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# Use of methanesulfonic acid as catalyst for the production of linear alkylbenzenes

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## Abstract

Methanesulfonic acid (MSA) was used as catalyst for the electrophilic addition of long-chain olefins such as 1-dodecene to benzene. The influence of the temperature, the ratios of the reactants, the amount of MSA, and the stirring of the reaction mixture were investigated. After a 3 h reaction time at 80 °C, a selectivity to the phenyldodecanes of more than 90% was obtained at 98% dodecene conversion. MSA could be recycled at least five times after a treatment with water and dichloromethane and a subsequent water removal. The presence of water in the reaction mixture was found to be detrimental for the activity of MSA. The inhibitory products formed during the reaction, as well as the crude organic phase, have been proved also as responsible for MSA deactivation. This method represents an environmentally benign alkylation route, because MSA could easily be separated from the reaction mixture via decantation and because it could be reused. In addition to that, MSA is biodegradable.

*Keywords:* Methanesulfonic acid; Linear alkylbenzene; LAB; Alkylation of aromatics

## 1. Introduction

The alkylbenzenes are widely used as raw materials in the manufacture of detergents [1]. In the past, two types of alkylates have gained industrial importance as intermediates for the production of anionic surfactants by a subsequent processing to alkylarylsulfonates [2]:

- The branched-chain alkylbenzenes. Their use decreased over the last decades, mainly because of the low rate of biodegradation [3].
- The linear alkylbenzenes (LAB). These are almost completely biodegradable [4], and their demand is still increasing.

The efficiency of linear alkylbenzene sulfonates as surfactants is well established [5,6], and they are among the safest and most cost-effective products in widespread commercial use. Among these linear alkybenzenes, the 2-phenyl isomer yields detergents of better emulsibility and biodegradability for several applications [7].

Most of the commercial plants for such alkylation reactions use HF or $AlCl_3$ as acid catalysts. These processes feature serious drawbacks: for example, HF is highly toxic, volatile, and corrosive; $AlCl_3$ is also toxic and corrosive, and it must be destroyed in the working-up procedure.

In order to overcome all the drawbacks in the use of HF or $AlCl_3$, new solid acid catalysts have been tested for such benzene alkylations. Various zeolites [8], pillared clays [9], heteropolyacids [10], sulfated zirconia [11], and immobilized ionic liquids [12] have shown good catalytic results (in terms of olefin conversion, LAB linearity, and catalyst life time) for benzene alkylation. A recent paper deals with the use of the zeolites H-MOR and MCM-22 for the LAB synthesis showing a high regioselectivity to 2- and 3-phenyldodecane [13]. Up to now these noted catalysts have not found industrial application [14].

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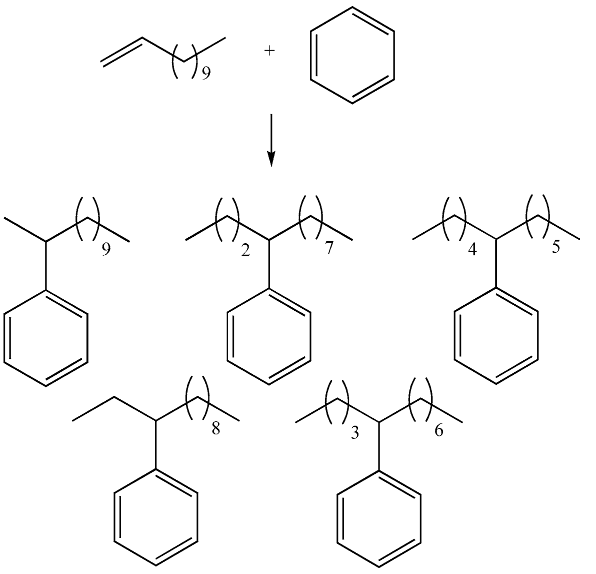

Fig. 1. Isomers which can be formed in the alkylation of benzene with 1-dodecene.

However, in 1992 UOP disclosed the DETAL technology as a novel process for the alkylation of benzene with heavy olefins, using solid acids such as HF supported on amorphous aluminosilicates or silica layers as catalysts in liquid-phase reactions [15–17]. The DETAL process, today successfully applied in three LAB plants [16], has required new production units to be built, as reactors used for the HF and $AlCl_3$-catalyzed manufacture cannot be used anymore for this kind of heterogeneously catalyzed process technology.

