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Super acid catalysis in supercritical fluid reaction media for the formation of linear alkyl benzenes

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High catalytic activity is demonstrated for the formation of linear alkylbenzenes using a perfluorosulfonic acid catalyst in supercritical fluid reaction media: enhanced alkylation activity is observed in fluoroform (CHF_3) compared to carbon dioxide.

Organic synthesis reactions in the chemical, polymer, and pharmaceutical industries are increasingly required to be highly selective, economical, and environmentally benign. As one means of developing such processes, the use of supercritical fluid (SCF) media as reaction solvents for catalysis has been the subject of increasing investigation over the last two decades because of a number of potential advantages afforded by these media over conventional liquid solvents and gaseous diluents.[1–3] In particular, SCFs provide a single reaction media in which the solvent and transport properties can be varied significantly and continuously.

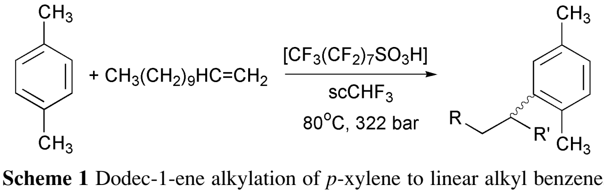
It is well known that the density-dependent properties of a SCF solvent (*e.g.* solubility, diffusivity, viscosity, and heat capacity) can be manipulated with relatively small changes in temperature and pressure. Polar solvents have the added feature of an adjustable dielectric constant. In catalysis applications, one can potentially exploit the resulting effects of these ‘tunable’ solvent features in a variety of ways; such as through enhancing component[4] and catalyst[5] solubilities, influencing kinetic rates through both temperature and pressure effects as well as shifting equilibrium constants to favor desired products,[6] increasing selectivity and yields (*e.g.* by manipulating the solvent dielectric constant[7] or viscosity[8]), reducing mass transfer limitations in diffusion-limited reactions,[9] controlling the temperature in highly exothermic reactions through adjustment of the solvent heat capacity,[10] minimizing heterogeneous catalyst deactivation through prevention of coking and extraction of fouling products,[11] and facilitating the separation and recovery of reaction products. Thus, the solvent environment can be optimized for a specific reaction application by tuning the various density-dependent fluid properties.[12] There is tremendous opportunity for successfully exploiting these potential advantages in economical, commercial processes.

There is a growing need in the Petroleum and Fine Chemicals markets for replacement of strong acid catalysts such as HF, BF_3, and $AlCl_3$ with economical alternatives that are more environmentally benign and ‘process friendly’. One reaction of interest is the alkylation of benzene with C_{12} olefins for the formation of linear alkyl benzenes (LABs). These materials, when sulfonated, represent the basis of the detergents industry. The development of new types of low cost catalysts for this class of reactions would be advantageous since the current commercial catalysts are HF and $AlCl_3$, both of which suffer from waste handling and process safety issues.[13] Hitzler *et al.*[14] have described a Friedel–Crafts alkylation in SCFs using a polysiloxane-supported solid acid catalyst. For the alkylation of mesitylene and anisole with propene and propan-2-ol, 100% selectivity to the mono-alkylated products was obtained with 50% conversion. Non-catalytic and selective alkylation of phenol with propan-2-ol in supercritical water has also recently been reported.[15] The use of SCF solvents combined with the super acid catalysts, perfluorosulfonic acids $[CF_3(CF_2)_nSO_3H]$,[16–18] is one further possibility to consider for applications in a variety of commercially important reactions such as linear alkylbenzene formation, acylations, olefin isomerizations, disproportionations, and oligomerizations. The longer chain acids ($> C_3$) are insoluble solids in SCF solvents at low temperatures, which allows easy separation of the catalyst from the reaction mixture.

Two potential limitations of these long chain perfluorosulfonic acid catalysts in liquid solvents are low solubility in non-polar liquids for homogeneous applications and low activity, which results from what is believed to be head-to-head clustering of the acid end groups. This clustering may inhibit access of reactants to the active acid sites. Conducting these reactions in SCF media could potentially overcome these limitations by (1) tailoring the length of the perfluorinated ‘tail’ to optimize catalyst solubility, and (2) pressure tuning the solvent strength and polarity of the fluid phase to minimize clustering of the acid end groups. We have found that the dodec-1-ene alkylation of *p*-xylene in supercritical fluoroform ($scCHF_3$) using $CF_3(CF_2)_7SO_3H$ as catalyst (Scheme 1) takes place with high yield to the desired alkylate. This represents a potential improvement over the present HF-based processes.

