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# Friedel−Crafts Alkylation of Anisole in Supercritical Carbon Dioxide: A Comparative Study of Catalysts

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## Abstract:

**The Friedel−Crafts alkylation of anisole with *n*-propanol was carried out over five different Brønsted solid acid catalysts using supercritical carbon dioxide as the reaction medium. The reaction temperature and pressure were evaluated in terms of selectivity for the monoalkylated products, conversion of the starting material, and the products' isomeric ratio. Desulfonation of the catalysts was observed when the temperature was increased above 150 °C for the organic supported catalysts investigated Amberlyst 15 and Purolite CT-175, and above 200 to 250 °C for the inorganic supported catalysts Nafion SAC-13 and Deloxan ASP I/7. A decrease in the catalytic performance of organic supported catalysts was observed with increasing pressure. This decrease was related to the phase behaviour of the reaction.**

## 1. Introduction

The Friedel−Crafts alkylation reaction is among the most fundamental and useful reactions for carbon−carbon bond formation in aromatic systems.[1] Although Friedel−Crafts chemistry is one of the most wasteful in terms of byproduct formation, atom efficiency,[2] and catalyst usage,[3] it is widely applied in the fine chemicals industry.[4] Typically, the reaction is performed using an alkyl halide in the presence of Lewis acids, such as $AlCl_3$ or $BF_3$,[5] or protic acids, such as HF or concentrated $H_2SO_4$.[6] In particular, anhydrous $AlCl_3$ has maintained its wide use in solution chemistry since it was introduced by Friedel and Crafts in 1877.[7]

Due to the importance of the Friedel−Crafts alkylation reaction in industry,[4] a variety of new, more environmentally friendly and efficient catalysts have been reported in the literature. Examples of these include *p*-toluensulfonic acid monohydrate (TsOH),[8] trifluoromethanesulfonic acid (TFSA) modified with trifluoroacetic acid (TFA) or water,[9] rare earth metal trifluoromethanesulfonates[10,11] all as homogeneous catalysis and mesoporous molecular sieves,[12,13] organic resins,[14,15] sulfated metal oxides,[16] clays,[17,18] and zeolites[4,13] for heterogeneously catalysed Friedel−Crafts alkylation reactions.

The advantages of using heterogeneous catalysts include reduced equipment corrosion, ease of product separation, less potential contamination in waste streams, recycling of the catalysts, and also the possibility of carrying out Friedel−Crafts reactions continuously with a fixed catalyst bed rather than in traditional batch reactors.[14,19] Continuous reactors are generally smaller and safer than batch reactors with equivalent production capacity.[20] In addition, batch reactions in $scCO_2$ are relatively difficult to scale up as a result of the high cost associated with the high-pressure vessels needed. Continuous fixed-bed catalytic flow reactors, using $scCO_2$ as the reaction medium, have already been scaled up to commercial scale by Thomas Swan & Co. Ltd.[21] This facility is a multipurpose plant; thus, changing the catalyst within the reactor changes the chemistry.

To investigate whether the catalytic activity of heterogeneous catalysts changes under supercritical conditions is of crucial importance for the chemical manufacturer in the event of scaling-up a particular process. In this investigation, the effect of $scCO_2$ on the catalytic activity of a variety of commercially available solid acid catalysts, by varying the reaction $p$ and $T$, was evaluated for the alkylation of anisole with *n*-propanol (Scheme 1).

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(1) Olah, G. A. *Friedel-Crafts and Related Reactions*; Wiley: New York, 1963−1964; Vol. I−IV.

(2) Constable, D. J. C.; Curzons, A. D.; Cunningham, V. L. *Green Chem.* **2002**, *4*, 521−527.

(3) Sheldon, R. A. *CHEMTECH* **1994**, *24*, 38−47.

(4) Tanabe, K.; Hölderich, W. F. *Appl. Catal., A* **1999**, *181*, 399−434.

(5) Singh, R. P.; Singh, V. K. *Tetrahedron* **2000**, *57*, 241−247.