High selectivity is one of the main targets in the field of alkylation reactions. High conversions can quite easily be obtained with an acid catalyst, but the product range can vary strongly, as, for example, in the LAB formation: in the alkylation of benzene with 1-dodecene, the desired products are the monoalkylated compounds, particularly 2-phenyldodecane because of its better emulsibility and its easy biodegradability (the sulfonated compound is an environmentally benign tenside).

During this alkylation five different isomers of the monoalkylated product, 2- to 6-phenyldodecane, can be formed. That is caused by a shift of the charge in the carbenium ion intermediate (see Fig. 1) [18]. The 1-phenyl isomer is not formed, as the reaction follows the Markownikow rule.

The isomer distribution changes depending on the catalyst used (Table 1).

Table 1
The isomer distribution of phenyldodecanes ($x$-Ph.-Dod.; $x = 1, 2, 3, 4, 5, 6$) in the alkylation of benzene with 1-dodecene over some homogeneous catalysts [20,21] and MSA catalyst ($T = 80\,^\circ C$, 1 eq MSA, $t = 24$ h)

| Catalyst | 1-Ph.-Dod. | 2-Ph.-Dod. | 3-Ph.-Dod. | 4-Ph.-Dod. | 5-Ph.-Dod. | 6-Ph.-Dod. |
|---|---|---|---|---|---|---|
| HF | 0 | 20 | 17 | 16 | 23 | 24 |
| $AlCl_3$ | 0 | 32 | 22 | 16 | 15 | 15 |
| $H_2SO_4$ | 0 | 41 | 20 | 13 | 13 | 13 |
| MSA | 0 | 29 | 19 | 16 | 19 | 17 |

Generally, all five products are formed. The product distribution obtained with $AlCl_3$ corresponds to the thermodynamical equilibrium of the different phenyl-positioned isomers at 35 °C [19]. Lewis acids such as $AlCl_3$ indeed have the ability to isomerize the phenylalkanes formed. In contrast, pure proton acids such as $H_2SO_4$ and HF only isomerize the olefins prior to the alkylation step [20–22]. Other products which have been found result from a possible dealkylation of the alkylated compounds, branching of the alkyl chain [23], transalkylations, and polyalkylations [24]. Other possible by-products are the isomerization and oligomerization products of the olefin.

Here we report on a new process for the alkylation of benzene with 1-dodecene using methanesulfonic acid as the catalyst. Methanesulfonic acid $CH_3SO_3H$ (MSA) is an alkanesulfonic acid, which has found numerous applications as, for example, as esterification or alkylation catalysts, as polymer solvents, in the electroplating and electrochemistry industry, etc. MSA is a strong acid ($pK_a = -1.9$), which is almost completely ionized at 0.1 M in an aqueous solution, and has a low tendency to oxidize organic compounds. It is, however, far less corrosive and toxic than the usual mineral acids. Under normal conditions aqueous solutions evolve no dangerous volatiles, making it safe to handle. Finally, it is readily biodegradable within 28 days, only forming $CO_2$ and sulfate, making it an environmentally benign material [25]. Furthermore, it has the advantage, as will be shown, that it can be separated readily from the reaction mixture and reused.

## 2. Experimental

Methanesulfonic acid (anhydrous grade > 99 wt%) was kindly provided by Atofina, Groupe de Recherche de Lacq. The reactions were carried out in a round-bottom flask equipped with a condenser under atmospheric pressure. Steel autoclaves were used for reactions under pressure. The benzene/1-dodecene molar ratio was adjusted at 8/1. The reaction took place either solvent free or with DMSO and THF, respectively, as the solvent (50 wt% of the solution). The amount of MSA varied: 0.25, 0.50, 1.00, and 2.00 M eq based on 1-dodecene. Temperatures between 20 and 84 °C have been chosen (the boiling point of the benzene/1-dodecene mixture was 84–85 °C) and kept stable by a silicon oil bath equipped with a thermostat and a magnetic stirrer and heated by a hotplate. The reactions were carried out under air or dry argon atmosphere.