The use of SCF solvents for conducting this reaction was first investigated using supercritical carbon dioxide ($scCO_2$) as the reaction media. The reactions were run in a high-pressure view cell reactor to allow visual observation of the solution phase behavior during the experiment. The catalyst $CF_3(CF_2)_7SO_3H$ was selected as representative of the perfluorosulfonic acids for evaluating their solubility and activity in $scCO_2$. The catalyst was prepared as described in the literature[16] with the following modification. The as-prepared catalyst was treated with an equal volume of thionyl chloride, which was removed under vacuum (this served to remove any traces of moisture from the catalyst). The catalyst was then purified by sublimation yielding a white, pure perfluorooctane sulfonic acid, which was subsequently handled in a dry box. The catalyst was found to be sparingly soluble (order of 0.015 M) in $scCO_2$ at the reaction conditions of 80 °C and 322 bar. The model alkylation reaction noted above was investigated to test the catalyst activity under these homogeneous reaction conditions. Only traces of the desired LAB reaction product were observed after 2 hours reaction time (Table 1). However, appreciable (68%) isomerization of the dodec-1-ene reactant to a mixture of internal olefins was seen, with 85% representing thermodynamic equilibrium.

These results indicate that $scCO_2$ solubilizes the long-chain perfluorosulfonic acid $CF_3(CF_2)_7SO_3H$ which initiates catalytic activity of these molecules. However, the poor conversion to the LAB product suggests that the availability of the acid sites is still limited at these conditions despite the apparent solubility of



Scheme 1 Dodec-1-ene alkylation of *p*-xylene to linear alkyl benzenes.

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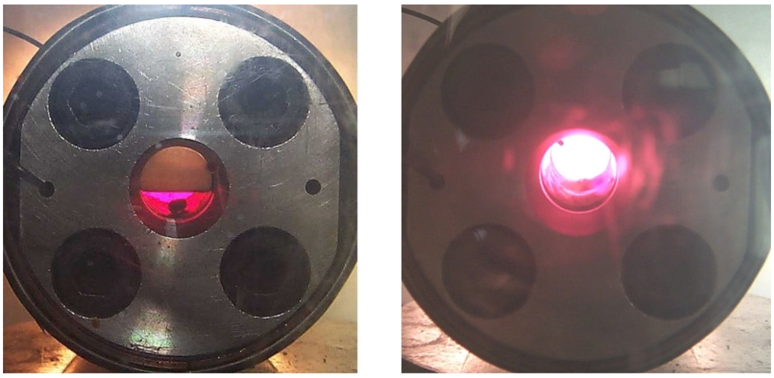
(a) (b)

Fig. 1 Transition to the SCF state at 80 °C: (a) 1 bar, and (b) 322 bar.

Table 1 Dodecene alkylation of *p*-xylene with $CF_3(CF_2)_7SO_3H$ catalyst[a]

Solvent	1-C_{12} Conv. to LAB	1-C_{12} Isomerization Products[b]
None[c]	0	< 1
CO_2[d]	1	68
CHF_3[d]	90	7–9

[a] Reactions conducted for 2 h using 0.010 mol dodec-1-ene, 0.030 mol *p*-xylene, and 0.15 g of catalyst. [b] Value shown represents conversion of the non-alkylated α-olefin to an internal olefin mixture with 85% being close to thermodynamic equilibrium. [c] 100 °C, 1 bar. [d] 80 °C, 322 bar.

the catalyst. This presumed clustering of end groups may affect both the number and strength of the available acid sites. Following removal of the CO_2, the acid precipitates from the products allowing easy separation and recovery.

