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Friedel-crafts Benzylation of Arenes over Mixed Oxides

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The replacement of liquid acid catalyst by solid acids for the Friedel-Crafts reaction of aromatic alkylation is a challenging task. Mixed oxide possessing spinel structures were found to catalyze the Friedel-Craft benzylation of arenes. It was found that the reaction was very fast at 80 °C, hence the reaction was studied with respect to more substrate. The significant point was even at this temperature monobenzylation, with the para isomer predominating, was achieved. Mixed oxides were prepared by co-precipitation method and were characterized by XRD technique.

Keywords: Mixed oxide; Spinel; Friedel-crafts; Benzylation; Co-precipitation.

INTRODUCTION

The Friedel-Crafts reaction of an aromatic compound with an alkyl halide requires a Lewis acid catalyst. During the past few years, many research groups have exploited the Friedel-Crafts benzylation of arenes using benzyl chloride. Friedel-Crafts alkylation can be performed extremely efficiently in the presence of spinels. The reasons why spinels are emerging as the catalyst of choice for Friedel-Crafts chemistry are due to high yield, high conversions, reduced reaction times, decerease of polyalkylation, lack of rearrangement and reduction in the amount of catalyst necessary. The benzylation of benzene and toluene[1] in particular are used for the preparation of substitutes of polychlorobenzenes, which are used as dielectrics. Diphenylmethane is also used in the preparation of diphenhydramine hydrochloride which is an antihistaminic compound. A number of reviews are available on the liquid phase and gas phase Friedel-Craft reaction using solid acids in general as catalyst.[2-11]

In the present work, benzylation of benzene and few other arenes has been carried out in presence of mixed oxide catalyst viz $Cu_{0.5}Zn_{0.5}Fe_2O_4$, $Zn_{0.5}Ni_{0.5}Fe_2O_4$, $Zn_{0.5}Co_{0.5}Fe_2O_4$, $Cu_{0.5}Co_{0.5}Al_2O_4$, $Cu_{0.5}Zn_{0.5}Al_2O_4$. Also a comparison was done with binary mixtures and simple oxide.

BENZYLATION OF BENZENE

Benzylation of benzene (**1**) with benzyl chloride (**2**) as an alkylating agent gives mainly diphenylmethane (**3**). As the Friedel-Crafts reaction is always accompanied by di- and poly-alkylations, due to higher reactivity of the product than the reactant, the benzylation reaction could also give dibenzylation products (**4**, **5**, **6**) as side products.

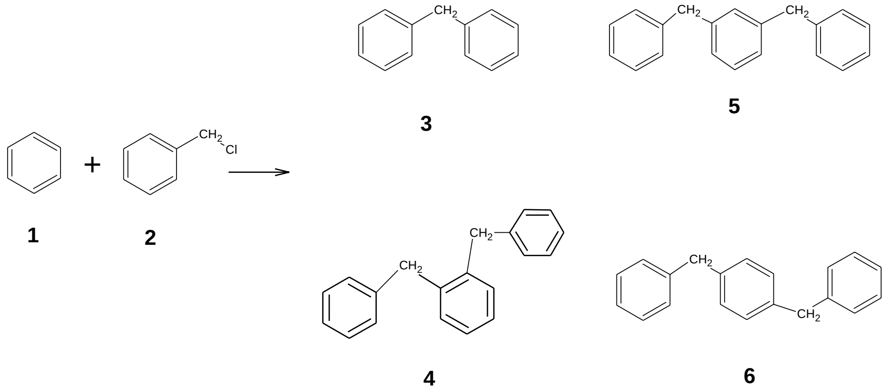

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Table 1. Comparison of Catalyst in Terms of Selectivity for Di-Phenyl Methane

