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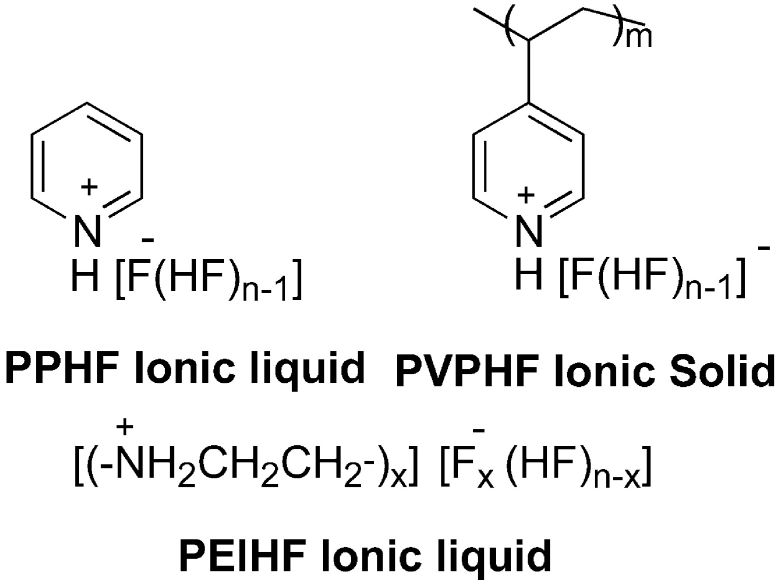

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# Ionic Liquid and Solid HF Equivalent Amine-Poly(Hydrogen Fluoride) Complexes Effecting Efficient Environmentally Friendly Isobutane−Isobutylene Alkylation

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***Abstract:*** Isoparaffin−olefin alkylation was investigated using liquid as well as solid onium poly(hydrogen fluoride) catalysts. These new immobilized anhydrous HF catalysts contain varied amines and nitrogen-containing polymers as complexing agents. The liquid poly(hydrogen fluoride) complexes of amines are typical ionic liquids, which are convenient media and serve as HF equivalent catalysts with decreased volatility for isoparaffin−olefin alkylation. Polymeric solid amine:poly(hydrogen fluoride) complexes are excellent solid HF equivalents for similar alkylation acid catalysis. Isobutane−isobutylene or 2-butene alkylation gave excellent yields of high octane alkylates (up to RON = 94). Apart from their excellent catalytic performance, the new catalyst systems significantly reduce environmental hazards due to the low volatility of complexed HF. They represent a new, “green” class of catalyst systems for alkylation reactions, maintaining activity of HF while minimizing its environmental hazards.

## Introduction

Ionic liquids are gaining increasing significance in chemistry.[1] Because of the toxic and hazardous nature of alkylation processes, including widely practiced isoparaffin-olefin alkylations in petrochemical industry, great need exists for developing “greener” and safer reaction systems. This has prompted the design of less toxic catalysts, which are not only safer but at the same time efficient and recyclable. Some of the recent reviews discuss the potential of ionic liquids as solvents for synthesis and catalysis.[2,3] Generally, ionic liquids are ionic salts (such as imidazolonium salts, vide infra), the melting points of which are lower than room temperature.[4] Walden in 1914 reported ethylammonium nitrate (mp 12−14 °C) as the first room-temperature ionic liquid formed by the reaction of ethylamine and nitric acid.[5] Many of the room-temperature ionic liquids are salts of organic cations such as tetraalkylammonium, tetraalkylphosphonium, *N*-alkylpyridinium, 1,3-dialkylimidazolium and trialkylsulfonium cations. Efforts by Osteryoung[2a,6] and Wilkes[7,8] in the 1970s and Hussey and Seddon[9,10] in the 1980s have given more insight into the properties and use of ionic liquids and resulted in further development as reaction media for organic synthesis as well as in biphasic catalysis.[11,12]

Since the reports by Wilkes and co-workers in the 1990s of air and moisture stable imidazolium salts based on tetrafluoroborate ($BF_4^-$) and hexafluorophoshate ($PF_6^-$),[13] there has been an exponential growth in the number and variety of ionic liquids in recent years. Though less studied than the quarternary nitrogen-based ionic liquids, their phosphorus-based analogues such as tetraalkylphosphonium tosylates are used as media for hydroformylation and tetraalkylphosphonium halides as solvents for palladium catalyzed Heck reaction and Suzuki cross coupling