Based on the first experiments optimal reaction conditions for high 1-dodecene conversion and high selectivities of monoalkylated phenyldodecanes were determined by means of an experimental testing plan, using the program Design Expert v.5 (Stat. Ease Corp.). The following limits have been chosen: $T = 60–80\,^\circ C$, MSA = 0.5–1.5 M

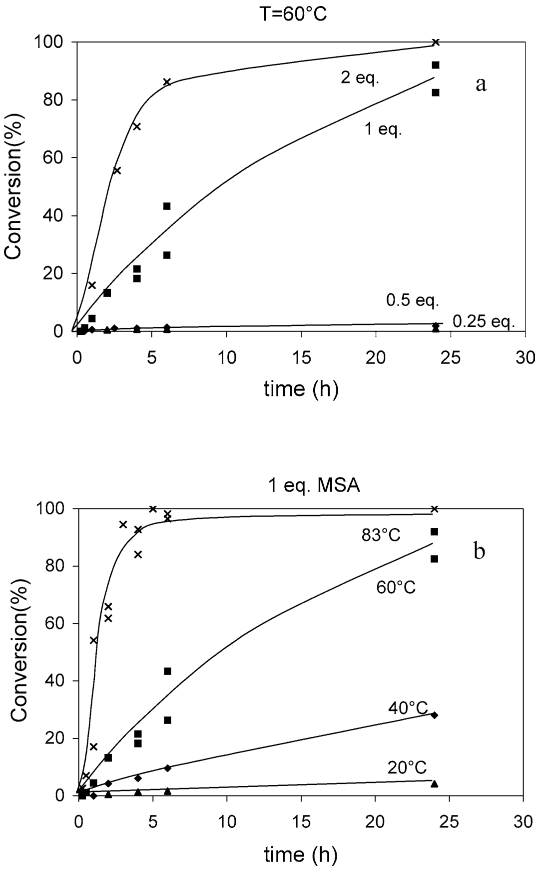

Fig. 2. The conversion of 1-dodecene: (a) for varying equivalents of MSA at 60 °C; (b) with increasing temperature using 1 eq of MSA.

eq, benzene/1-dodecene = 5–10 M eq, $t = 2$–6 h, which resulted in 30 experiments with 6 centerpoints.

The influence of the agitation was investigated by comparing the stirring using a magnetic bar with a dissolver tooth-edge circular stirring.

For comparison reasons HF and $AlCl_3$ were also used as catalysts, with somewhat different reaction conditions. For the HF catalyst the conditions are: amount of HF = 10 M eq, $T = 50\,°C$, $t = 10$ min; for $AlCl_3$ catalyst, amount of $AlCl_3 = 0.1$ M eq, $T = 0$–35 °C, $t = 30$–45 min; and for MSA catalyst, amount of MSA = 1 M eq, $T = 80\,°C$, $t =$ 240–300 min.

For reusability tests the MSA was separated from the reaction mixture, diluted with water, and washed three times with dichloromethane. After that the water was removed by distillation. The influence of the presence of water on the activity was investigated by preparing a 10 wt% MSA/water mixture. Then, different concentrations were adjusted by subsequent addition of MSA. The influence of the inhibitory products strongly adsorbed on MSA and the presence of a crude organic phase were studied comparatively, as well. Thereby, fresh MSA was blended with 0.2 g of the residue obtained after evaporation of the dichloromethane phase used in the reactivation procedure, or with 0.2 g of crude organic phase.