(6) Harmer, M. A.; Sun, Q.; Vega, A. J.; Farneth, W. E.; Heidekum, A.; Hoelderich, W. F. *Green Chem.* **2000**, *2*, 7−14.

(7) Friedel, C.; Crafts, J. M. *Comptes Rendus* **1877**, *84*, 1392−1450.

(8) Mahindaratne, M.; Wimalasena, K. *J. Org. Chem.* **1998**, *63*, 2858−2866.

(9) Olah, G.; Torok, B.; Prakash, S. *Appl. Catal., A* **1996**, *146*, 107−117.

(10) Kawada, A.; Mitamura, S.; Matsuo, J.; Tsuchiya, T.; Kobayashi, S. *Bull. Chem. Soc. Jpn.* **2000**, *73*, 2325−2333.

(11) Kobayashi, S.; Sugiura, M.; Kitagawa, H.; Lam, W. W. L. *Chem. Rev.* **2002**, *102*, 2227−2302.

(12) Selvaraj, M.; Pandurangan, A.; Seshadri, K. S.; Sinha, P. K.; Krisnashami, V.; Lal, K. B. *J. Mol. Catal. A: Chem.* **2002**, *186*, 173−186.

(13) Clark, M. C.; Subramaniam, B. *Ind. Eng. Chem. Res.* **1998**, *37*, 1243−1250.

(14) Harmer, M. A.; Sun, Q. *Appl. Catal., A* **2001**, *221*, 45−62.

(15) Hart, M.; Fuller, G.; Brown, D. R.; Park, C.; Keane, M. A.; Dale, J. A.; Fougret, C. M.; Cockman, R. W. *Catal. Lett.* **2001**, *72*, 135−139.

(16) Ginosar, D. M.; Thompson, D. N.; Coates, K.; Zalewski, D. J. *Ind. Eng. Chem. Res.* **2002**, *41*, 2864−2873.

(17) Cseri, T.; Bekassy, S.; Kenessey, G.; Liptay, G.; Figueras, F. *Thermochim. Acta* **1996**, *288*, 137−154.

(18) Miller, J. M.; Goodchild, M.; Lakshmi, L. J.; Wails, D.; Hartman, J. S. *Mater. Lett.* **2000**, *44*, 164−169.

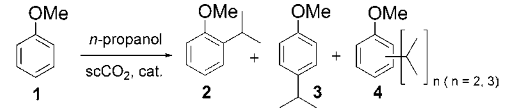
(19) Haag, J. S. *Handbook of Heterogeneous Catalysis*; Wiley-VCH: Weinheim, 1997; Vol. 5.

(20) Tundo, P. *Continuous Methods in Organic Synthesis*; Ellis Horwood: Chichester, 1991.

(21) Licence, P.; Ke, J.; Sokolova, M.; Ross, S. K.; Poliakoff, M. *Green Chem.* **2003**, *5*, 99−104.

10.1021/op050044y CCC: $30.25

***Scheme 1.*** **Friedel-Crafts alkylation of anisole, 1, with *n*-propanol over solid acid catalysts to form *o*-isopropylanisole, 2, *p*-isopropylanisole, 3, and polyalkylated derivatives, 4**



The catalysts investigated included the following: commercially available organic acidic ion-exchange resins (Amberlyst 15 and Purolite CT-175), inorganic supported catalysts (Nafion SAC-13 and Deloxan ASP I/7) in addition to a zeolite (Zeolyst CBV 600). The use of $scCO_2$ as a solvent in our reactions may offer the following advantages: enhancement of the reaction rate and selectivity,[22] enhancement of mass and heat transfer rates, an increase in the catalyst lifetime due to the extraction of coke precursors, and easier separation of the products from the solution after reaction.[23]

There have been a small number of published examples of continuous alkylation reactions using heterogeneous catalysts in $scCO_2$ in the literature,[16,24,25] which demonstrated that aromatic substrates could undergo continuous and sustainable Friedel−Crafts alkylation in supercritical fluids over solid acid heterogeneous catalysts with high selectivity towards the product of interest. However, although the literature shows that Friedel−Crafts alkylation reactions can be carried out in the supercritical phase and in the presence of heterogeneous catalysts, there is no true understanding of the reaction parameters required to perform more productive and selective alkylations.

