Organic Process Research & Development **1998**, *2,* 221–225

Articles

Enhanced Selectivity in the Preparation of Linear Alkylbenzenes Using Hexagonal Mesoporous Silica Supported Aluminium Chloride[1]

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Abstract:

For decades sulphonated linear alkylbenzenes have been one of the worlds most important detergents. Industrially, their preparation involves the use of either aluminium chloride or hydrogen fluoride as catalysts in the alkylation stage of the reaction. The use of these catalysts presents severe problems in terms of both their environmental impact and their lack of selectivity towards the desired product. Solid acids, such as zeolites, can overcome these problems but at the expense of activity. It has now been discovered that by chemically supporting aluminium chloride on a MCM-41 type silica a reuseable catalyst is produced. It can be easily separated from the products and is environmentally benign. In addition, the new catalyst exhibits significant improvements in selectivity towards both the monoalkylated product and the preferred 2-phenyl isomer. Selectivity can be further increased by maximizing the relative activity of the catalytic sites situated within the pores of the catalyst.

Introduction

Over the past few decades linear alkylbenzene sulphonate has been one of the most widely used detergent surfactants.[2,3] It is prepared from benzene, simple derivatives of *n*-paraffins (extracted from kerosine), and sulphur trioxide (or sulphuric acid). The low cost of these raw materials used in its synthesis, together with its biodegradability properties, has led to it almost completely replacing the branched alkylbenzene sulphonate.[4,7]

There are two major processes for the manufacture of linear alkylbenzenes (LAB), which is the precursor to LAS.[3,4] The first involves aluminium chloride as the catalyst to alkylate benzene with chloroalkanes. The second process, and most widely used, involves hydrofluoric acid as the catalyst to alkylate benzene with olefins. In both instances *n*-paraffins of chain length $C_{12}-C_{16}$ are used, these are either chlorinated, for the $AlCl_3$ process, or dehydrogenated, for the HF process.

However, both processes suffer from a number of drawbacks. The first is caused by side reactions, such as polyalkylation, dimerisation of the alkene, and cycloalkylation. These side reactions result in a variety of by-products, or “heavy alkylates”, being formed.[3] While the majority can be removed by distillation, the cycloalkylated products and the branched alkylbenzenes are difficult to remove due to their similar molecular weight, thus leading to impurities in the final product. The position of the phenyl group on the alkyl chain and the length of the alkyl chain are also important as they affect the properties of the final product.[2−6] Generally, the middle chain isomers give the best foam stability; however, a high 2-phenyl isomer content is preferred for better biodegradation and solubility properties. Both processes exhibit low selectivity towards the 2-phenyl isomer; the $AlCl_3$ catalyst results in 30% 2-phenyl and 20% 3-phenyl down to ∼15% for the middle chain isomers. The HF process is less selective, giving an even isomer distribution of 17−20%. The second problem is caused by the catalysts themselves. HF is extremely hazardous, requiring specialist equipment to handle it. $AlCl_3$, although easier to handle, is difficult to separate from the products and results in the production of a large amount of waste effluent.

In recent years attention has turned towards solid acid catalysts as a means of overcoming the problems of low selectivity and waste production in alkylation reactions.[3−7] Zeolites have been investigated, and although some give great improvements in selectivity towards both the *mono*alkylated product and the 2-phenyl isomer, their activity is significantly lower than both $AlCl_3$ and HF, requiring high temperatures and pressures.[3,5] Further problems are encountered due to adsorption of heavy by-products causing catalyst deactivation. Recently, a solid acid process, DETAL, has been commercialised by UOP for production of LAB involving a fluorided silica−alumina as the catalyst.[4] The catalyst is more selective towards the 2-phenyl isomer than the HF

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(1) Clark, J. H.; Price, P. M.; Martin, K.; Bastock, T. W. UK Patent Appl. P96302GB, March 1997.