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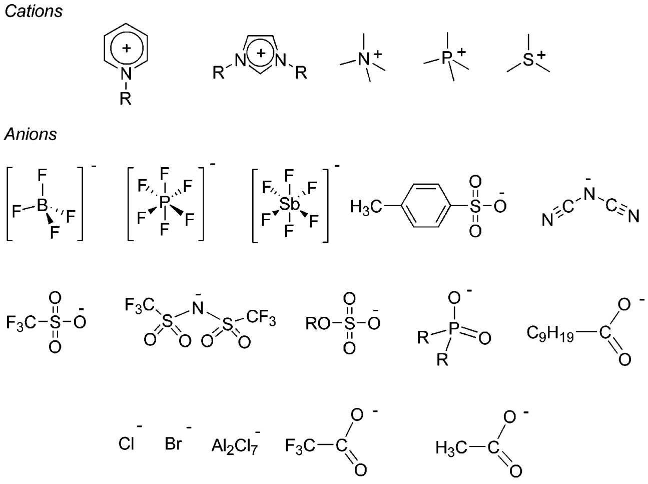
**Scheme 1**



reactions. Recently, Bradaric et al. have developed a diverse range of new products by pairing tetraalkylphosphonium cations with various counterions to produce ionic phosphonium liquids.[14] Wide range of ionic liquids containing various tetraalkylammonium and phosphonium cations with a diverse array of anions are shown in Scheme 1. Many of the alkylammonium halides are either commercially available or can be easily prepared by reacting the corresponding haloalkane with amines. Pyridinium and imidazolium halides, [emim]Cl (emim$^+$ is 1-ethyl-3-methylimidazolium cation), [bmim]Cl (bmim$^+$ is 1-butyl-3-methylimidazolium cation) etc., can be prepared accordingly.[15−17] Merck KGaA has developed a number of halogen free ionic liquids with highly improved physical properties, which can have wide application in catalysis, extraction, metal deposition, and batteries.

Ionic liquids being environmentally benign reaction media, open up exciting challenges and opportunities to clean catalytic processes. They can be considered as “green” solvents due to their low volatilities. Their chemical and physical properties can be altered by the judicious selection of the components. Over the years, some of us have explored the use of amine-poly(hydrogen fluoride) as convenient fluorinating agents. These materials are also ionic liquids in their own right.[18]

Our work began with search for convenient fluorinating agents using less volatile complexes of HF with varied *n*-donor bases. In our extensive studies on amine-HF complexes, we found that pyridine and its analogues forms remarkably stable solutions with anhydrous hydrogen fluoride to give pyridinium poly(hydrogen fluoride) (**PPHF, Olah’s reagent**)[19,20] Since its introduction in 1973, its properties as an ionic liquid have, however, not been extensively explored. Olah and co-workers found that hydrogen fluoride, which itself is highly associated in the liquid phase,[21] gives poly-hydrogen fluorides not only with pyridine or picoline, but with many alkyl and arylamines and their derivatives. These ionic liquids of pyridine, picoline, triethylamine, or triethanolamine containing up to 70 wt % of HF give stable solutions which do not lose hydrogen fluoride noticeably up to 50 °C. The 70% hydrogen fluoride/30% pyridine solution studied in detail was found to be pyridinium poly(hydrogen fluoride) containing a small amount of free hydrogen fluoride in equilibrium acting as a reservoir of HF and an equivalent of HF reagent. The 70/30 wt % composition was found to be a convenient and an efficient fluorinating agent in many organic fluorination reactions. Studies on physical properties such as density,[22] electrical conductivity,[23] etc. of amine-poly(hydrogen fluoride) ionic liquids have also revealed their complexed ionic nature. Our investigations of these onium poly(hydrogen fluoride) complexes, however, revealed that higher HF content is needed for suitable catalytic activity for alkylations and Friedel−Crafts type reactions. Therefore, these compositions constitute a prominent class of ionic liquids which can also act as very specific HF equivalent strong acid catalysts.

