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An efficient method for the alkylation of α-methylnaphthalene with various alkylating agents using methanesulfonic acid as novel catalysts and solvents

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Friedel-Crafts alkylations of α-methylnaphthalene with various alkylating agents were first carried out in the presence of methanesulfonic acid (MeSA). The Brønsted acid catalyst MeSA exhibited outstanding catalytic performance, and was found to be excellent catalyst and solvent for alkylation reaction of aromatic hydrocarbon. It's found that alkenes can be used as excellent alkylating agent for alkylation of α-methylnaphthalene. The effects of various reaction parameters like type of alkylating agent, dosages of catalysts, reaction temperature and reaction time were investigated in detail. Moreover, the performance of reuse for catalysts was also studied. It's found that, under the optimal reaction conditions, more than 90% of conversion for olefins and 100% of selectivity for the desired products were obtained. Compared with traditional catalysis technology, the reaction, catalyzed by MeSA catalyst, no volatile solvents needed, good selectivity for desired products could be obtained. The catalyst can be isolated easily from the reaction mixtures by decantation, and was successfully reused. The methanesulfonic acid could be considered as environmentally friendly novel catalyst and solvent for long-chain alkylation of α-methylnaphthalene with alkenes. The catalytic reaction mechanism for alkylation in the presence of MeSA was proposed as well.

KEY WORDS: alkylation; methanesulfonic acid; brønsted acid catalyst; α-methylnaphthalene; reaction mechanism.

1. Introduction

There exists abundant methylnaphthalene distillation cut in both pyrolysis gas oil and coal-tar cleaning oil, whose downstream products need to be exploited urgently. Studies on the alkylation of α-methylnaphthalene with long-chain alkenes possess double objective. One is to meet the urgent demand for exploiting downstream products of methylnaphthalene distillation; the other is preparing long-chain alkylmethylnaphthalenes, the core intermediates for alkylnaphthalene sulfonate anionic surfactants. Alkylnaphthalene sulfonates are one of the most important anionic surfactants for all kinds of industrial purposes. By using them as a chemical oil-displacing agent for enhanced oil recovery, satisfactory results could be obtained and the ultralow interfacial tension between oil and water could be achieved [1,2]. Moreover, because of their eminent surface activity, they may be used in many fields such as cleaning, dying and printing, emulsifying, ore milling and nanotechnology [3]. To date, the long-chain alkylation of benzene has already been widely and thoroughly investigated [4–6], but not for naphthalene and its derivatives [7]. To our knowledge, scarcely any relative studies for the long-chain alkylation of methylnaphthalene have been reported [8].

The alkylations of aromatic hydrocarbon with long-chain olefins, alkyl halide and aliphatic alcohol, are typical Friedel-Crafts reaction, and may be catalyzed conventionally by homogeneous acid catalysts, such as H_2SO_4, BF_3, HF, $AlCl_3$, $FeCl_3$, etc., which give rise to many problems concerning the handing, health, safety, corrosion and waste disposal of the catalysts [9]. In order to overcome these problems, many efforts have been devoted to the search of various heterogeneous acid catalysts to replace the homogeneous acid catalysts, including zeolite [10,11], heteropoly acid [9,12] and ionic liquids [13–16] etc. However, there exist some shortages towards the above catalysis technology. Catalyzed by zeolite catalysts, the reactions need a series of rigorous reaction conditions, besides the catalysts are easy to deactivation. The heteropoly acid catalysts are also easy to deactivation, whereas they possess high catalysis activation under weak reaction conditions. In recent years, the ionic liquids are being more and more regarded as relatively clean catalysts and solvents. As far as alkylation is concerned, considerable attention has been focused on the use of chloroaluminate ionic liquids, which indicate an excellent catalysis performance. However, the chloroaluminate ionic liquids are sensitive to water and air, which leads to lose their catalysis activation. In the present report, to my knowledge, the methanesulfonic acid (figure 1) is first used as both environmentally friendly novel catalysts and green solvents for Friedel-Crafts reaction. Our aim is to find an

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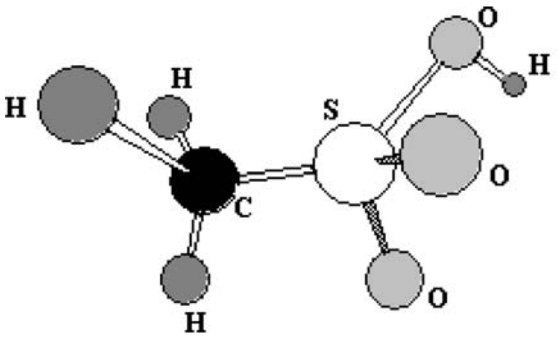
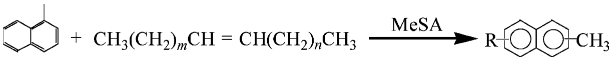


Figure 1. 3D molecular model of MeSA.

excellent and novel green catalyst for alkylation of arenes. The present report describes a new thought for alkylation.