(2) Berna, J. L.; Cavalli, L.; Renta, C. *Tenside Surf.* **1995**, *32* (2), 122−127.

(3) de Almeida, J. L. G.; Dufaux, M.; Ben Taarit, Y.; Naccache, C. *J. Am. Oil Chem. Soc.* **1994**, *71* (7), 675−694 and references therein.

(4) Lawson, R. J.; Fritsch, T. R. LAB Production Experience DETAL vs $AlCl_3$ and HF. Presented, at Solid Acid/Base ’97.

(5) Wugeng, L.; Yong, J.; Zhiqing, Y.; Zhanwen, W.; Bingbing, H.; Mingyuan, H.; Enze, M. *Zeolites* **1996**, *17*, 297−303.

(6) Sivasanker, S.; Thangaraj, A. *J. Catal.* **1992**, *138*, 386−390.

(7) Wugeng, L.; Yong, J.; Zhiqing, Y.; Zhanwen, W.; Zao, W.; Mingyuan, H.; Enze, M. *J. Chem. Technol. Biotechnol.* **1995**, *62*, 98−102.

S1083-6160(98)00017-6 CCC: $15.00

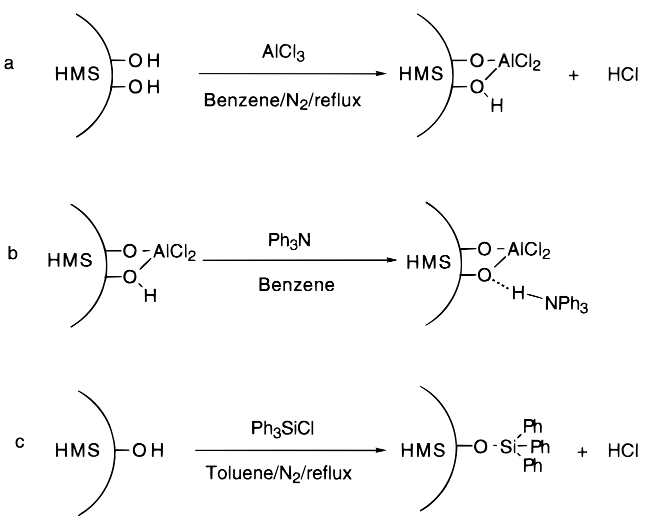

Figure 1. **Preparation of supported aluminium chloride catalysts: (a) General preparation. (b) Poisoning of catalyst site using triphenylamine. (c) Modification of HMS with triphenylchlorosilane.**

catalyst and produces less waste, although the low activity of the solid acid again means that the process operates at high temperatures and pressures.

We now report the development of a new solid acid catalyst with comparable activity to $AlCl_3$ but with significant improvements in selectivity towards both *mono*alkylation and the 2-phenyl isomer. The catalyst is prepared by supporting $AlCl_3$ on hexagonal mesoporous silica (HMS),[1,8] a silica with a well-ordered pore structure possessing a narrow pore size distribution. Modification of the catalyst by elimination of external catalytic sites further improves the catalyst selectivity.

Results and Discussion

In total, five catalysts were investigated. These were based on supporting $AlCl_3$ on hexagonal mesoporous silica of two different pore sizes, 16 and 24 Å, and are denoted $AlCl_2-HMS_{16}$ and $AlCl_2-HMS_{24}$, respectively. Modification of these catalysts by treatment with triphenylamine ($AlCl_3$:Ph_3N ratio = 5) gave $AlCl_2-HMS_{16}-Ph_3N$ and $AlCl_2-HMS_{24}-Ph_3N$, respectively. A final catalyst was prepared by pretreatment of the HMS_{24} with triphenylchlorosilane prior to supporting $AlCl_3$. Figure 1 summarises the preparation method for the catalysts. To relate catalyst performance to LAB production, the prepared catalysts were tested by alkylating benzene with a variety of *n*-1-alkenes with chain lengths in the range C_6-C_{16} and the results compared with homogeneous $AlCl_3$.