The 70−95% HF containing modified poly(hydrogen fluoride) ionic liquids and related solid polymeric resins have helped to alleviate the volatility and toxicity of neat anhydrous HF to a great extent. A specific application that we report now is the isobutane-isobutylene/2-butene alkylation using pyridinium poly(hydrogen fluoride) (**PPHF**) as a catalyst and ionic reaction medium. This and related systems are very efficient catalysts for the alkylation process for producing high octane alkylate (The basis of UOP’s **Alkad process**).[20]

## Results and Discussion

**Application of Amine-(HF)$_n$ Ionic Liquids (Onium Poly-Hydrogen Fluorides) in Alkylation.** Alkylation of isobutane with various alkenes is a major process in petroleum industry. The major alkylation plants utilize anhydrous hydrogen fluoride or sulfuric acid based technology.[24] These technologies however, carry serious environmental and safety risks. In this context, extensive efforts have been made to modify the existing processes and to develop new catalysts, which are environmentally more benign and stable.[25] Isomerization of $C_{5-8}$ paraffinic hydrocarbons has been achieved with ionic liquids derived from trialkylamine-HCl−$AlCl_3$ combination.[26] Similar catalysts have been found to be useful for the alkylation of isobutane with butenes.[27] However, these systems due to the ionic combinations

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*Table 1.* Alkylation of Isobutane with Isobutylene and 2-Butene Catalyzed by Pyridine/HF (1:22) Complex

| exp no. | I | II | III | IV |
|---|---|---|---|---|
| olefin/alkane | isobutylene/isobutane | | | 2-butene/isobutane |
| ratio | 1/12 | 1/12 | 1/12 | 1/12 |
| time (min.) | 3 | 20 | 40 | 3 |
| $T$ (°C) | 36 | 36 | 32 | 36 |
| $C_5$ | 6.9 | 7.5 | 6.0 | 9.3 |
| $C_6$ | 6.4 | 7.0 | 5.8 | 2.6 |
| $C_7$ | 6.6 | 7.5 | 6.2 | 2.7 |
| $C_8$ | 51.7 | 61.1 | 65.8 | 41.3 |
| 2,2,4-TMP | 29.8 | 34.5 | 38.9 | 13.4 |
| sum $C_5-C_8$ | 71.6 | 83.1 | 83.8 | 55.9 |
| $C_9^+$ | 28.5 | 17 | 16.2 | 44.1 |
| RON | 87.3 | 90.3 | 91.1 | 85.9 |

*Table 2.* Alkylation of Isobutane with Isobutylene and 2-butene Catalyzed by Poly(ethylenimine)/HF (1:22) Complex

| exp no. | I | II | III | IV | V |
|---|---|---|---|---|---|
| olefin/alkane | isobutylene/isobutane | | 2-butene/isobutane | | |
| ratio | 1/12 | 1/24 | 1/12 | 1/24 | 1/12 |
| time (min.) | 3 | 3 | 3 | 3 | 10 |
| $T$ (°C) | 36 | 36 | 36 | 36 | 36 |
| $C_5$ | 4.6 | 3.7 | 5.7 | 3 | 5 |
| $C_6$ | 5.1 | 4.5 | 5.7 | 4.1 | 5.5 |
| $C_7$ | 6 | 5.9 | 6.5 | 5.2 | 6.6 |
| $C_8$ | 64.1 | 76.2 | 66.6 | 79.8 | 67.3 |
| 2,2,4-TMP | 35.8 | 42.8 | 28.6 | 35.2 | 29.9 |
| sum $C_5-C_8$ | 81.6 | 90.3 | 84.6 | 92.1 | 84.4 |
| $C_9^+$ | 18.4 | 9.7 | 15.4 | 7.9 | 15.6 |
| RON | 90.8 | 93.3 | 91.4 | 93.7 | 91.7 |

in the involved ionic liquids can give complex products. As mentioned earlier, we have been interested for some time in ionic poly(hydrogen fluoride) complexes and developed, for example a 30/70 pyridinium poly(hydrogen fluoride) based liquid fluorinating agent. This system, however, is not suitable as an HF equivalent catalysts for isobutane-isobutylene or 2-butene alkylation process to give high octane alkylates. As reported in the present paper only compositions containing higher ratios of HF effect alkylations. Complexation of HF with amines reduces the volatility significantly, making it a safer and more convenient catalyst system for isoparaffin-olefin alkylation. In the case of accidental release to the atmosphere, toxic HF aerosol cloud formation is greatly reduced or diminished (up to 95%) and the acid can be easily neutralized and washed off. The **PEIHF** complex generated from ethyleneimine polymer (**PEI**) is highly water soluble, and is still more advantageous in the synthesis of alkylates. Our recent studies[28a,b] have shown that modified HF equivalent systems contain sufficient amount of immobilized HF, which provides sufficient acidity for the isomerization of pivalaldehyde to methyl isopropyl ketone.