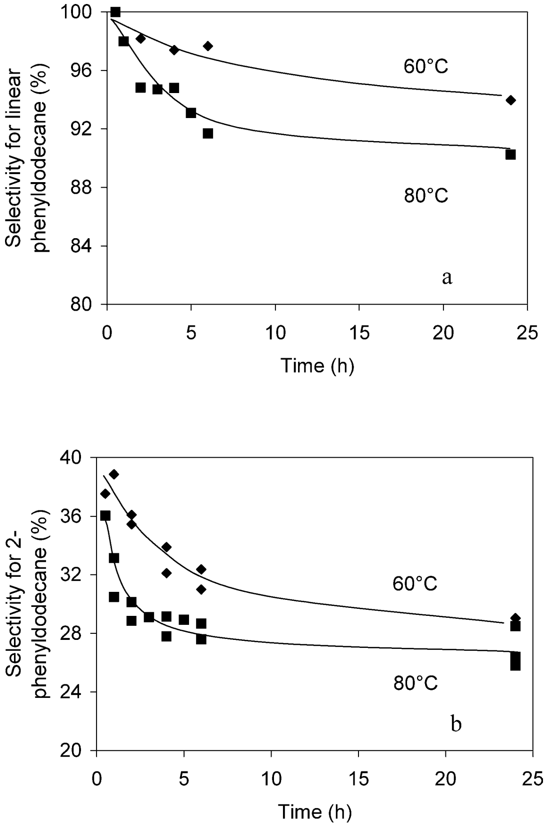

Fig. 3. The selectivity based on 1-dodecene achieved by 1 eq MSA at 60 and 80 °C: (a) for the linear alkylbenzenes and (b) for 2-phenyldodecane.

Samples were taken at regular intervals and analyzed by gas chromatography (HP6890) on a 60 m SE-54 column (15 min 140 °C, 10 °C/min to 270 °C, 30 min 270 °C).

## 3. Results and discussion

Fig. 2 shows the catalytic activity in the alkylation of benzene with 1-dodecene at 60 °C over different amounts of MSA (Fig. 2a) and at different reaction temperatures (Fig. 2b) over 1 eq MSA as function of the reaction time.

As illustrated in Fig. 2a, at least a stoichiometric amount of MSA was needed to achieve an almost complete 1-dodecene conversion after 24 h at 60 °C and for a benzene/1-dodecene ratio of 8/1. At lower amounts of MSA only minor conversions were found. With 2 eq of MSA conversions of about 90% could be obtained already after 6 h.

The 1-dodecene conversion was also strongly influenced by the temperature. Fig. 2b indicates that in the presence of 1 eq MSA there was hardly any conversion at 20 °C after 24 h, whereas at 83 °C (refluxing conditions) nearly full 1-dodecene conversion was achieved already after 5 h.

When using a solvent (50 wt% of DMSO or THF) the reaction rate slowed down dramatically. Therefore, no solvents were used in further experiments.

Fig. 3 illustrates the selectivity to the linear alkylbenzenes (Fig. 3a) and to 2-phenyldodecane (Fig. 3b), respectively,

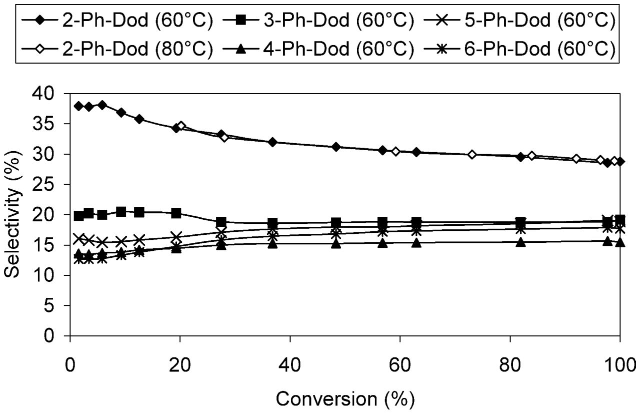

Fig. 4. The selectivity based on 1-dodecene to all linear phenyldodecanes at 60 °C and to 2-phenyldodecane at 80 °C.

based on 1-dodecene transformed over 1 eq MSA at 60 and 80 °C as a function of reaction time.

The selectivity to the linear alkylbenzenes decreased from 100% to about 94% at 60 °C, or to 90% at 80 °C; there was an up to 10% selectivity for branched compounds. It is obvious that an increase of the temperature caused an increase in the 1-dodecene conversion, as well as an increased amount of branched alkylbenzenes (see Fig. 3a). In the first hours mainly 2-phenyldodecane was formed (see Fig. 3b). The drop in selectivity was stronger at 80 °C than at 60 °C; at higher temperatures the rate for branched isomers increased.

Fig. 4 shows the selectivity based on 1-dodecene to all the linear phenyldodecanes at 60 °C and alone to 2-phenyldodecane at 80 °C as function of conversion.

Thereby, the selectivity to 2-phenyldodecane was the same at 60 and 80 °C at the same conversions. The selectivity to 2-phenyldodecane at 100% conversion was 28%, and the total selectivity to all linear phenyldodecanes was 92%.