Table 1. **Selectivity towards LAB using $AlCl_2-HMS$ catalysts compared with homogeneous $AlCl_3$**

catalyst[a]	alkene	reaction time (*t*/h)	LAB	heavy alkylate[b]
$AlCl_3$	hex-1-ene	0.5	58.7	41.3
$AlCl_2-K10^c$	hex-1-ene	2.5	69.2	30.8
$AlCl_2-HMS_{24}$	hex-1-ene	0.5	72.0	28.0
$AlCl_2-HMS_{16}$	hex-1-ene	0.5	74.7	25.3
$AlCl_3$	oct-1-ene	0.5	64.1	35.9
$AlCl_2-K10^c$	oct-1-ene	2.0	76.3	23.7
$AlCl_2-HMS_{24}$	oct-1-ene	0.5	80.3	19.7
$AlCl_2-HMS_{16}$	oct-1-ene	0.5	81.0	19.0
$AlCl_3$	dodec-1-ene	0.5	66.1	33.9
$AlCl_2-K10^c$	dodec-1-ene	2.0	77.3	21.3
$AlCl_2-HMS_{24}$	dodec-1-ene	0.5	81.3	18.7
$AlCl_2-HMS_{16}$	dodec-1-ene	0.5	85.7	14.3
$AlCl_3$	tetradec-1-ene	0.5	67.3	31.2
$AlCl_2-HMS_{24}$	tetradec-1-ene	0.5	86.9	13.1
$AlCl_2-HMS_{16}$	tetradec-1-ene	0.5	88.9	11.1
$AlCl_3$	hexadec-1-ene	0.5	77.2	22.8
$AlCl_2-K10^{c,d}$	hexadec-1-ene	4.5	71.0	14.5
$AlCl_2-HMS_{24}$	hexadec-1-ene	0.5	92.0	8.0
$AlCl_2-HMS_{16}^e$	hexadec-1-ene	1.0	92.5	5.1

[a] $AlCl_3$ loading = 1.5 mmol g^{-1}, unless otherwise stated; equivalent amount of $AlCl_3$ used in homogeneous reaction. [b] Heavy alkylate consists mainly of polyalkylated benzene; some branched alkylated benzene is present for longer chain alkenes due to impurities in the starting material. [c] $AlCl_3$ loading = 0.75 mmol g^{-1}. [d] Reaction only 85% complete. [e] Reaction 99% complete.

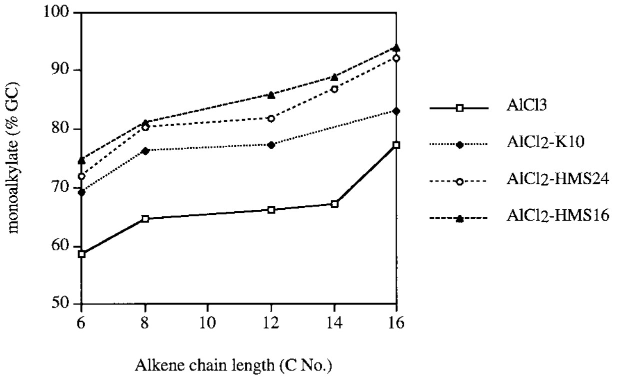

Figure 2. **Selectivity towards monoalkylation for the unmodified catalysts compared with homogeneous $AlCl_3$ and $AlCl_3$ supported on acid-treated clay.**

Supporting $AlCl_3$ on Hexagonal Mesoporous Silica. Table 1 shows the results obtained for $AlCl_3$, $AlCl_2-K10$[9] (K10 is an acid-treated montmorillonite clay), $AlCl_2-HMS_{16}$, and $AlCl_2-HMS_{24}$ catalysts using a range of linear alkenes. The catalytic activities for both the $AlCl_2-HMS$ catalysts compare favourably with that of homogeneous $AlCl_3$ (reaction is complete upon final addition of the alkene). Activity is only reduced for the $AlCl_2-HMS_{16}$ catalyst when alkylating with hexadec-1-ene. This is likely to be a result of a lower diffusion rate of reactants caused by the small pore diameter of the catalyst. The heavy alkylates produced consist mainly of polyalkylated benzene, the majority of which is dialkylbenzene. No trialkylbenzene is produced with the heterogeneous catalysts for alkenes larger than oct-1-ene. Small amounts of branched alkylbenzenes are formed for alkenes $C_{12}-C_{16}$; however, this is likely to be due to impurities present in the starting alkene.