All presently studied HF complexes of selected poly(ethylenimine) (linear, low molecular weight and high molecular weight) afforded high quality alkylate. The possible HF contamination of the alkylate is minimal or can be eliminated by aqueous washing. The reaction conditions were optimized using **PEIHF** and **PPHF** as typical ionic liquid catalysts with such variables as temperature, residence time, hydrocarbon ratio, etc. (See Tables 1 and 2). The useful onium poly(hydrogen fluoride) ionic liquid systems studied had up-to-a ratio 22:1 of HF:pyridine (or **PEI**) and were found to be effective for isoparaffin−olefin alkylation giving high octane alkylate. The studied systems are highly efficient and economic HF equivalent catalysts as well as efficient ionic liquid media for alkylation.

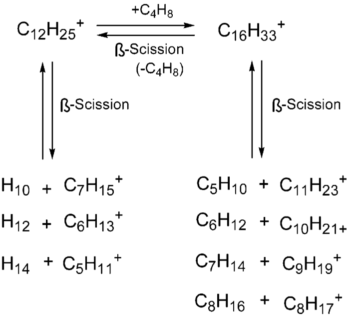
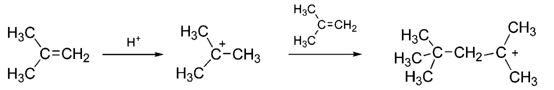
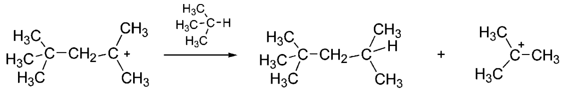


*Figure 1.* Pathway for the formation of light and heavy products in the isobutane/butene alkylation.

Acid catalyzed alkylation is mechanistically considered as a chain process as shown by eqs 1 and 2. In isobutane-isobutylene alkylation, efficiency of alkylation is manifested through the formation of high amounts of 2,2,4-trimethylpentane (2,2,4-TMP, research octane number = 100). It is formed through an intermediate $i$-$C_8^+$ cation that abstracts hydride from isobutane forming the *tert*-butyl cation, which keeps the catalytic cycle going.


(1)


(2)

At the same time, a variety of side reactions can occur depending on the reaction conditions. The $i$-$C_8^+$ ion can undergo isomerization through skeletal and nonbranching rearrangements caused by hydride and methyl shifts giving various isomeric cations leading to the formation of different octane isomers. The ion can add to isobutylene to form higher homologues , $i$-$C_{12}^+$, $i$-$C_{16}^+$, etc. These cations lead to the formation of heavier alkanes (by hydride abstraction) or alkenes (by deprotonation). The larger isomeric carbocations also tend to cleave into smaller carbocations ($C_5^+$, $C_6^+$, and $C_7^+$) and alkenes. These cleavage reactions, through a $\beta$-scission pattern, can be considered as the reverse process of the addition of carbocations to alkenes (eqs 1−3 and Figure 1).[29]

$$i\text{-}C_{12}H_{25}^+ \rightarrow i\text{-}C_5H_{11}^+ + i\text{-}C_7H_{14} + i\text{-}C_6H_{13}^+ + i\text{-}C_6H_{12} \quad (3)$$

It is well recognized that the alkylation of isobutane with olefins depends on the acid strength. Catalyst acidity may affect differently the major reaction pathway and the side reactions. The acidity of the onium poly(hydrogen fluoride) complexes depends on their composition affecting the equilibrium with free HF, so does their catalytic activity for alkylation. In all of the alkylation reactions, there was a 98−100% conversion of the olefin. The alkylate composition and quality varied depending

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***Table 3.*** Stability (Volatility) of HF and Onium Poly(Hydrogen Fluorides)

| HF or amine: HF complex | amine: HF wt % | amine: HF molar ratio | threshold HF volatility temp. ($\rho$, °C) |
|---|---|---|---|
| HF | 0:100 | 0:100 | 18 |
| pyridine:HF | 15:85 | 1:22 | 32 |
| | 20:80 | 1:16 | 36 |
| | 25:75 | 1:12 | 42 |
| | 30:70 | 1:9 | 50 |
| triethylamine:HF | 18.7:81.3 | 1:22 | 30 |
| | 22.7:77.3 | 1:17 | 36 |
| | 25:75 | 1:15 | 40 |
| | 27.4:72.6 | 1:13 | 50 |
| poly(ethylenimine):HF | 8.9:91.1 | 1:22 | 23 |
| | 15:85 | 1:12 | 34 |
| | 17.7:82.3 | 1:10 | 39 |
| aniline:HF | 17.7:82.3 | 1:22 | 32 |
| | 20:80 | 1:18 | 34 |
| *N*,*N*-dimethylaniline:HF | 22:78 | 1:20.3 | 32 |
| 4-picoline:HF | 17.6:82.4 | 1:22 | 32 |
| imidazole:HF | 14:86 | 1:21 | 33 |
| quinoline:HF | 26.3:73.7 | 1:18.1 | 37 |
| poly(vinylpyridine):HF | 19.5:80.5 | 1:22 | 24 |

on the different conditions employed. At 36 °C, in 3 min complete conversion of the olefin was observed.