To achieve a highly selective Friedel−Crafts alkylation in $scCO_2$, a large number of parameters must be investigated and optimised; namely, pressure ($p$), temperature ($T$), alkylating agent, flow rates of $scCO_2$ and substrate, choice of catalyst, and the effect of $scCO_2$ on their catalytic activity. Minor modification of the reaction conditions could lead to dramatic changes to the outcome of the reaction, mainly in terms of selectivity and conversion. For this reason, a deeper knowledge and control of the process is highly desirable from both an industrial and academic point of view.

The main chemical challenge in conventional Friedel−Crafts alkylation reactions is to achieve selective monoalkylation of the substrate. Unfortunately, the addition of the first alkyl group activates the substrate so that subsequent alkylation is made easier.[26] Consequently, reaction parameters have to be controlled precisely, often with high dilution and low temperatures to minimise the formation of polyalkylated products.[25]

## 2. Experimental Section

All of the experiments reported were carried out using **1** and *n*-propanol in a molar ratio of 3:1, and the concentration of the organic mixture in the $scCO_2$ was 10%w/w unless otherwise stated.

***Table 1.*** **Supplier and properties of the commercially available catalysts investigated**

| catalyst | supplier | surface area ($m^2$/g) | loading (meq/g) | $T$ stability (°C) | typical amount loaded[a] (g) |
|---|---|---|---|---|---|
| Amberlyst 15[b] | Rohm & Haas | 47 | 4.80 | 130 | 4.8 |
| Purolite CT-175[b] | Purolite Int. | 30 | 5.00 | 150 | 5.7 |
| Nafion SAC-13[c] | DuPont | 200 | 0.15 | 280 | 3.7 |
| Deloxan ASP I/7[d] | Degussa | 510 | 1.10 | 200 | 4.7 |
| Zeolyst CBV 600[e] | Zeolyst Int. | 660 | 1.60 | − | 3.3 |

[a] Amount needed to fill a 10-mL reactor volume. [b] Organic supported catalysts as a result of the copolymerisation of styrene and DVB. The degree of cross-linking was 20−25%. [c] Silica composite with 13% w/w of Nafion particles entrapped within the porous framework. [d] Deloxan is a macroporous polysiloxane with alkylsulfonic acid groups. This catalyst was manufactured by Degussa, but sadly, it is no longer available. [e] Type Y zeolite ($H^+$) with a Si/Al ratio of 5.2.

**2.1. Catalysts.** Five commercially available Brønsted-type solid acid catalysts have been studied in this research, Amberlyst 15, Purolite CT-175, Nafion SAC-13, Deloxan ASP I/7, and Zeolyst CBV 600. Table 1 shows some of their properties as well as the different suppliers. Samples of “fresh” catalyst were used to study the performance of the different catalysts across the temperature range at different pressures.

The catalysts were loaded into the reactor and used “as supplied” by the manufacturer. Before pumping of the organic substrate was started, the catalysts were dried in situ by flowing $scCO_2$ at the reaction temperature for a period of 1 h. This pretreatment should, in principle, remove any water entrapped within the catalyst particles.

**2.2. Supercritical Fluid Continuous Flow Apparatus.** A diagram of the supercritical fluid continuous flow apparatus is shown in Figure 1. The $scCO_2$ pump compresses the $CO_2$ to above the desired system pressure. The system pressure is then controlled by the pressure regulator. The organic substrate is pumped using a standard HPLC pump. The supercritical fluid and the organic substrate are mixed in a static mixer, before entering the reactor, which contains the catalyst. The catalyst is held inside the reactor by a frit placed at the bottom of the reactor. Thermocouples placed inside the catalyst bed, in the reactor heating block and in the product stream, are used to monitor the reaction. The pressure is then reduced stepwise to separate the product(s) from the fluid using an expansion module. The flow of the exhaust gases is measured by a flowmeter which is connected to the vent line. The flow rate of the gases was set to 0.65 L/min of $CO_2$ at room temperature and pressure which corresponds to 1.06 g/min.