Catalyst selectivities of the four catalysts towards linear alkylbenzene are compared in Figure 2. For all catalysts a general increase in selectivity is observed as the chain length of the alkene increases. Supporting $AlCl_3$ on K10 results in a large increase in selectivity, and further significant increases are gained when the HMS material is used as the support. Indeed, there is almost complete conversion to the mono-

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(8) Clark, J. H.; Price, P. M.; Martin, K.; Macquarrie, D. J.; Bastock, T. W. *J. Chem. Res.* **1997**, 430−431.

(9) Clark, J. H.; Martin, K.; Teasdale, A. J.; Barlow, S. J. *Chem. Commun.* **1995**, 2037−2040.

Table 2. **Comparison of reaction selectivities using the modified $AlCl_2-HMS$ catalysts**

catalyst[a]	alkene	reaction time (*t*/h)	LAB	heavy alkylate[b]
$AlCl_2-HMS_{24}-Ph_3N$	hex-1-ene	0.5	82.5	17.5
$AlCl_2-HMS_{16}-Ph_3N$	hex-1-ene	0.5	82.0	18.0
$AlCl_2-HMS_{24}-TPS$[c]	hex-1-ene	0.5	73.3	26.7
$AlCl_2-HMS_{24}-Ph_3N$	oct-1-ene	0.5	84.0	16.0
$AlCl_2-HMS_{16}-Ph_3N$	oct-1-ene	0.5	84.9	15.1
$AlCl_2-HMS_{24}-TPS$[c]	oct-1-ene	0.5	83.0	17.0
$AlCl_2-HMS_{24}-Ph_3N$	dodec-1-ene	0.5	86.4	13.6
$AlCl_2-HMS_{16}-Ph_3N$	dodec-1-ene	1.5	89.7	10.3
$AlCl_2-HMS_{16}-TPS$[c]	dodec-1-ene	0.5	84.7	15.3
$AlCl_2-HMS_{24}-Ph_3N$	tetradec-1-ene	0.5	95.3	4.7
$AlCl_2-HMS_{16}-Ph_3N$	tetradec-1-ene	5.0	91.2	8.8
$AlCl_2-HMS_{24}-TPS$[c]	tetradec-1-ene	0.5	89.4	10.6
$AlCl_2-HMS_{24}-Ph_3N$[d]	hexadec-1-ene	20.0	14.4	4.7
$AlCl_2-HMS_{16}-Ph_3N$	hexadec-1-ene			
$AlCl_2-HMS_{24}-TPS$[c,e]	hexadec-1-ene	0.5	95.1	4.4

[a] $AlCl_3$ loading = 1.5 mmol g^{-1}, unless otherwise stated. [b] Heavy alkylate consists mainly of polyalkylated benzene; some alkene dimers and branched alkylated benzene are present. [c] $AlCl_3$ loading = 0.75 mmol g^{-1}. [d] Reaction 19% complete. [e] Reaction 99.5% complete.