To find out if MSA can isomerize the phenyldodecanes, or if the isomerization took place on 1-dodecene before alkylation, a mixture of linear phenyldodecanes with a high 2-phenyldodecane content (37%) was treated with MSA. The composition of this mixture did not change, showing that MSA only isomerized the 1-dodecene, and not the phenyldodecanes. This is in agreement with the fact that MSA is a pure proton acid such as HF, which also does not isomerize the phenyldodecanes.

Using the first data set the optimal reaction conditions were determined by means of an experiment setup developed with the program Design Expert v.5 (30 experiments, with 6 center points; $T = 60$–$80\,^\circ\mathrm{C}$, amount of MSA = 0.5–1.5 M eq, benzene/1-dodecene ratio = 5–10 M eq, $t = 2$–6 h). To achieve a conversion of 98% and a linear phenyldodecanes selectivity of 92% (a yield of 90%) the following reaction conditions should be used:

$T = 70$–$74\,^\circ\mathrm{C}$;

MSA amount = 1.4–1.5 M eq;

benzene to dodecene ratio = 8.0–8.5;

time = 255–285 min.

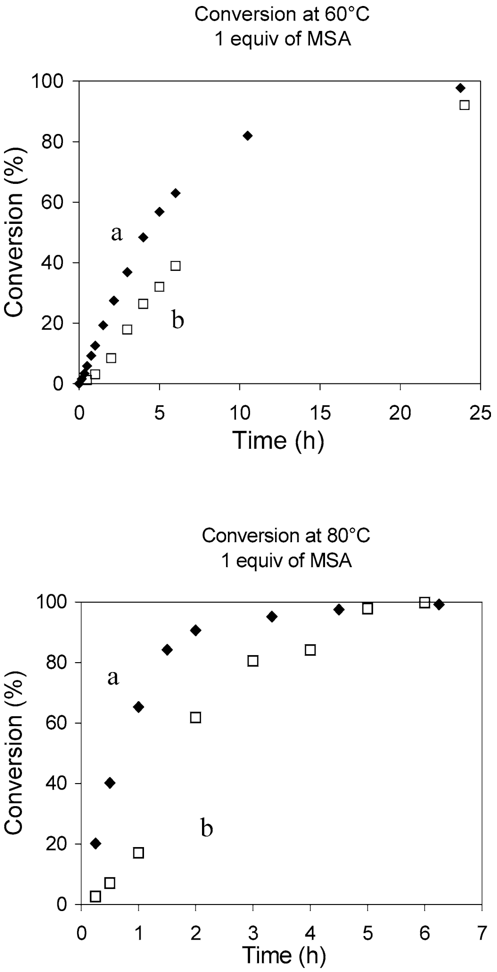

Fig. 5. The influence of the stirrer type on the 1-dodecene conversion at 60 and 80 °C: (a) dissolver type tooth–edge circular stirrer and (b) magnetic stirring bar.

The biphasic reaction mixture (the organic phase and the methanesulfonic acid phase) allows an easy separation. However, this fact causes strong diffusion limitations. Therefore stirring/mixing of the reaction mixture is an important parameter. The influence of two different types of stirrers on the 1-dodecene conversion was investigated, comparing stirring with a magnetic stirring bar (b) with a dissolver-type tooth edge circular stirrer (a) in a reactor equipped with breakers at both 60 and 80 °C (see Fig. 5).

The conversions increased when using the dissolver type stirrer: at 80 °C a quantitative conversion was found already after 3 h instead of 4–5 h in case of the magnetic stirring bar.

The catalytic performance over the three alkylation catalysts—MSA, HF, and $AlCl_3$—was investigated. A direct comparison is somewhat difficult because different reaction conditions were used, because MSA is not as reactive as $AlCl_3$ and HF. For MSA the reaction temperature and the reaction time had to be increased. The results obtained using $AlCl_3$, HF, or $H_2SO_4$ (see Tables 1 and 2) were in agreement with the observation of Forni and Bonini [20] and Ullmann's Chemical Encyclopaedia [21].