**Stability of the Onium Poly(Hydrogen Fluoride) Complexes.** The volatility of anhydrous hydrogen fluoride catalyst can be substantially decreased or eliminated by forming complexes with organic bases such as ammonia, alkylamines, pyridine, and varied organic bases. HF complexes of a number of bases were prepared and the stablility of these ionic liquids have been studied (as defined by the threshold volatility temperature). The temperature at which the complex loses more than 1% weight is referred to as the threshold temperature of HF-release. The data in Table 3 show that the threshold temperature of volatility increases with increasing molar ratio of bases to HF but changes little with the use of different bases (mentioned in Table 3) in same molar ratio. Threshold volatility temperature ($\rho$) of HF (18 °C) increases to 32 °C with the addition of 15% (by weight) of pyridine.

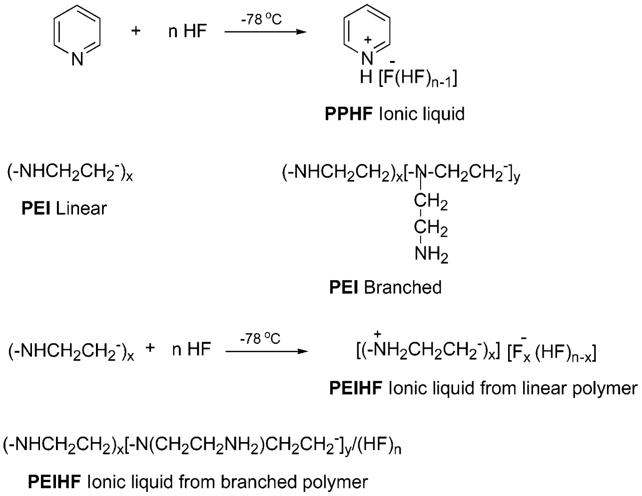
We found that there are no simple relationships between the basicity of the used additives and the stability of its corresponding onium poly(hydrogen fluoride) ionic liquids formed with the same molar ratio. For example, aniline, and *N*,*N*-dimethylaniline (p$K_a$ of $BH^+$ 3−5) are much weaker bases compared to pyridine (p$K_a$ of $BH^+$ 9) and alkylamines (p$K_a$ of $BH^+$ 10−12). However, aniline:HF (molar ratio 1:22) and pyridine:HF (molar ratio 1:22) complexes have equal threshold decomposition temperature of 32 °C. The process of the formation of onium poly(hydrogen fluoride) can be divided into two steps, i.e., the formation of $BH^+$ and $F^-$ in the gas phase by reacting one mole base with one mole HF (reaction 4) and the process of transferring the $BH^+$ and $F^-$ ions from the gas phase into the poly(hydrogen fluoride) liquid phase (eq 5).

$$B_{(g)} + HF_{(g)} \rightarrow BH^+_{(g)} + F^-_{(g)}\ \Delta G_{(g)} \qquad (4)$$

$$BH^+_{(g)} + F^-_{g} + nHF_{(l)} \rightarrow BH^+F(HF)^-_{n(l)}\ \Delta G_{(l)} \qquad (5)$$

Obviously basicity is a determining factor for the thermodynamics of $BH^+$ formation. However, the stability of the onium poly(hydrogen fluoride) probably largely depends on the interaction of $BH^+$ ion and fluoride ion with the bulk hydrogen fluoride (network of hydrogen bonding).[19d,21,30] This may not have a simple correlation with the basicity of the original conjugate base. Instead, such interactions can be best characterized by the free energy changes ($\Delta G_{(l)}$) for transferring the $BH^+$ and fluoride ion from gas phase into the hydrogen fluoride solution.