**2.3. Characterisation Techniques.** The identification and quantification of the products obtained in all the experiments reported were carried out using GC and GC−MS. The GC analysis was carried out using a Shimadzu GC-17a with an AOC 20i autosampler. Helium was used as carrier gas, and the detector was an FID. The GC−MS instrument employed was a Thermo-Finnegan Polaris Q ion trap GC-MSn. The column used in both instruments was a RTX-5 (30 m length, 0.52 mm i.d. and 0.25 $\mu$m film thickness).

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(22) Baiker, A. *Chem. Rev.* **1999**, *99*, 453−473.
(23) Hyde, J. R.; Licence, P.; Carter, D. N.; Poliakoff, M. *Appl. Catal., A* **2001**, *222*, 119−131.
(24) Santana, G. M.; Akgerman, A. *Ind. Eng. Chem. Res.* **2001**, *40*, 3879−3882.
(25) Hitzler, M. G.; Smail, F. R.; Ross, S. K.; Poliakoff, M. *Chem. Commun.* **1998**, 359−360.
(26) Vollhardt, K. P.; Schore, N. E. *Organic Chemistry*, 2nd ed.; W. H. Freeman and Company: New York, 1994.

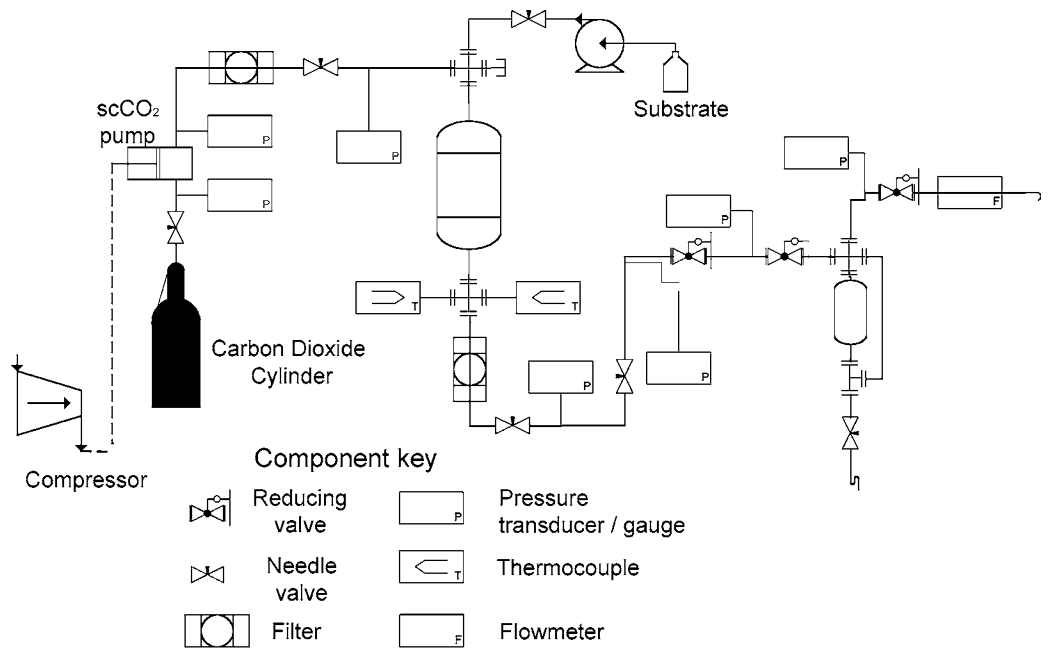
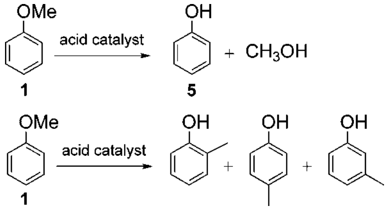


***Figure 1.*** **Schematic of the supercritical fluid continuous flow equipment.**

***Scheme 2.*** **Formation of phenol 5 and Fries rearrangement of 1 to form *o*-cresol, *p*-cresol, and *m*-cresol in the presence of an acid catalyst**



## 3. Results and Discussion

The influence of the reaction temperature and pressure on the catalyst performance was evaluated in terms of the selectivity for monoalkylated products (**2** + **3**), the absolute conversion of **1**, and the isomeric ratio for monoalkylated species (**2** and **3**).