The reaction was repeated in $scCHF_3$ which was selected as an alternative polar solvent since it has a similar critical temperature to CO_2 (T_{c,CO_2} = 31 °C, T_{c,CHF_3} = 26 °C). Fig. 1 shows the reaction vessel and the transition to the SCF state. Fig. 1(a) shows the clear phase separation of the reactants and the CHF_3 solvent at 80 °C and low pressure. On increasing the pressure above the mixture critical point, a single, homogeneous phase is obtained, as shown in Fig. 1(b). The catalyst appeared completely soluble at 0.015 M concentration. Table 1 shows the results of the catalytic runs. These results demonstrate that conducting this reaction in $scCHF_3$ results in significant activation of the catalyst and appreciable yields of the LAB product at a catalyst concentration comparable to that of the reaction in CO_2. The high conversion (90%) with the C_8 perfluorosulfonic acid catalyst is particularly significant since, to the authors' knowledge, activation of this catalyst for linear alkylbenzene formation has not previously been accomplished in conventional liquid-phase reactions**.** Values for the LAB product distribution are as follows: 2-Ø(28%), 3-Ø(19%), 4-Ø(16%), 5-Ø(17%), and 6-Ø(20%), where Ø denotes phenol and the number refers to the substitution on the dodec-1-ene.

In summary, we have found that the dodec-1-ene alkylation of *p*-xylene using SCF fluoroform as solvent proceeds in high yield. In contrast, isomerization of the α-olefin is primarily observed using $scCO_2$ with only a small yield of the alkylated product. This demonstrates tuning of the reaction pathway depending upon the solvent characteristics within the SCF media. For this case of perfluorsulfonic acids, the detailed effect of these solvents is not understood, but is believed to be associated with disruption of clustering of the acid end groups. This example illustrates use of a SCF solvent to define reaction chemistry in a catalysis application.

Notes and references

1 *Chemical Synthesis Using Supercritical Fluids*, ed. P. G. Jessop and W. Leitner, Wiley-VCH, Weinheim, Germany, 1999.

2 K. W. Hutchenson, in *Supercritical Fluid Technology in Materials Science and Engineering*, ed. Y.-P. Sun, Marcel Dekker, New York, in press.

3 R. S. Oakes, A. A. Clifford and C. M. Rayner, *J. Chem. Soc., Perkin Trans. 1*, 2001, 917.

4 Y. Sun, R. N. Landau, J. Wang, C. LeBlond and D. G. Blackmond, *J. Am. Chem. Soc.*, 1996, **118**, 1348.

5 P. G. Jessop, T. Ikariya and R. Noyori, *Chem. Rev.*, 1999, **99**, 475.

6 K. P. Johnston, *Nature*, 1994, **368**, 187.

7 D. C. Wynne and P. G. Jessop, *Angew. Chem., Int. Ed. Engl.*, 1999, **38**, 1143.

8 T. Aida and T. G. Squires, in *Supercritical Fluids: Chemical and Engineering Principles and Application*, ACS Symposium Series No. 329, ed. T. G. Squires and M. E. Paulaitis, American Chemical Society, Washington, D.C., 1987, p. 58.

9 P. G. Jessop, T. Ikariya and R. Noyori, *Nature*, 1994, **368**, 231.

10 D. J. Bochniak and B. Subramaniam, *AIChE J.*, 1998, **44**, 1889.

11 B. Subramaniam and A. Jooma, in *Innovations in Supercritical Fluids: Science and Technology*, ACS Symposium Series No. 608, ed. K. W. Hutchenson and N. R. Foster, American Chemical Society, Washington, D.C., 1995, p. 246.

12 C. A. Eckert and K. Chandler, *J. Supercrit. Fluids*, 1998, **13**, 187.

13 K. Tanabe and W. F. Holderich, *Appl. Catal. A*, 1999, **181**, 399.

14 M. G. Hitzler, F. R. Smail, S. K. Ross and M. Poliakoff, *Chem. Commun.*, 1998, 359.

15 T. Sato, G. Sekiguchi, T. Adschiri and K. Arai, *Chem. Commun.*, 2001, 1566.

16 X. Fu, M. He, Q. Lei and B. Luo, *Syn. Commun.*, 1991, **21**, 1273.

17 X. Fu, W. Pu, B. Luo and C. Deng, *Chin. J. Chem.*, 1993, **4**, 307.

18 H. Choukroun, A. Germain, D. Brunel and A. Commeyras, *Nouv. J. de Chimie*, 1981, **5**, 39.