***Scheme 2***



**HF Immobilized on Solid Polymeric Amines as Alkylation Catalysts.** Attempts to replace liquid acid catalysts by solids for efficient alkylation process have not yet been fully successful.[31] A wide variety of solid acids such as Nafion-H/silica nanocomposite,[32] sulfated zirconia and heteropoly acid derivatives[33] have been tested. Despite promising laboratory results, fast deactivation of the catalyst impeded industrial application. However, due to its enormous potential and practical importance, solid acid catalysis is still in the forefront of alkylation research.[34] The immobilization of hydrogen fluoride with polymers was first reported by Zupan and co-workers[35] with limited success. More recently, we reported the preparation of a well immobilized form of hydrogen fluoride, i.e., poly(4-vinylpyridinium) poly(hydrogen fluoride) (**PVPHF**, Scheme 4) and its use as versatile fluorinating agent.[36] Herein, we also report the development and application of related environmentally friendly solid HF complexes as alkylation catalysts to produce high octane gasoline. Their use minimizes the environmental hazards and provides easy and safe handling as these catalysts can easily be separated from the alkylate and recycled.[37]

As a convenient solid catalyst base, commercially available polymeric poly(4-vinylpyridine) (**PVP**) resin has been selected giving the corresponding poly(hydrogen fluoride) complex (**PVPHF**). The catalyst for alkylation reactions can be prepared easily by following our earlier method.[36] The alkylation of

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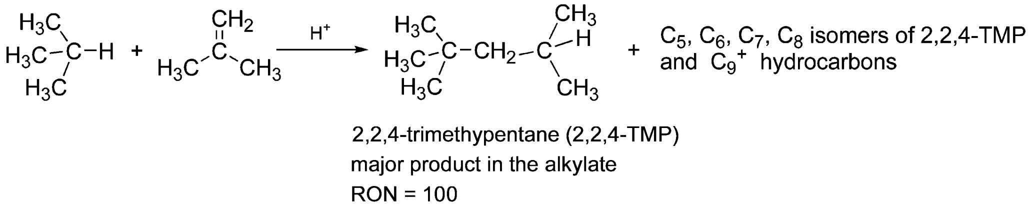
*Scheme 3*



*Scheme 4*

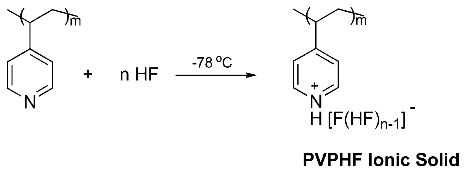


***Table 4.*** Effect of Experimental Variables on the Alkylation of Isobutane with Isobutylene/2-Butene Catalyzed by PVPHF Complex

| exp no. | I | II | III | IV | V | VI | VII |
|---|---|---|---|---|---|---|---|
| olefin/alkane | isobutylene/isobutane | | 2-butene/isobutane | | | | |
| ratio | 1/12 | 1/24 | 1/12 | 1/24 | 1/12 | 1/12 | 1/24 |
| time (min.) | 3 | 3 | 3 | 3 | 10 | 10 | 10 |
| $T$ (°C) | 36 | 36 | 36 | 36 | 36 | 22 | 7 |
| $C_5$ | 5.1 | 3.8 | 4.4 | 2.9 | 4.1 | 3.6 | 7.4 |
| $C_6$ | 5.3 | 4.5 | 4.5 | 3.5 | 4.7 | 2.7 | 2.1 |
| $C_7$ | 6.2 | 5.7 | 5.5 | 4.9 | 6 | 4.2 | 2.6 |
| $C_8$ | 67.9 | 74.5 | 73.7 | 81.8 | 70 | 73.7 | 68.8 |
| 2,2,4-TMP | 39.9 | 44.4 | 33.1 | 38.8 | 31.7 | 32.3 | 27.4 |
| sum $C_5-C_8$ | 84.5 | 88.5 | 88 | 93.1 | 84.7 | 84.2 | 80.9 |
| $C_9^+$ | 15.5 | 11.5 | 12 | 6.9 | 15.3 | 15.8 | 19.1 |
| RON | 91.3 | 92.9 | 92.5 | 94 | 91.3 | 93 | 93.4 |