**3.1. Effect of Temperature.** The range of temperatures at which the catalysts were investigated was from 100 to 250 °C. As a general observation, formation of phenol **5** and cresols occurred (Scheme 2). The formation of these derivatives, particularly **5**, increased significantly when the temperature was raised above 200 °C.

Formation of cresols was a result of protonation of the O-Me group and the rearrangement of **1** (Fries rearrangement) in the presence of an acid catalyst. In some cases, the reaction can proceed by simple heating without a catalyst.[27] The phenol formed can also react with *n*-propanol to form phenol-alkylated products, thereby decreasing the overall selectivity for **2** and **3**. The formation of ethers (*N*-*n*-propyl ether and *n*-propyl−isopropyl ether) was also observed when the reaction was performed at mild temperatures (100−150 °C). Formation of ethers from alcohols in the presence of a solid acid catalyst in $scCO_2$ was first described by Gray et al.[28] The formation of propylene was also observed as a result of the formation of the carbocation and the subsequent elimination of a proton to form the double bond.

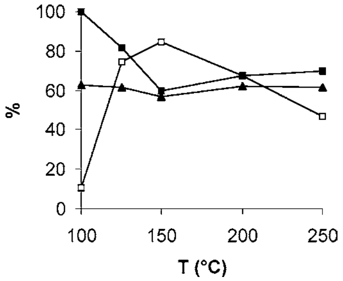


***Figure 2.*** **Conversion of 1 (□), selectivity for 2 and 3 (■), and ratio of 2 to 3 (▲) for the alkylation of 1 with *n*-propanol over Amberlyst 15 at 200 bar in $scCO_2$.**

Figure 2 shows the catalytic activity of Amberlyst 15 for the alkylation reaction at 200 bar and across the range of temperatures. The conversion of **1** was maximized at 150 °C, although the selectivity for monoalkylated products was poor. Above 150 °C the conversion of **1** dropped dramatically with the reaction running time, as a result of a desulfonation process of the catalyst.[29]

Sulfur microanalysis measurements on a sample of untreated catalyst and catalyst exposed to the reaction conditions confirmed the desulfonation of the catalyst (Table 2). The loading found for the untreated sample of catalyst was 4.3 mequiv/g of $-SO_3H$ groups (13.67% S), whereas the loading for the catalysts after use at 150 °C and 200 °C were 10% and nearly 50% lower, respectively. Purolite CT 175 showed a behavior similar to that shown by Amberlyst 15. However, no reaction was observed at low temperatures

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[27] March, J. *Advances in Organic Chemistry*; Wiley-Interscience: New York, 1985.

[28] Gray, W. K.; Smail, F. R.; Hitzler, M. G.; Ross, S. K.; Poliakoff, M. *J. Am. Chem. Soc.* **1999**, *121*, 10711−10718.

[29] Rhodes, C. N.; Brown, D. R.; Plant, S.; Dale, J. A. *React. Funct. Polym.* **1999**, *40*, 187−193.

***Table 2.*** **Sulfur content by microanalysis in untreated and treated samples of Amberlyst 15**

| catalyst | sulfur detected (%) | meq of $-SO_3H$/ g catalyst |
|---|---|---|
| untreated | 13.67 | 4.3 |
| 150 °C/200 bar | 12.33 | 3.9 |
| 200 °C/200 bar | 6.90 | 2.2 |

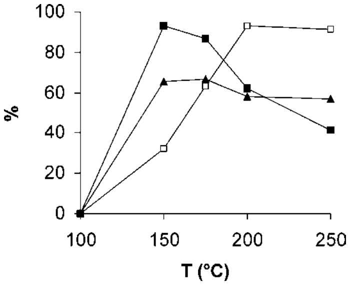

***Figure 3.*** **Conversion of 1 (□), selectivity for 2 and 3 (■), and ratio of 2 to 3 (▲) for the Friedel−Crafts alkylation of 1 with *n*-propanol at 200 bar in $scCO_2$ and using Nafion SAC-13 as catalyst.**

(100 °C) most likely due to the high moisture content of this catalyst (~53%w/w).

