelderich, Spec. Publ. Soc. Chem. 266 (2001) 242.
[19] S. Laforge, P. Ayrault, D. Martin, M. Guisnet, Appl. Catal. A 279 (1–2) (2005) 79.
[20] K. Yamamoto, T. Tatsumi, Micropor. Mesopor. Mater. 44–45 (2001) 459.
[21] K.-M. Choi, S. Ikeda, S. Ishino, K. Ikeue, M. Matsumura, B. Ohtani, Appl. Catal. A 278 (2) (2005) 269.
[22] A. Corma, H. Garcia, Adv. Synth. Catal. 348 (2006) 1391.
[23] J.D. Sunseri, W.T. Cooper, J.G. Dorsey, J. Chromatogr. A 1011 (2003) 23.
[24] A. Corma, H. Garcia, Chem. Rev. 103 (2003) 4307.
[25] http://www.rohmhaas.com.
[26] K. Arata, Adv. Catal. 37 (1990) 165.
[27] R.S. Drago, N. Kob, J. Phys. Chem. B 101 (17) (1996) 3360.
[28] A. Sakthivel, N. Saritha, P. Selvam, Catal. Lett. 72 (3–4) (2001) 225.
[29] J. Gui, H. Ban, X. Cong, X. Zhang, Z. Hu, Z. Sun, J. Mol. Catal. 225 (2005) 27.
[30] D.E. López, J.G. Goodwin Jr., D.A. Bruce, E. Lotero, Appl. Catal. A 295 (2005) 97.
[31] R.A. Boyse, E.I. Ko, Appl. Catal. A 177 (1999) L131–L137.
[32] K. Tanabe, T. Nishizaki, in: F.C. Tompkins (Ed.), Proc. 6th Int. Congress on Catalysis, The Chemical Society, London, 1977.
[33] L.H. Klemm, C.E. Klopfenstein, J. Shabtai, J. Org. Chem. 35 (1970) 1069.
[34] D.E. López, K. Suwannakarn, D.A. Bruce, J.G. Goodwin Jr., J. Catal. 247 (2007) 43.
[35] J. Matta, J.-F. Lamonier, E. Abi-Aad, E.A. Zhilinskaya, A. Aboukaïs, Phys. Chem. Chem. Phys. 1 (1999) 4975.
[36] W.-D. Sun, Z.-B. Zhao, C. Guo, X.-K. Ye, Y. Wu, Ind. Eng. Chem. Res. 39 (2000) 3717.
[37] (a) J.G. Santiesteban, J.C. Vartuli, S. Han, R.D. Bastian, C.D. Chang, J. Catal. 168 (1997) 431;
(b) M. Scheithauer, R.K. Grasselli, H. Knozinger, Langmuir 14 (1998) 3019.
[38] M.L. Occelli, S. Biz, A. Auroux, G.J. Ray, Micropor. Mesopor. Mater. 26 (1998) 193.
[39] (a) A. Corma, V. Fornes, M.T. Navarro, J. Perez-Pariente, J. Catal. 148 (1994) 569;
(b) B. Chakraborty, B. Viswanathan, Catal. Today 49 (1999) 253.
[40] M.J. Climent, A. Corma, S. Iborra, S. Miquel, J. Primo, F. Rey, J. Catal. 76 (1999) 783.
[41] S. Triwahyono, T. Yamada, H. Hattori, Appl. Catal. A 242 (2003) 101.
[42] F.-W. Küpper, Appl. Catal. A 264 (2004) 253.