***Table 5.*** Comparison of N-Containing Polymer Immobilized HF Catalysts with HF and Sulfuric Acid in the Isobutane−Isobutylene Alkylation

| catalyst | HF | $H_2SO_4$ | PPHF | PEIHF | PVPHF |
|---|---|---|---|---|---|
| olefin/alkane | isobutylene/isobutane | | | | |
| ratio | 1/12 | 1/12 | 1/12 | 1/24 | 1/24 |
| time (min.) | 3 | 20 | 40 | 3 | 3 |
| $T$ (°C) | 36 | 36 | 32 | 36 | 36 |
| $C_5$ | 4.1 | 9.0 | 6.0 | 3.7 | 3.8 |
| $C_6$ | 3.7 | 8.1 | 5.8 | 4.5 | 4.5 |
| $C_7$ | 5.0 | 8.4 | 6.2 | 5.9 | 5.7 |
| $C_8$ | 77.5 | 39.2 | 65.8 | 76.2 | 74.5 |
| 2,2,4-TMP | 48.4 | 14.2 | 38.9 | 42.8 | 44.4 |
| sum $C_5-C_8$ | 90.4 | 64.7 | 83.8 | 90.3 | 88.5 |
| $C_9^+$ | 9.6 | 35.3 | 16.2 | 9.7 | 11.5 |
| RON | 93.6 | 86.4 | 91.1 | 93.3 | 92.9 |

isobutane with isobutylene/2-butene was carried out in a pressurized well stirred closed batch reactor.[38] The solid catalyst was found to be stable at room temperature for prolonged times and was repeatedly reused.

The structure of the polymeric resin expectedly has a significant effect on the complex formation with HF. Linear (non cross-linked) PVP did not give practically useful poly(hydrogen fluoride) complex, it did not swell but formed only a highly viscous and sticky material. Cross-linked samples can immobilize limited amounts of HF, the swelling of the 25% cross-linked sample is strongly limited due to the rigid backbone. PVP with 2% cross-linking was found to be most suitable for poly(hydrogen fluoride) complex preparation for catalytic purpose, since it could immobilize high amount of HF (up to a HF to PVP weight ratio ~5) still remaining as a convenient solid. As a result, alkylations were carried out using commercial (Sigma-Aldrich) 2% cross-linked PVP. For reported fluorination reactions PVPHF complex containing about 7 equivalents of hydrogen fluoride to one equivalent of 4-vinylpyridine unit was used.[36] However, PVPHF complex containing 22 equivalents of hydrogen fluoride to one equivalent of 4-vinylpyridine unit has been used for alkylations due to the higher acidity requirement of the reaction. As shown in Table 4, the product distribution gradually changes with change in temperature. Increase in temperature resulted in higher amount of light products ($C_5-C_7$ fractions), with decrease in the amounts of higher oligomers ($C_9^+$ fraction). These changes are due to the increasing acidity of the catalyst system, which initiates more cracking. Since the HF alkylation reactions are carried out in practice at 35−37 °C, we carried out majority of these reactions at 36 °C except for temperature dependence studies.

The effect of residence time and temperature of the reaction can be identified from change in the yield and quality of the alkylate within given limits (Table 4). The alkylate quality increases with longer reaction time and higher temperature (7−36 °C). However, this increase becomes limited after 20 min reaction time. Most likely the system reaches a close-to-equilibrium state and the product distribution does not change significantly further. One of the most important parameters is the ratio of the alkane:alkene hydrocarbon mixture. Under standard conditions isobutane: isobutylene ratio (molar) of 12:1 was used. Increase in this ratio to 24:1 significantly increased the alkylate quality. As shown, the distribution of the most valuable $C_8$ fractions and isooctane increased considerably. This enhancement is due to the dilution effect by the higher amount of isobutane (hydride source), which increases the efficiency of hydride-transfer to the cations formed, and suppresses the oligomerization reactions responsible for higher $C_9^+$ hydrocarbons. Since the acidity of HF (containing some moisture) is $\sim H_0 = -11$ (This is $-15.1$ if completely devoid of water), the addition of polymeric organic bases in relatively small amounts (usually in HF/N = 22 ratio) does not decrease the acidity below the known optimum, that is $\sim H_0 = -10.8$[39] for alkylation reactions.

Since the catalyst's lifetime, regeneration and recycling are also important factors in the evaluation of new catalyst system, we tested the catalyst recycling in the alkylation reactions. The PVPHF catalyst was reused in several concecutive reactions by removing the alkylate from it and introducing the new reactant mixture. The catalyst showed similar performance in the first four reactions though noticeable change in selectivity/product quality with higher ratio of $C_9^+$ fraction was observed in further reactions. This is most likely due to acidity decrease by slow

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HF leaching from the catalyst. The PVPHF systems have catalytic efficiency comparable to that of HF with substantial decrease of HF volatility. The alkylate quality obtained with the amine based HF catalysts considerably exceeds that obtained with $H_2SO_4$ and is very close to that obtained with neat HF (Table 5). All the alkylates have suitable high octane characteristics.