Desulfonation of the catalyst also occurred above 150 °C, leading to a poor conversion of **1**. In contrast, the inorganic supported catalysts showed a higher optimum temperature range than that observed for the organic supported catalysts. Figure 3 shows that a 90% conversion of **1** and 60% selectivity for **2** plus **3** was achieved at 200 °C using Nafion SAC-13 as catalyst. However, at temperatures above 250 °C desulfonation of the catalyst was observed. Deloxan ASP I/7 showed an optimum reaction temperature of 200 °C; however, desulfonation was noted at temperatures above that temperature. Finally, maximum conversion of **1** (73%) was achieved at 200 °C using Zeolyst CBV 600, but selectivity to **2** + **3** decreased to 60%.

**3.2. Effect of Pressure.** An increase in the system pressure causes an increase in the $CO_2$ density as well as an increase in the mean residence time of the organic substrate in the catalyst bed. This effect might be expected to increase the absolute conversion of the starting material and decrease the selectivity for the product(s), but only if the reaction has not reached its final conversion inside the catalyst bed at the reference conditions. This was observed for the inorganic supported catalysts investigated (Figures 4 and 5), but the organic supported catalysts showed the opposite effect (Figures 6 and 7).

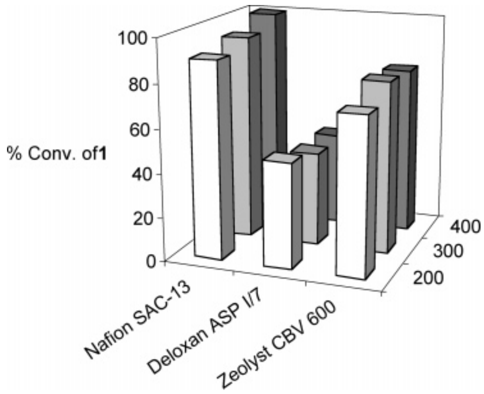

***Figure 4.*** **Effect of pressure on the conversion of 1 at 200 °C over inorganic supported catalysts in $scCO_2$.**

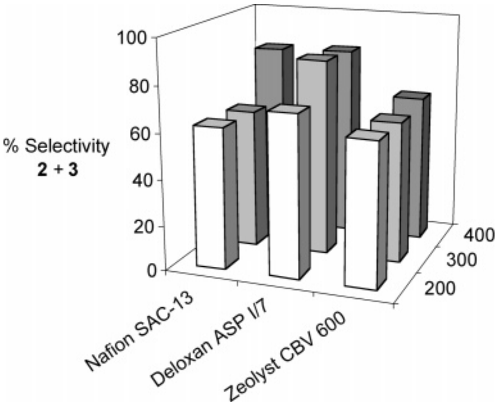

***Figure 5.*** **Effect of pressure on the selectivity for 2 + 3 at 200 °C over Nafion SAC-13 Deloxan ASP I/7 and Zeolyst CBV 600 in $scCO_2$.**

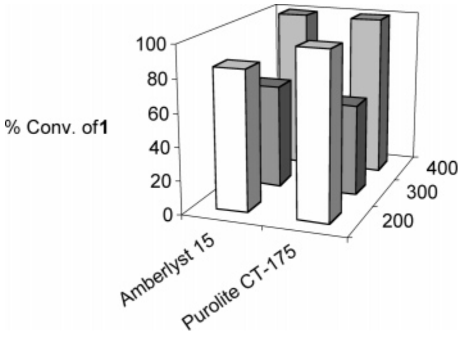

***Figure 6.*** **Effect of pressure on the conversion of 1 at 150 °C over Amberlyst 15 and Purolite CT-175 in $scCO_2$.**