Table 2
Comparative selectivity to phenyldodecanes for the alkylation of benzene with 1-dodecene over different homogeneous catalysts according to Forni and Bonini [20] and MSA catalyst

| Catalyst | Equivalents of olefin | Temperature (°C) | Time (min) | Selectivity to phenyldodecanes |
|---|---|---|---|---|
| HF | 10 | 50 | 10 | ~ 90% |
| $AlCl_3$ | 0.1 | 0–35 | 30–45 | ~ 70% |
| $H_2SO_4$ | 0.1 | 0–10 | 120 | ~ 70% |
| MSA | 1 | 80 | 240–300 | ~ 90% |

Table 1 presents the distribution of the linear phenyldodecanes obtained over the catalysts HF, $AlCl_3$, $H_2SO_4$, and MSA ($T = 80\,°C$, 1 eq MSA, $t = 24$ h).

The isomer distribution achieved with MSA is approximately the same as that found for $AlCl_3$. More of the desired 2-phenyldodecane was found than in the case of HF. Furthermore, the use of MSA obviously results in higher selectivity to the phenyldodecanes compared with the performances of $AlCl_3$ and $H_2SO_4$, but at a comparable selectivity as found over HF (see Table 2). However, for the latter a 10-fold amount of catalyst was necessary. The regioselectivity obtained with MSA is roughly the same, but is obviously not improved.

A strong disadvantage of the homogeneous systems $AlCl_3$ and HF is the costs of the reactor because of its aggressiveness. A disadvantage of MSA is the longer reaction time needed for high conversion. For the HF-based system a reaction time of 10 min was found to be sufficient. However, in the case of MSA 5 to 6 h are needed.

Finally, the reusability of the MSA was investigated. The MSA was separated from the reaction mixture and reused up to 5 times directly with fresh 1-dodecene and benzene mixtures at 60 and 80 °C. As can be seen in Fig. 6 MSA suffered under a strong loss of activity, especially at lower temperatures.

As MSA showed a loss in activity, the reactivation was investigated. First, MSA was diluted with water and washed three times with dichloromethane in a weight ratio of 1:2:1. Subsequently, the water was removed by distillation, obtaining anhydrous MSA. Such treatment resulted in the possibility of reusing the MSA at least up to five times (see Fig. 7). In experiments in which reactivated MSA was used, the catalyst was essentially as active as fresh material. This observation demonstrates that MSA can be recycled after a reactivation by a treatment with water and dichloromethane before the next run. This reactivation procedure is more complicated than the industrial ones for $AlCl_3$ (settling) and HF (settling and stripping) and might be more cost intensive also due to probably higher catalyst consumption.

The deactivation of MSA seems to be a result of the presence of water in the reaction mixture. If the alkylation was done under a dry argon atmosphere the deactivation behavior was the same; therefore, moisture from the ambient atmosphere could not be the water source. If indeed water caused the deactivation it could only stem from the reactants. The water content of benzene for example was < 0.03%, and the MSA (even though it was anhydrous grade > 99 wt%) contained small amounts of water, too.

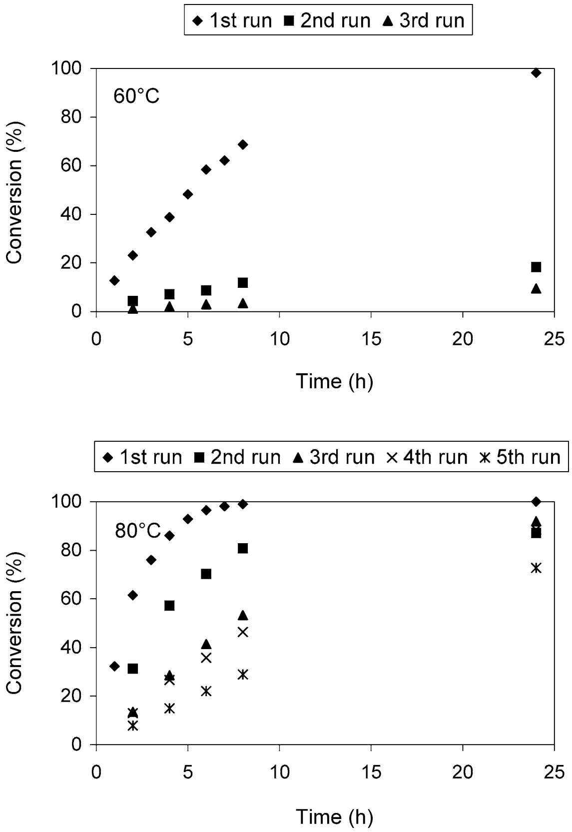

Fig. 6. The reusability of MSA at 60 and 80 °C without reactivation.