## Conclusion

In conclusion, new environmentally safe, immobilized liquid and solid modified HF catalysts were developed and used for isobutane-olefin alkylations. Being ionic complexes of amines and anhydrous HF, the ionic liquid compositions are efficient media and HF equivalent catalysts for alkylations. They decrease the volatility of anhydrous HF and as a result, HF release to the atmosphere in case of accidents is decreased allowing easy neutralization. The handling, use, recycling and regeneration of the catalysts are convenient. Both the liquid and solid polymer based poly(hydrogen fluoride) catalysts can be advantageously applied in alkylation process representing environmentally benign and safer conditions readily adaptable to the existing refinery alkylation units.

## Experimental Section

**Materials and Methods.** ***Caution!*** *HF and HF-amine complexes are highly corrosive and can cause severe damages to eyes, skin and lungs. Precautions have to be taken (wearing proper safety masks, gloves and glasses) while handling them.* Isobutane, isobutylene and 2-butene were commercially available from Matheson (>99% purity) and Sigma-Aldrich and used without further purification. Anhydrous HF (Matheson, >99.5% purity) was condensed in an acetone-dry ice bath and was used in liquid form. Pyridine, poly(ethylenimine) (Linear, low molecular weight or high molecular weight) Poly(4-vinylpyridine) (2% cross linked) and all amines were purchased from Aldrich and used as received.

The catalysts were prepared on the basis of methods described earlier.[19d,36] Pyridine (15 g) was taken into a 250 mL Nalgene bottle and cooled in a dry ice-acetone bath (−78 °C). Liquid HF (85 g) was added carefully in small portions (a few drops initially and increase the amount slowly) at −78 °C. Complex is stored in a refrigerator.

**Typical Alkylation Procedure.** An autoclave (**A**, 600 mL, Monel) equipped with a dropping tube reaching to half of the height of the reactor was purged with argon and loaded with 100 g PPHF catalyst at −78 °C. It was then warmed to 36 °C under stirring (720 rpm). In a second autoclave (**B**, 600 mL, Monel) equipped with a dip tube reaching to the bottom of the reactor 186 mL isobutane and 14 mL isobutylene (12:1 molar ratio isobutane:isobutylene) were mixed at −78 °C. **B** was than pressurized with argon to 500 psi and allowed to reach room temperature. The dip tube of **B** was connected to the addition tube of **A** and the isobutane/isobutylene mixture added to the acid phase under stirring (720 rpm), maintaining the temperature of **A** at 36 °C using a cooling loop. Addition valve was closed after a pressure of 200 psi was reached in **A**. After 3 min, stirring was turned off and reaction mixture was cooled to −78 °C (15 min). The pressure was slowly released and the 2 phases were separated in a Nalgene separatory funnel. The organic phase was placed in a 125 mL Nalgene flask over a known amount of PVP to remove any amount of HF present in the alkylate, allowed to reach 0 °C (ice bath) and stored in a freezer.

GC analysis was performed on a Varian 3400 chromatograph equipped with a FID and a petrocol DH 50.2 column (50 m × 0.2 mm × 0.5 $\mu$m column head pressure 35 psi Helium) with temperature program: 70 °C for 12 min, 15 °C/min to 220 °C, 10 min at 220 °C. Prior to use the syringe was placed in a freezer to enable injection of the cold alkylate.

The actual amount of alkylate obtained after reaction was determined by subtracting the amount of isobutane present in the organic phase (determined by GC). Once the alkylate amount ($C_5-C_9^+$) is known the yield in $C_5$ and $C_5-C_8$ can be determined. Identification of the $C_5$, $C_6$, $C_7$, and $C_8$ hydrocarbons was based on comparison with authentic samples, while heavier hydrocarbons, except 2,2,5-trimethylhexane, were not individually identified and treated as $C_{9+}$ fraction. The numerical results are given in wt % and the research octane numbers were calculated as described in the literature.[38]

**Determination of the Threshold Temperature of HF-Release of Amine-HF Complexes.** Into a 100 mL Nalgene bottle was charged 70 g of the onium poly(hydrogen fluoride) and fitted at its top with a polyethylene tube (diameter, 2 mm) which was kept under $N_2$ at atmospheric pressure. The bottle was then kept in a thermostatically controlled bath at the chosen temperature for 1 h. The weight change after the treatment was measured. The bath temperature was raised by increments of 1 °C until more than 1% weight loss was found at a given temperature. The temperature at which the complex loses more than 1% weight is referred to as the threshold temperature of HF-release.

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