A possible explanation for this effect on both parameters, could be related to the different nature of the support of these catalysts under high pressure. Recent studies have shown the ability of $scCO_2$ to diffuse into a polymeric matrix. The $CO_2$ causes swelling and changes in the mechanical and physical properties of the polymer. The most important result is a reduction in the glass transition temperature ($T_g$) of glassy polymers in the presence of $scCO_2$. This is generally termed plasticization.[30,31] A plasticization process may also have been taking place in the catalysts investigated in the presence of $scCO_2$, since they possess a polymeric matrix which could interact with $CO_2$ with a decrease in the $T_g$ of the polymer. A decrease in the $T_g$ of the polymer might modify the polymer matrix decreasing the number of available acidic groups which in turn would impair the catalyst performance when the amount of $CO_2$ in our system increased. However, $CO_2$ can dissolve polystyrene (PS) at pressures above 500 bar and 100 °C[32] if the molecular weight of the PS is less

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(30) Kazarian, S. G.; Vincent, M. F.; Bright, F. V.; Liotta, C. L.; Eckert, C. A. *J. Am. Chem. Soc.* **1996**, *118*, 1729−1736.

(31) Kazarian, S. G. *Polym. Sci., Ser. C* **2000**, *42*, 78−101.

(32) McHugh, M. A.; Krukonis, V. J. *Supercritical Fluid Extraction: Principle and Practice*, 2nd ed.; Butterworth-Heinemann: Boston, 1994.

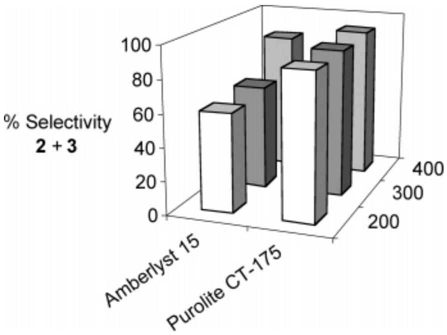

***Figure 7.*** **Effect of pressure on the selectivity for 2 + 3 at 150 °C over Amberlyst 15 and Purolite CT-175 and across the pressure range in $scCO_2$.**

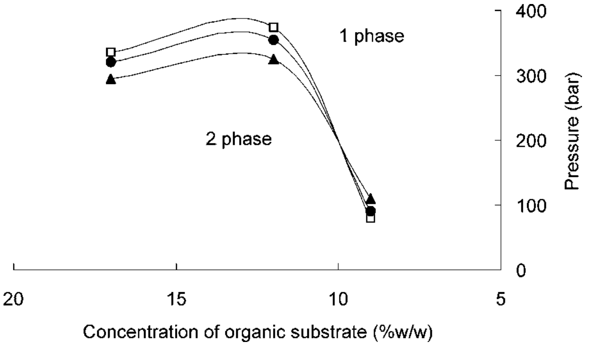

***Figure 8.*** **Phase diagram showing the effect of %w/w of organic material in $scCO_2$ at 150 °C (▲), 175 °C (●), and 200 °C (□). The organic mixture is for the alkylation of 1 with *n*-propanol at 3:1 molar ratio at different temperatures in $scCO_2$. The phase measurements were conducted in a variable volume view cell with a visual inspection of the cell contents via a boroscope and a video camera system.**

than 1000. In contrast, PS of a higher molecular weight (106 000 $gmol^{-1}$) shows very low solubility even at 225 °C and 2100 bar which demonstrates that a plasticization process is unlikely to be happening to our catalyst due to the low solubility that $scCO_2$ exhibited in PS.

Phase behaviour studies of our reaction (see Figure 8) suggested why lower pressures (100 bar) might lead to an apparent increase in the activity of the organic supported catalysts leading to an increase in the conversion of the starting material and a decrease in selectivity for the products of interest. The low solubility of the reactants (**1** + *n*-propanol) in $scCO_2$ and the lipophilicity of the catalysts due to their organic nature (styrene−divinylbenzene copolymer (S-DVB)) could favour the formation of a thin film of the organic material on the surface of the catalyst.[33] Thus, an increase in the concentration of organic material in the proximity of the catalyst active sites would occurred (*pseudoconcentration* effect).[34]