In the present paper, a practical and efficient procedure for alkylation of α-methylnaphthalene with long-chain alkenes (mixed alkenes, m + n = 7 and 8, mass ratio of C11 to C12 is 45/55) and other alkylating agents is reported, using a MeSA as recyclable catalyst and solvent (scheme 1). The effects of various reaction parameters like type of alkylating agents, dosages of catalysts, reaction temperature and reaction time were investigated in detail. Moreover, the performance of reuse for catalysts was also studied. On the basis of the prevenient studies [15–18], the 5:1 molar ratio of α-methylnaphthalene to alkylating agents were adopted in all cases.



Scheme 1. The main reaction.

2. Experimental

All commercial chemicals were used as received. A certain amount of α-methylnaphthalene (>98%) and alkylating agents (alkalenes, 1-dodecanol and *n*-bromododecane) were put into a 100 ml 3-neck flask equipped with a stirrer, a reflux condenser with drying pipe and a thermometer. The alkenes include a 1-dodecene and the mixed olefins C_{11-12} (weight ratio 45/55, afforded by Fushun Petrochemical Company, China). After stirring for about 30 min at room temperature, a certain amount of MeSA were added. Then the mixture was heated to the required reaction temperature. And to record the reaction time at once. The reaction mixtures were stirred at 273–373 K for about 0 min–8 h, depending on each specific reaction. After the completion of alkylation reaction, the upper solvent layer containing the alkylated products and unreacted reactants was separated from the MeSA layer at the bottom of flask simply by decantation.

All samples were characterized [19,20] qualitatively with HP6890/5973 GC/MS equipped with a HP-5MS column, 30 m × 0.25 mm × 0.25 μm; quantitative analyses were carried out with HP6890GC equipped with a HP-5column, 30 m × 0.32 mm × 0.25 μm. The concentrations of reactants and products were directly given by the system of GC chemstation (in this departmental laboratory) according to the area of each chromatograph peaks.

3. Results and discussion

3.1. *Effect of alkylating agent type*

In the present study, alkylation of α-methylnaphthalene with various alkylating agents like alkalenes, 1-dodecanol and *n*-bromododecane gave 100% selectivity for the desired products, a series of isomers of monoalkylmethylnaphthalene. In all cases, no alkylated byproducts were detected. MeSA exhibited an excellent catalysis performance.

Table 1 shows the effects of type of alkylating agents on the alkylation. The alkylation of α-methylnaphthalene with various alkylating agents in the presence of $Et_3NHCl–AlCl_3$ (0.71 molar fraction of aluminum trichloride) ionic liquids has been contrastively studied besides catalyzed by MeSA.

As can be seen that, there exists obvious difference in the effect of alkylating agent on the alkylation in the two catalysis systems. Catalyzed by both ionic liquids and MeSA, 100% of conversion for 1-dodecene was obtained. But the reaction could hardly take place when the aliphatic alcohol was used as alkylating agent. The possible reason is that the produced water destroys the catalysis systems. When the *n*-bromododecane is used as alkylating agent for the alkylation of α-methylnaphthalene, the reaction goes through Lewis catalyzed mechanism. The higher conversion was obtained in the presence of ionic liquids, but not MeSA. Therefore, alkenes can be used as excellent alkylating agent for alkylation of α-methylnaphthalene. The alkylation of α-methylnaphthalene with alkenes go through a carbonium ion mechanism, the possible mechanism is shown in scheme 2. On the basis of the above studies, the

Table 1

Effect of type of alkylating agent on the alkylation of α-methylnaphthalene

Alkylating agent	Conversion of alkylating agent (%)	
	By ionic liquids	By MeSA
1-Dodecene	100.0	100.0
1-Dodecanol	6.2	1.0
n-Bromododecane	97.8	0

The dosage of ionic liquids is 12% of reagents; the mole ratio of MeSA catalyst to alkylating agent is 8. $T = 353$ K, $t = 30$ min.

alkylation of α-methylnaphthalene with $C_{11–12}$ mixed alkenes in the presence of MeSA were further studied as follows:

3.2. *Effect of dosage of MeSA catalyst*

The effect of the dosage of MeSA catalyst on the alkylation reaction was studies by varying molar ratio of MeSA to alkenes from 0.4 to 15.0. The results are shown in figure 2.

As can be seen from figure 2 that, there exists an obvious increase in conversion of alkenes from 12.3 to 92.8% when the molar ratio of MeSA catalyst to alkenes is increased from 0.4 to 10.0. A slight change takes place when the dosage of catalyst was further increased. More than 90% of conversion can be obtained as long as the dosage of catalyst is not less than 7.0.

