

SYNTHESIS OF SUPPORTED ALUMINUM CHLORIDE AND CHLOROALUMINATE IONIC LIQUID CATALYST FOR ALKYLATION OF BENZENE

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Summary

AlCl_3 and triethylaminopropyl chloroaluminate, bonded on silica gel catalysts were prepared, characterized and were found highly active for benzene alkylation with 1-dodecene. The product consisted of five isomers of linear alkylbenzenes from 2-LAB to 6-LAB and selectivity of the 2-LAB was 45% for supported catalyst, which was much larger than for unsupported AlCl_3 catalyst (~33%). Both catalysts were successfully run for 500 hours in packed bed reactor under argon atmosphere. Molecular modeling of the catalysts was performed on GAUSSIAN 03 using B3LYP/6-31G** method and the results match well with experiments.

Keywords

Green CRE, computational catalysis, novel functional materials.

Introduction

Linear alkylbenzenes (LABs) are used to produce detergents and was carried out by alkylation of the benzene with long chain olefins (C_{10} - C_{14}) in the presence of AlCl_3 , HF and H_2SO_4 as a catalyst [1]. These catalysts lead to the formation of isomeric products from 2-LAB to 6-LAB, where 2- and 3-LABs are biodegradable. Considerable effort was spent on increasing the selectivity of the biodegradable LABs using zeolites [2]. Recently ionic liquids have made an impact as green catalysts for Friedel-Craft reactions [3]. In this work we report the synthesis of AlCl_3 bonded silica gel (SG- AlCl_3) and triethylaminopropyl chloroaluminate bonded silica gel (SG- $\text{N}^+(\text{CH}_3)_3\text{-Al}_2\text{Cl}_7^-$) catalysts for the benzene alkylation. These catalysts have shown increased selectivity as compared to homogeneous AlCl_3 and retain their activity up to 500 hours of the usage in packed bed reactor under argon atmosphere.

Experimental

1) Catalyst synthesis

a) SG- AlCl_3 catalyst was prepared by taking 5 gram of calcined silica gel (100-300 micron) which was treated with AlCl_3 vapor for a period of 5 hours at 150C.

b) SG- $\text{N}^+(\text{CH}_3)_3\text{-Al}_2\text{Cl}_7^-$ was prepared as follows: A solution of 3-chloropropyl triethoxysilane (7.2g) and triethylamine (2ml) in toluene (15ml) was refluxed for 2 hrs. To this, a prepared mixture containing ammonium chloride salt, 9.1g of calcined silica gel was added and refluxed at 90C for 8 hours. The resulting silica was

washed with acetonitrile in a Soxhlet apparatus for 12 hours and dried at 150C for 5 hrs. Finally AlCl_3 vapor was deposited on triethylaminopropyl silica chloride at 150C for 5 hours.

2) Catalyst characterization

The BET surface area and pore volumes were determined from N_2 adsorption-desorption experiments on Coulter SA 3100. The FT-IR spectra of the catalysts were taken by Bruker-IFS113V FT-IR apparatus. The acidic nature (Bronsted and Lewis) of the catalysts were characterized by FTIR spectroscopy with chemisorbed pyridine. The ^{29}Si and ^{27}Al MAS-NMR of the samples was done on DSX-300/AV-III 500 NMR spectrometer. The SEM micrographs of the samples were obtained by JEOL 840A Scanning Electron Microscope which showed the deposition of AlCl_3 on the surface of silica gel.

3) Catalytic reaction of benzene with 1-dodecene

The apparatus consisted of a round bottomed flask (100ml) serving as a batch reactor. Initial mole ratios of benzene and 1-dodecene were varied from 10:1 to 2:1 respectively. Undecane (10% by weight of total reaction mixture) was used as internal indicator for the analysis of the samples in Gas Chromatograph. The amount of catalyst was 10% by weight of the reaction mixture.

Results and Discussion

The decrease in BET surface area (~30%) and pore volume (~20%) in both the catalysts was associated with adsorption of the AlCl_3 and triethylaminopropyl chloroaluminate within the pores of the silica gel. The FT-

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IR spectra showed the characteristic peaks of the catalysts with Si-O-Si asymmetric and symmetric bond stretching at 1122 and 850 cm^{-1} respectively as shown in Table 1.