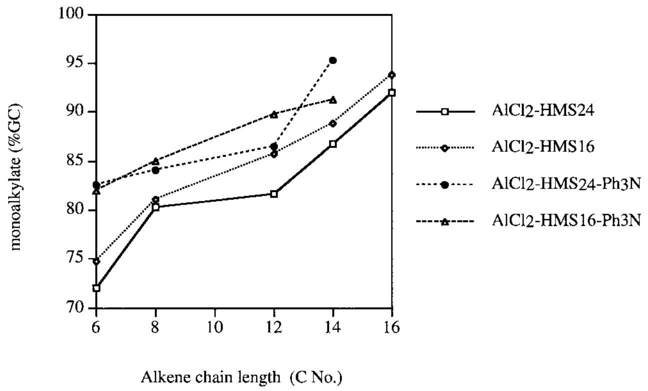

Figure 3. **Comparison of catalyst selectivities between poisoned catalysts and unmodified catalysts.**

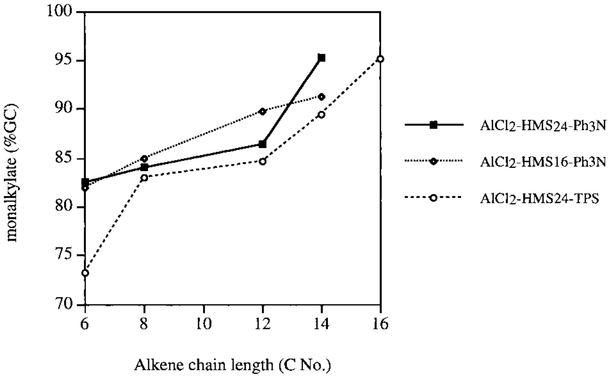

Figure 4. **Comparison of modified catalysts.**

hexadecylbenzene when $AlCl_2-HMS_{16}$ catalyst is used. The increase in selectivity of the $AlCl_2-HMS$ catalysts may be attributed to catalysis taking place mainly within the small, well-defined pores of the HMS and thus affording some degree of shape selectivity.

Enhancement of Catalyst Selectivities. To increase selectivity towards monoalkylation, the contribution from catalytic sites within the pore structure of the $AlCl_2-HMS$ catalysts was enhanced by reducing the effect of the external sites. Two methods were employed. The first involved poisoning the catalysts with a bulky amine (triphenylamine) so as to selectively remove the external catalytic sites. The second method, based on the same principle, involved elimination of the external silanol groups of the HMS_{24} material by reacting them with a bulky silane (triphenylchlorosilane) prior to catalyst preparation. Table 2 shows the results for the modified catalysts. The catalysts poisoned with triphenylamine exhibit a gradual loss in activity with increasing chain length of the alkene. This is consistent with the catalyst pore openings being restricted by the triphenylamine groups, thus leading to a decrease in the diffusion rate as the alkene chain length increases. It is interesting to note that there is no observable loss of activity with the $AlCl_2-HMS_{24}-TPS$ catalyst despite having half the $AlCl_3$ loading, suggesting that the pore openings are not sufficiently restricted to lower the diffusion rate. The selectivities for both the poisoned and the unmodified catalysts are compared in Figure 3. A significant increase in selectivity towards the monoalkylated product is achieved by poisoning the catalyst. The increase is likely to be caused by catalysis taking place almost exclusively within the pores. Overall, the $AlCl_2-HMS_{16}-Ph_3N$ catalyst shows the best results; however, selectivity is lost for the alkylation with tetradec-1-ene, where an increase in the amount of dimerisation was observed. This may be attributed to the combination of two effects. First, diffusion of the alkene is reduced, leading to a concentration of alkene at the external surface. Second, despite the external sites being poisoned, they still possess some Lewis acid character and it is these Lewis acid sites which can cause the alkene dimerisation. Indeed, it has been observed that increasing the level of triphenylamine poisoning leads to an increase in alkene dimerisation, as well as a general decrease in activity. Figure 4 compares the selectivities of the three modified catalysts, and it can be seen that both the catalysts poisoned with triphenylamine give better results than the triphenylsilylated catalyst. This suggests that the catalyst still possesses some externally active sites, thus leading to a decrease in selectivity.