Catalyst	Induction time in min	Reaction time in min	Benzyl chloride % conversion	DPM % selectivity
$Cu_{0.5}Zn_{0.5}Fe_2O_4$	30	80	100	92.8
$Zn_{0.5}Ni_{0.5}Fe_2O_4$	-	10	100	93.7
$Zn_{0.5}Co_{0.5}Fe_2O_4$	-	15	100	93.9
$CuFe_2O_4$	45	120	100	91.8
$NiFe_2O_4$	10	60	100	91.6
$CoFe_2O_4$	5	50	100	93
$ZnFe_2O_4$	-	5	100	92.8
ZnO		120	42	91
Fe_2O_4		20	100	92.6

Temperature: 80 °C
Benzene: 20 mL
Benzyl chloride: 5 mL

Thus dibenzylbenzene, tribenzylbenzene, etc. may be formed in the reaction, dibenzylbenzene being the most prominent side product.

EXPERIMENTAL

Catalyst Preparation

Catalysts were prepared by co-precipitation method.[12,13] The starting materials were analytical reagent grade sulphates. An aqueous solution containing the desired ions in the required molar proportion was prepared by dissolving the salts in the stoichiometric proportion in distilled water. It was precipitated by adding sodium hydroxide and the pH of the solution was maintained between 9 to 9.5. The solution was kept on a water bath maintained at 80 °C for 3 hours and then oxidized by adding the required amount of 30% H_2O_2 dropwise with constant stirring. After the reaction was over the re-