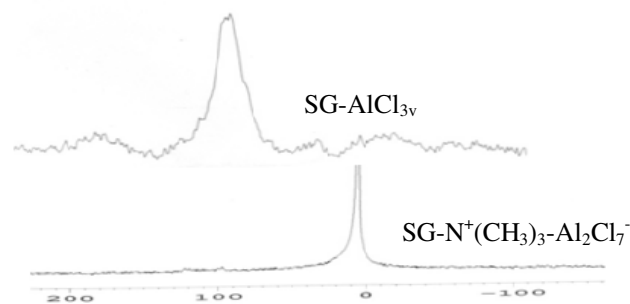


Fig 1: ^{27}Al MAS-NMR of the catalyst

The MAS-NMR of the catalyst SG-AlCl_{3v} and $\text{SG-N}^+(\text{CH}_3)_3\text{-Al}_2\text{Cl}_7^-$ are shown in Fig 1. The peak at 96.578 ppm is attributed to 4-coordinated Al species present in the SG-AlCl_{3v} catalyst. In case of $\text{SG-N}^+(\text{CH}_3)_3\text{-Al}_2\text{Cl}_7^-$ the peak appears at 6.987 ppm which is due to presence of 6-coordinated Al species.

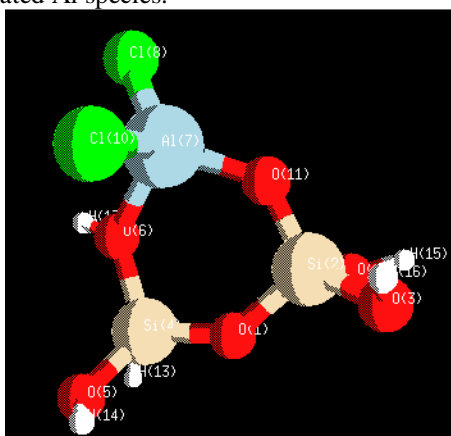


Fig 2: Optimized geometry of AlCl_3 vapor treated silica gel complex catalyst

Molecular modeling of the catalysts complex was performed on GAUSSIAN 03 using B3LYP method and 6-31G** basis set. The optimized structure is shown in the Fig 2. This optimization is found in good agreement as obtained by Xu et al [4]. Vibrational analysis of the catalyst complex is carried out by frequency optimization using the same method and basis set as employed for geometry optimization. The experimental and predicted wavenumber for the corresponding bond stretch are well matched as shown in Table 1.

Table 1: Vibrational frequencies of SG-AlCl_{3v} catalyst

S.No.	Bond	Frequency(cm^{-1}) experimental	Frequency(cm^{-1}) predicted
1	O-H	3500	3537
2	Si-O(sym)	1122	1137
3	Si-O(asym)	850	828

Both the catalyst SG-AlCl_{3v} and $\text{SG-N}^+(\text{CH}_3)_3\text{-Al}_2\text{Cl}_7^-$ were loaded in packed bed reactor and a mixture of benzene and 1-Dodecene (10:1mole ratio) was fed from the top. The catalyst was successfully run for 500 hours with slight decrease in activity of the catalyst as shown in Fig 3.

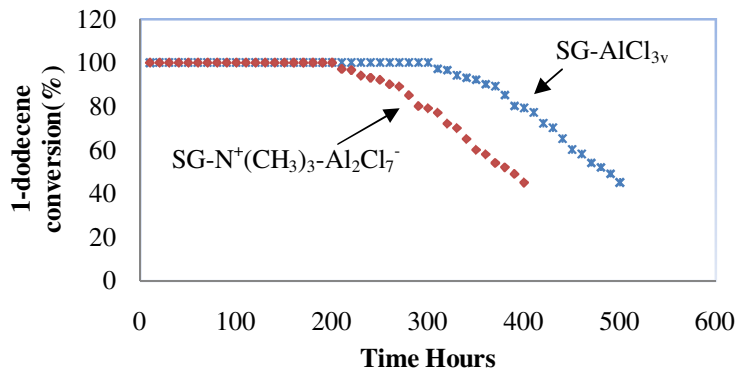


Fig 3: Catalyst life curve

Conclusions

The SG-AlCl_{3v} and $\text{SG-N}^+(\text{CH}_3)_3\text{-Al}_2\text{Cl}_7^-$ catalyst showed the high activity and increased selectivity for LABs synthesis. Moreover the life of both the catalysts was much higher than the unsupported AlCl_3 . Molecular modeling gave an insight into catalyst complex formation.

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