Selectivity towards the 2-Phenyl Isomer. As previously mentioned, LAB is made up of a number of isomers, with the 2-phenyl being preferred as it gives the best biodegradability and solubility properties. Table 3 compares the selectivity towards this isomer from using the various catalysts over the $C_{12}-C_{16}$ alkene range. Supporting $AlCl_3$ on the HMS materials results in a significant increase in the 2-phenyl isomer content, and further increases are gained on elimination of the external catalytic sites. Despite being small, these increases are consistent with those observed for selectivity towards monoalkylation. The catalysts compare favourably with HZSM-4, a large pore zeolite, even though the reaction for the zeolite was run at twice the benzene/alkene dilution. It is interesting to note that the alkylation with dodec-1-ene using the $AlCl_2-HMS_{24}$ catalyst at a 4:1 dilution gives very similar selectivity to HZSM-4, and the latter requires high temperature and pressure for a reasonable reaction rate to be maintained.[3]

Table 3. **Comparison of catalyst selectivities towards the 2-phenyl isomer for alkenes $C_{12}-C_{16}$**

	2-phenyl isomer (% LAB)		
catalyst[a]	C_{12}	C_{14}	C_{16}
$AlCl_3$	30	30	35
$AlCl_2-HMS_{24}$	34 (38)[b]	34	35
$AlCl_2-HMS_{16}$	34	35	37
$AlCl_2-HMS_{24}-TPS$[c]	35	35	38
$AlCl_2-HMS_{24}-Ph_3N$	35	37	
$AlCl_2-HMS_{16}-Ph_3N$	39	37	
ZSM-4[b,d]	38		

[a] $AlCl_3$ loading = 1.5 mmol g^{-1}, unless otherwise stated. [b] Benzene−alkene ratio = 4. [c] $AlCl_3$ loading = 0.75 mmol g^{-1}. [d] Results from ref 3.

Table 4. **Reuse study of the $AlCl_2-HMS_{24}$ catalyst in the alkylation of benzene with dodec-1-ene**

		product (% GC)		
no. of reuses[a]	time (min)	dodec-1-ene	LAB	heavy
initial reaction	30		85	15
1	30		86	14
2	30		83	17
3	30		86	14
4	60	1	87	12
5[b]	60	48	45	7

[a] Once the reaction was complete, the products were decanted off, the reaction was then repeated. [b] No further reaction was observed.

Catalyst Reuse Studies. The reuseability of the $AlCl_2-HMS_{24}$ catalyst was investigated in the alkylation of benzene with dodec-1-ene. Table 4 shows the results obtained from a series of reactions. It can be seen that the catalyst can be reused three times without any loss in either activity or selectivity; although there is a small loss in activity on the fourth reuse, it is still reasonably high, with almost complete conversion after 1 h. On the fifth reuse the reaction only proceeds to 50% completion with no further reaction after 30 min. TGA analysis of the spent catalyst shows a large weight loss between 200 and 500 °C, indicating adsorption of heavier organic products on the catalyst surface, accounting for the sudden stop in catalysis. This poisoning of the catalyst by the adsorption of such heavier materials has been observed for the same reaction using zeolites.[5] However, the poisoning occurred frequently, requiring the catalyst to be washed with benzene in order to regenerate the catalyst.

Conclusion

Aluminium chloride supported on hexagonal mesoporous silica results in a catalyst that exhibits substantial improvements in selectivity, without loss of activity, towards linear alkylbenzenes compared with traditional homogeneous catalysts. Further improvements in selectivity can be gained by reducing the effect of the external catalytic sites, either by direct poisoning or by pretreatment of the HMS material. The catalysts also give small improvements in selectivity towards the preferred 2-phenyl isomer compared with both $AlCl_3$ and HF, with the results comparable to those achieved with the best zeolites.

Together with the improved performance, the catalysts can be easily filtered from the reaction mixture without the need for laborious and costly separation processes. Indeed, the catalyst can be reused several more times without any loss in activity or selectivity.