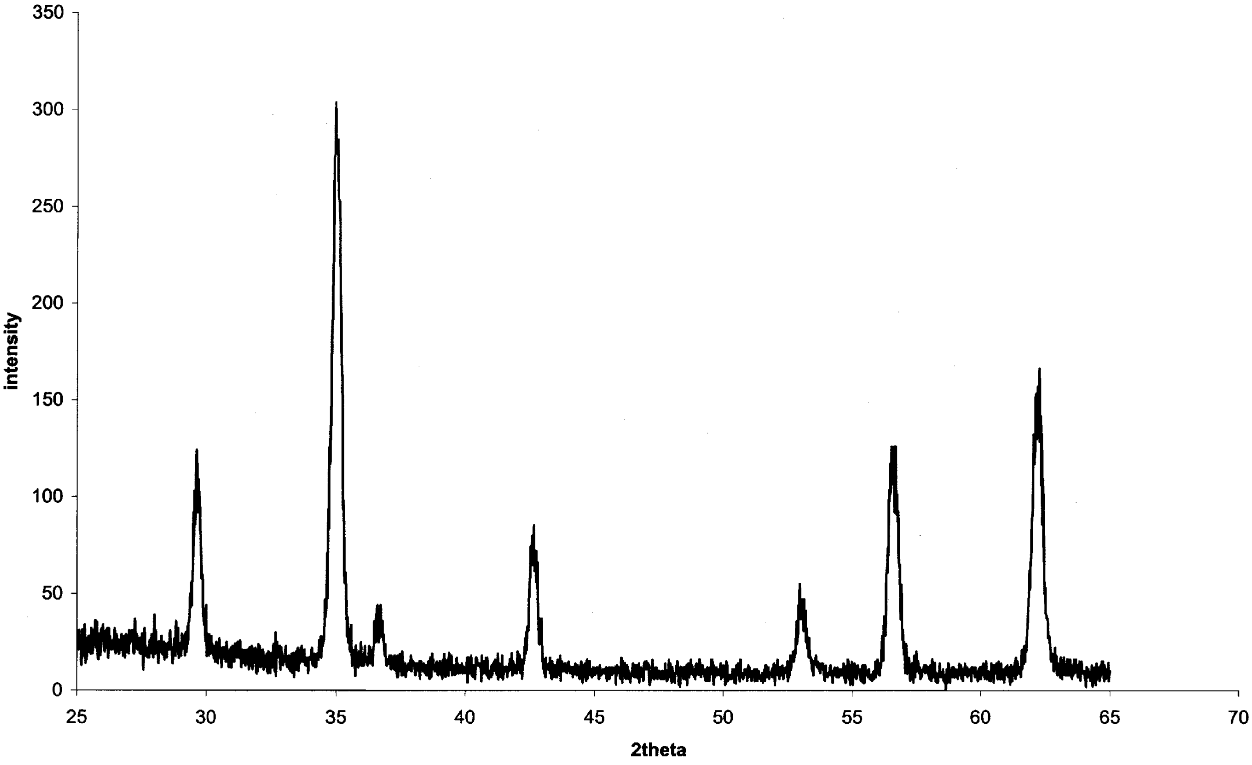

Fig. 1. XRD pattern of $ZN_{0.5}Ni_{0.5}Fe_2O_4$.

Table 2. Effect of Substitution of Fe^{+3} by Al^{+3}

Catalyst	Reaction time in min	Benzyl chloride % conversion	DPM % selectivity
$Cu_{0.5}Zn_{0.5}Al_2O_4$	180	71	92.8
$Cu_{0.5}Co_{0.5}Al_2O_4$	180	-	-
$ZnAl_2O_4$	120	78	91.6
$NiAl_2O_4$	120	-	-
$CoAl_2O_4$	120	-	-

Temperature: 80 °C
Amount of Benzene: 20 mL
Amount of Benzyl chloride: 5 mL

sultant precipitate was filtered and washed with distilled water to remove excess of alkali and sulphate ions. The precipitate was dried at 110 °C for 3 hours. The dried precipitate was calcined at 900 °C for 10 hours. The formation of single spinel phase was determined by XRD. Spinels prepared by this method have high surface area.

Catalyst Characterization

The catalysts were characterized by X-ray diffraction technique. XRD patterns were recorded on Siemens D-500 Kristalloflex diffractometer with a microprocessor controller using Cu K_α radiation with nickel filter. All diffractograms were recorded at room temperature. The X-ray pattern of all the compositions indicated the formation of a single-phase spinel[12,14] and match well with standard JCPDS patterns.

Reaction Procedure

The reaction was carried out in a flat bottom reactor containing baffles to which 20 mL of arene, 5 mL of benzyl chloride and 0.2 gm of catalyst was added. The flask was then sealed and was kept in an oil bath maintained at a desired temperature. The reaction mixture was stirred with an overhead stirrer. After every 2 min the sample from the reaction mixture was removed to measure the induction period. The reaction mixture was filtered and was analyzed by gas chromatography (Column OV-17 & FID Detector).

Thus benzyl chloride was reacted with benzene, toluene, ethyl benzene, cumene, anisole and chloro benzene. During the substrate study it was been found that para product was the predominating product. This may be due to the electron density at para position.