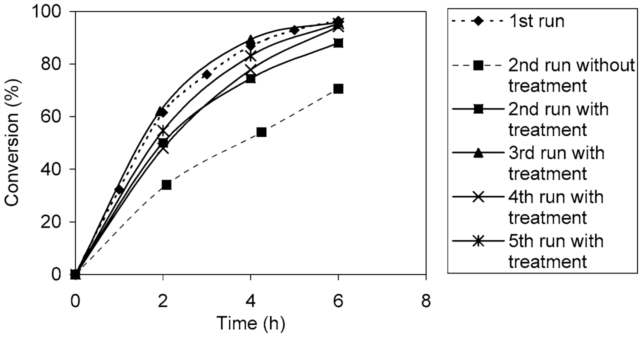

Fig. 7. The activity of reactivated MSA ($T = 80\,°C$, benzene: 1-dodecene:MSA ratio = 8:1:1).

To investigate if water could indeed be responsible for the deactivation, and to determine the influence of the amount of water on the deactivation behavior, a 10 wt% water containing MSA solution was prepared. Out of that, mixtures with lower water contents were prepared by the addition of appropriate amounts of MSA.

The 1-dodecene conversion dependent upon the added water content is presented in Table 3.

There was a strong decrease in the activity if the MSA contained more than 0.25 wt% of water. The removal of wa-

Table 3
Influence of the amount of water added in the reaction mixture on the conversion of 1-dodecene in the alkylation of benzene with 1-dodecene over MSA catalyst ($T = 80\,^\circ\mathrm{C}$, benzene:1-dodecene:MSA ratio = 8:1:1, $t = 5$ h)

| Water content (%) | 0 | 0.10 | 0.25 | 0.50 | 1 | 2.50 | 5 | 10 |
|---|---|---|---|---|---|---|---|---|
| Conversion (%) | 88.00 | 85.23 | 80.69 | 56.87 | 46.35 | 12.11 | 1.89 | 0.34 |

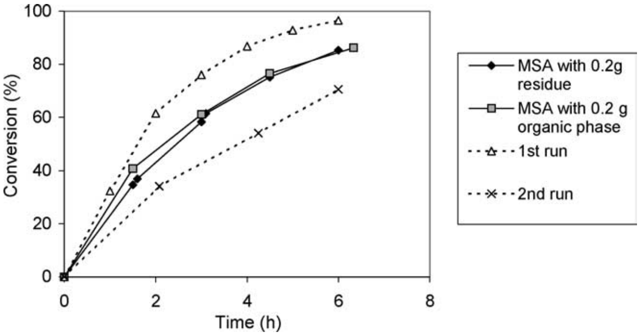

Fig. 8. The influence of strongly adsorbed species on activity of MSA (residue of extraction or crude organic phase at $T = 80\,^\circ\mathrm{C}$ for a benzene:1-dodecene:MSA ratio = 8:1:1).

ter from recycled MSA was clearly essential for obtaining a catalytically active material. However, the amount of water from reactants present in the system is not enough for the observed strong deactivation.

In order to explain the drop of 1-dodecene conversion during successive catalytic runs over MSA, the influence of the presence of an inhibitory product formed during the reaction or crude organic phase was investigated. To test this assumption, comparative catalytic tests over MSA differently blended (one with 0.2 g residue extracted with dichloromethane in reactivation procedure and one with 0.2 g of crude organic phase) were carried out.

Fig. 8 presents comparatively the 1-dodecene conversion over these two differently blended MSA as a function of reaction time at 80 °C.

Both blended MSA give lower conversion than pure MSA, without a significant difference between them.

The premise that simultaneous processes of deactivation induced by water, as well as by strongly and irreversibly adsorbed high boiling compounds amassing in the system during successive catalytic runs, can explain the observed MSA deactivation. Also, these catalytic results confirm the right choice of the successive steps of the reactivation procedure (dichloromethane washing and water removal) in order to recover completely the catalytic performance of MSA.