Experimental Section

Products were analysed using a Hewlett-Packard 6890 gas chromatograph using a DB5 capillary column. GC−MS spectra were obtained on a Varian 3400CX gas chromatograph using a DB5 capillary column interfaced to a Finnigan Mat Magnum mass spectrometer. Diffuse reflectance infrared spectra of the catalysts were obtained using a Perkin-Elmer 1720 FTIR spectrometer interfaced to a PC station. Surface areas and pore size distributions were obtained using a Quantasorb surface area analyser.

Preparation of Hexagonal Mesoporous Silica.[10] Octylamine or dodecylamine (0.0054 mol) was added to a solution of deionized water (11.8 mol) and absolute ethanol (3.6 mol) in a conical flask. The solution was stirred for 20 min, and tetraethoxysilane (0.4 mol) was added slowly. A white precipitate slowly formed over a period of 15 min, and the resulting mixture was aged for 18 h. The mixture was then filtered and dried on a rotary evaporator and was finally calcined in air at 873 K for 4 h to remove the template.

$AlCl_3-HMS$ (General Preparation). The HMS (2 g) was dried for 18 h in an oven at 573 K; it was then cooled slightly in a desiccator containing P_2O_5 and added to dry benzene (20 cm^3, 0.2 mol) in the reaction vessel in a N_2 atmosphere. To this suspension was added aluminium chloride (0.4 g, 0.003 mol). The mixture was refluxed for 1 h, with N_2 passing through the system removing any HCl produced. Once cooled to room temperature, the catalyst may be used in situ or can be isolated by removing the benzene on a Schlenk line.

Catalyst Modification I (Elimination of External Catalytic Sites). The catalyst was prepared as above. Once the catalytic mixture was at room temperature, triphenylamine (0.147 g, 6×10^{-4} mol) was added in a 1 cm^3 solution of benzene. The mixture was then stirred in a water bath for 30 min, resulting in the catalyst changing from pale yellow to blue/green. As before, the catalyst can either be used in situ or isolated.

Catalyst Modification II (Elimination of External Silanol Groups). The HMS material (24 Å pore size) was prepared as above and dried for 18 h at 573 K. The HMS_{24} (2 g) is cooled slightly in a desiccator over P_2O_5 and then added to dry toluene (40 cm^3) in the reaction vessel flushed with N_2. To this was added triphenylchlorosilane (17.7 g, 0.06 mol); the mixture was then refluxed under a N_2 atmosphere for 18 h. The resulting $HMS_{24}-TPS$ was filtered, washed with acetone, and dried on a rotary evaporator. $HMS_{24}-TPS$ was finally dried at 473 K for 18 h to remove any physisorbed water. The dried support was then used to prepare a catalyst, following the above method but using only half the amount of $AlCl_3$.

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(10) Tanev, P. T.; Pinnavaia, T. J. *Science* **1995**, *267*, 865.

General Procedure for the Alkylation of Benzene. To a suspension of the catalyst (2.4 g) in dry benzene (0.2 mol) was added alkene (0.1 mol) over a period of 30 min. Samples were taken after the final addition of the alkene and at subsequent 30 min intervals. The products were identified by GC−MS.

Reuse study of the $AlCl_2$−HMS_{24} Catalyst. The initial alkylation (using dodec-1-ene) was carried out as previously described. On completion of the reaction, the catalyst was allowed to settle out and the liquid decanted off. The reaction vessel was recharged with fresh benzene, the mixture stirred for 10 min, and the fresh dodec-1-ene was again added dropwise over a period of 30 min. This procedure was repeated until no further reaction was observed.

Acknowledgment

We thank Contract Chemicals Ltd., EPSRC, the Royal Academy of Engineering (for a Fellowship to J.H.C.), and the Royal Society (for a University Research Fellowship to D.J.M.) for their financial support and other members of the Envirocats and York Green Chemistry Groups for helpful discussions.

Received for review February 11, 1998.

OP980017Q