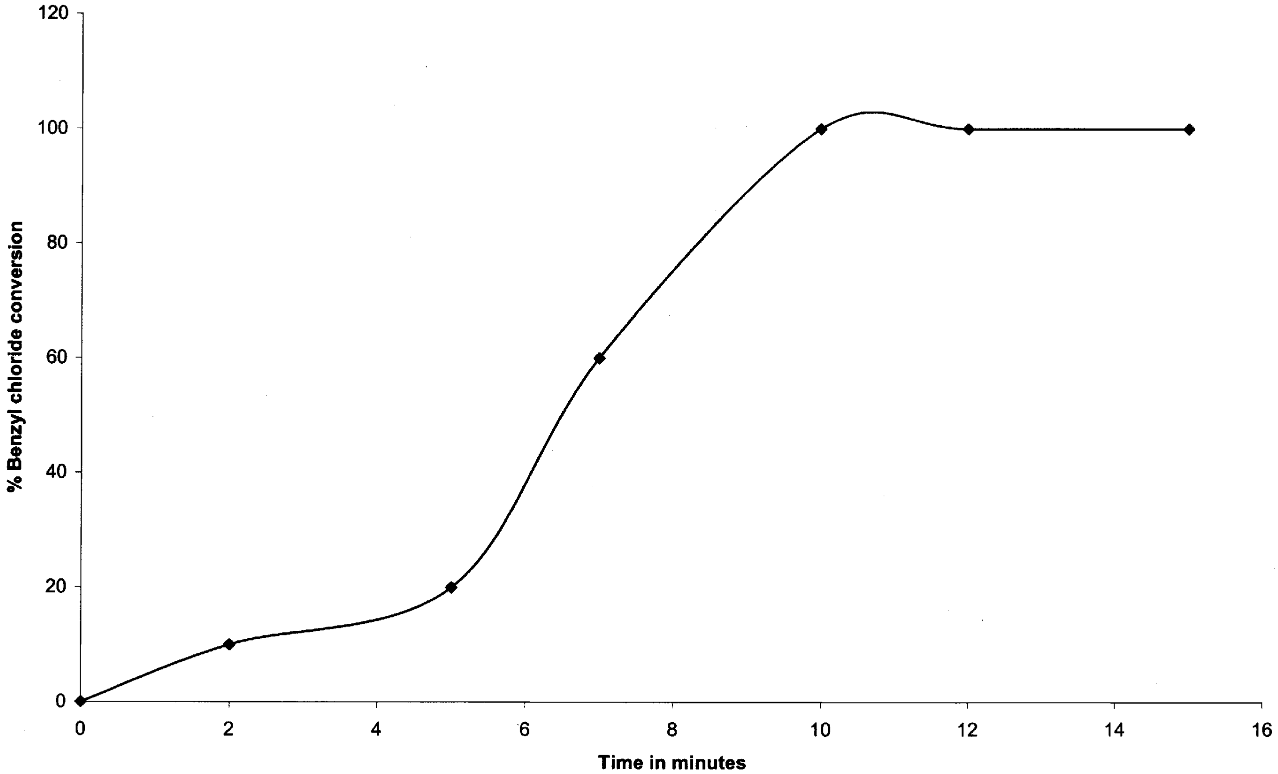

Fig. 2. Time required for benzyl chloride conversion over $Zn_{0.5}Ni_{0.5}Fe_2O_4$.

Table 3. Alkylation of Substrate on $ZnFe_2O_4$

Substrate	Reaction time in min	Benzyl chloride % conversion	Product		
			Ortho	Meta	Para
Toluene	5	100	8.2	-	91.8
Anisole	10	100	46.4	-	53.6
Chlorobenzene	40	100	36.5	-	63.5

Temperature: 80 °C
Amount of substrate: 20 mL
Amount of benzyl chloride: 5 mL

Table 4. Alkylation of Various Substrates over $Zn_{0.5}Ni_{0.5}Fe_2O_4$

Substrate	Benzyl chloride % conversion	Time in min	Product		
			Ortho	Meta	Para
Chlorobenzene	100	30	25.7	-	74.3
Toluene	100	5	7.2	-	92.8
Anisole	100	5	43.2	-	56.8
Cumene	100	25	16.7	21.4	61.9
Ethyl benzene	100	30	43	-	57.0

Temperature: 80 °C
Amount of substrate: 20 mL
Amount of benzyl chloride: 5 mL

RESULTS AND DISCUSSION

Catalyst Characterization

The X-ray pattern of all the compositions indicated the formation of a single-phase spinel[12,14] and match well with standard JCPDS patterns.

Reusability of the Catalyst

Reusability of the catalyst was tested by carrying out repeated runs of the reaction on the same batch on the catalyst system without any pretreatment. It was observed that catalyst could fairly sustain the initial reactivity up to five runs.

CONCLUSION

The ternary mixture $Zn_{0.5}Ni_{0.5}Fe_2O_4$ and binary mixture $ZnFe_2O_4$ showed good catalytic properties in alkylation of benzene with benzyl chloride leading to increase in para alkylated product and decrease in polyalkylated product. The catalyst also showed good reusable properties.

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