## 4. Conclusions

Benzene could be alkylated with 1-dodecene to the linear phenyldodecanes with a selectivity of 90% using methanesulfonic acid as catalyst. The selectivity to 2-phenyldodecane was about 28%. As side products only some branched compounds were found. With increasing amounts of MSA the reaction proceeded faster; for a complete conversion at least 1 M eq of MSA was needed. The conversion was also strongly dependent on the temperature and on the stirrer type. The optimal conditions, determined with a statistical experiment setup based on 30 experiments with 6 centerpoints, were: $T = 70$–$74\,^\circ\mathrm{C}$, 1.4–1.5 eq of MSA, benzene/1-dodecene ratio = 8–8.5, $t = 255$–$285$ min. MSA could be recycled at least up to five times after a reactivation treatment with water and dichloromethane.

As this process is based on the noncorrosive, easily biodegradable MSA, it is environmentally benign, and in this respect might have advantages in contrast to processes based on the homogeneous catalysts such as HF, $AlCl_3$, or $H_2SO_4$. However, the less activity and the more complicated reactivation of MSA show some disadvantages. An advantage of this new MSA-based process in comparison to the environmentally friendly heterogeneously catalyzed DETAL process is that the same reactors as for the HF or $AlCl_3$-based processes can be used. However, it was not the intention of the authors to present an economic comparison of all the known and currently applied process technologies with this MSA-based procedure.

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## References

[1] J.L.G. de Almeida, M. Dufaux, Y. Ben Taarit, C. Naccache, J. Am. Oil Chem. Soc. 71 (1994) 675.
[2] U. Schoenkaes, Chim. Oggi 16 (1998) 9.
[3] R.C. Tarring, Air Water Pollut. 9 (1965) 545.
[4] G.G. Robeck, J.M. Cohen, W.T. Sayers, R.L. Woodward, J. Water Pollut. Control Fed. 35 (1963) 1225.
[5] W.A. Sweeney, A.C. Olson, J. Am. Oil Chem. Soc. 41 (1964) 815.
[6] J. Rubinfeld, E.M. Emery, H.D. Cross III, J. Am. Oil Chem. Soc. 41 (1964) 822.
[7] K.L. Matheson, T.P. Matson, J. Am. Oil Chem. Soc. 60 (1983) 1693.
[8] S. Sivasanker, A. Thangaraj, J. Catal. 138 (1992) 386.
[9] J.L. Berna Tejero, A.M. Danvila, US patent 5,146,026 (1992), to Petroquimica Espanola S.A. (PETRESA) Spain.
[10] R.T. Sebulsky, A.M. Henke, Ind. Eng. Chem. Proc. Des. Dev. 10 (1971) 272.
[11] J.H. Clark, G.L. Monks, D.J. Nightingale, P.M. Price, J.F. White, J. Catal. 193 (2000) 348.
[12] C. de Castro, E. Sauvage, M.H. Valkenberg, W.F. Hoelderich, J. Catal. 196 (2000) 86.
[13] T.-C. Tsai, I. Wang, S.-J. Li, J.-Y. Liu, Green Chem. 5 (2003) 404.
[14] C. Perego, P. Ingallina, Catal. Today 73 (2002) 3.
[15] J.A. Kocal, US patent 5,196,574 (1993), to UOP.
[16] K. Tanabe, W.F. Hoelderich, Appl. Catal. A 181 (1999) 399.
[17] J.A. Kocal, B.V. Vora, T. Imai, Appl. Catal. A 221 (2001) 295.
[18] H.R. Alul, Ind. Eng. Chem. Prod. Res. Dev. 7 (1968) 7.

[19] H.R. Alul, J. Org. Chem. 33 (1968) 1522.
[20] L. Forni, D.S. Bonini, Chim. Ind. 61 (1979) 533.
[21] Ullmann's Chemical Encyclopaedia, vol. A1, VCH, Weinheim, 1985, p. 195.
[22] A.C. Olson, Ind. Eng. Chem. 52 (1960) 833.
[23] L. Cavalli, A. Landone, C. Divo, G. Gini, M. Galli, E. Bareggi, J. Am. Oil Chem. Soc. 53 (1976) 704.
[24] R.D. Swisher, E.F. Kaelble, S.K. Liu, J. Org. Chem. 26 (1961) 4066.
[25] M.D. Gernon, M. Wu, T. Buszta, P. Janney, Green Chem. 3 (1999) 127.