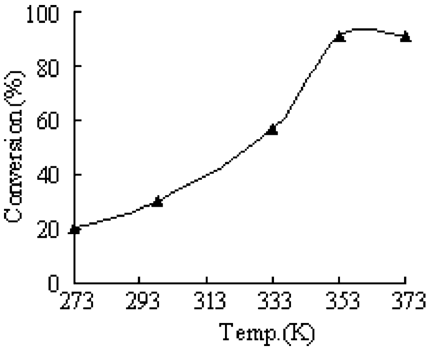
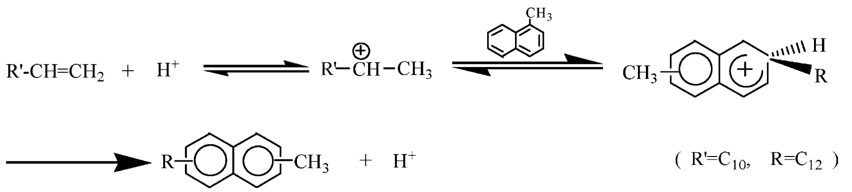


Figure 3. Effect of reaction temperature on the alkylation reaction (molar ratio of MeSA to alkenes = 8.0, t = 30 min).



Scheme 2. The mechanism of long-chain alkylation of α-methylnaphthalene with 1-dodecene in the presence of MeSA.

3.3. *Effect of reaction temperature*

The effect of temperature change on the conversion of alkenes was studied in the temperature range of 273–373 K. The results are given in figure 3.

It's obviously seen from that, the conversion of alkenes increased with an increase in temperature from 273 to 353 K, then slight decrease take places when the temperature is further increased. The maximum conversion of alkenes is obtained when the temperature is 353 K.

3.4. *Effect of reaction time*

A series of reactions were carried out to establish the effect of reaction time on the alkylation of α-methylnaphthalene with alkenes in the presence of 8.0 molar ratio of catalyst amount at 353 K. The reactions were performed under exactly the same conditions except varying the reaction time from 0 to 480 min. The results are shown in figure 4.

It's found from figure 4 that there exists a dramatic increase in conversion of alkenes as the reaction time increases from 0 to 30 min. A slight increase in conversion takes place when the reaction time is further increased. The 93.3% of maximum conversion is obtained when the reaction time is 240 min.

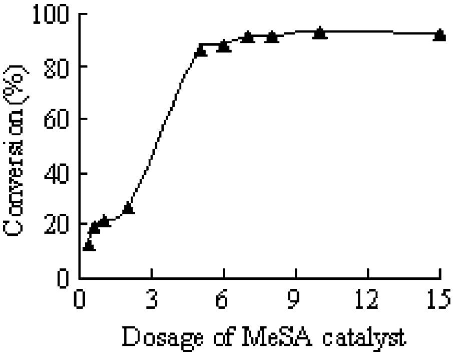


Figure 2. Effect of dosage of MeSA catalyst on the alkylation reaction (T = 353 K, t = 30 min).

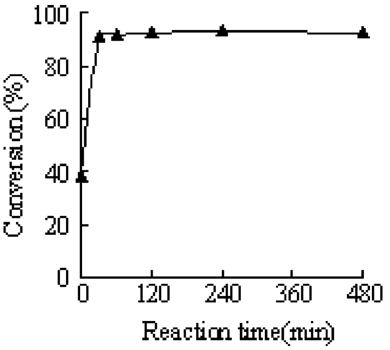


Figure 4. Effect of reaction time on the alkylation reaction (molar ratio of MeSA to alkenes = 8.0, T = 353 K).

Table 2
The results of the reuse of catalysts

Run times	C_L%	S_{AMN}%
1	92.8	100
2	89.6	100
3	86.5	100

Molar ratio of MeSA catalyst to alkenes = 5:1, $T = 353$ K, $t = 120$ min.

3.5. Reusability of MeSA catalyst

The products and unreacted reactants do not dissolve in the MeSA, and therefore they could be isolated easily by decantation, which makes it is possible for MeSA catalyst to be reused. Here the primary studies on the reusability of MeSA catalyst were carried out, and the results are shown in table 2.

As can be seen from the table that, the MeSA may be reused as novel catalysts and solvents for alkylation of α-methylnaphthalene with long-chain alkenes, which provides a new route for exploiting novel catalyst systems for alkylation of aromatic hydrocarbon.

4. Conclusions

The long-chain alkylation of α-methylnaphthalene was successfully carried out first in a batch mode in the presence of MeSA. The long-chain alkenes can be used as excellent alkylating agent for alkylation of α-methylnaphthalene. The alkylation of α-methylnaphthalene with long-chain alkenes catalyzed by MeSA goes through a carbonium ion mechanism. The present study indicates that MeSA could be considered as a novel environmentally friendly alternative to the existing homogeneous catalysts for Friedel-Crafts alkylation. Under the optimal reaction conditions, more than 90% of conversions for alkenes, and about 100% of selectivity towards the desired products were obtained, and no volatile organic solvents needed. The products and unreacted reactants do not dissolve in the MeSA, and therefore they could be isolated easily by decantation. MeSA could be used as novel reaction medium for Friedel-Crafts alkylation of arenes.

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