Furthermore, at low pressures, the reactor would operate as a trickle bed reactor, in which the residence time of the liquid phase across the catalyst bed would be longer than the residence time of the single supercritical phase formed at higher pressures. In this way, the reaction rate of all processes will increase, leading to a higher conversion of anisole but to a decrease in the selectivity for the desired products. An increase in pressure (300−400 bar) leads to a single-phase system, in which all the organics would be dissolved and diluted within the $scCO_2$. The diffusion resistance of this single phase into the catalytic active sites would determine the overall rate. An increase in pressure from 300 to 400 bar would increase the residence time across the catalyst bed leading to an increase in the conversion of the starting material. The selectivity for the reaction could be explained as follows: in the two-phase region, the organic material, in the liquid phase, would take longer to diffuse into the polymeric matrix, react. and diffuse back out to the reaction stream, allowing further alkylation reactions and other side reactions to take place. By contrast, in the one-phase region, the diffusion of the organic material into the polymeric particles would occur more rapidly since the organic material is dissolved in the $scCO_2$. The inorganic supported catalysts may not display such a marked *pseudoconcentration* effect at low pressures, since the surface may not be so easily wetted when the reaction mixture is biphasic. Consequently, an increase in the working pressure should increase the conversion of the starting material due to the longer residence time across the catalyst bed. In the single phase, the diffusion into the active sites would probably be the rate-determining step, as all the organic material would be dissolved and diluted within the $scCO_2$.

## 4. Conclusions

The organic supported catalysts investigated, Amberlyst 15 and Purolite CT-175, performed best within the temperature range from 100 to 150 °C. Above 150 °C, a decrease in the conversion of the starting material with time occurred as a result of desulfonation of the catalyst. By contrast, the inorganic supported catalysts, Nafion SAC-13, Deloxan ASP I/7, and Zeolyst CBV 600, showed a higher optimum temperature range. As a general trend, the higher the reaction temperature, within the optimum temperature range found for each catalyst, the higher the conversion of the starting material. However, the reaction became less selective towards the monoalkylated products.

The effect of pressure on the reaction performance was found to correlate with the phase behaviour of the reaction. Thus, when the organic supported catalysts were employed in the reaction in the two-phase region, a *pseudoconcentration* effect appeared to modify the behaviour of the catalyst bed, thus increasing the reaction rate for all processes leading to a higher conversion of **1** and decreasing the selectivity for monoalkylated products. In the single-phase region, the organic material would be dissolved and diluted with $scCO_2$. The diffusion of the single phase into the catalytic active sites would determine the overall rate of the reaction. However, when inorganic supported catalysts were employed, increases in the working pressure produced corresponding increases in the conversion of the starting material as a consequence of an increase in the residence time across the catalyst bed. Furthermore, the acidic terminal $-CF_2CF_2-SO_3H$ group in Nafion SAC-13, has been shown to be $scCO_2$-

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(33) Desikan, S.; Doraiswamy, L. K. *Chem. Eng. Sci.* **2000**, *55*, 6119−6127.
(34) Hodge, P. *Chem. Soc. Rev.* **1997**, *26*, 417−424.

philic,[35] and therefore an enhancement in the diffusion of the single phase formed by the organic material dissolved within the $scCO_2$ into the catalytic sites would be expected. Despite the high surface area of Deloxan ASP I/7, this catalyst behaved very similarly to the organic supported catalysts previously described, when the pressure was varied. The low conversion of the starting material achieved across the temperatures and pressures tested was a result of the low loading of the catalyst. The *o-/p-* ratio was found to be largely independent of temperature, pressure, and catalyst type.

This investigation has shown that Friedel−Crafts alkylation of simple aromatics, such as anisole, can successfully be carried out over Brønsted-type solid acid catalysts with different catalytic supports, in $scCO_2$, with very high conversion of starting material in conjunction with high selectivities for the product(s) of interest. Phase behavior measurements have proved to be of crucial importance to truly understand and predict the reaction outcome when employing supercritical fluids as the reaction media.

An extensive catalyst lifetime investigation, however, is required to scale up this process to commercial scale.

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(35) Harmer, M. A.; Hutchenson, K. W. *Chem. Commun.* **2002**, 18−19.