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Friedel-Craft's Acylation of Deactivated Benzenes over Solid Acid Catalysts

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ABSTRACT

The cobalt manganese ferrospinels with the general formula $CoxMn(1-x)Fe2O4(x = 0.0, 0.2, 0.4, 0.6, 0.8$ and 1.0 has been successfully synthesized by controlled low temperature hydroxide co-precipitation method. The cobalt manganese ferrospinels exhibit a well defined crystalline structure with high surface area. The physicochemical properties of the ferrospinels are characterized by X-ray diffraction, Inductively coupled plasma analysis and surface area determination by BET method. The stoichiometry of the samples was in good agreement with the theoretical values. The surface acidity of the systems was determined by NH3-TPD method. The addition of cobalt ions into the pure manganese ferrospinels enhances the acidity in the weak and medium regions. These ferrospinel systems were found to be active for the liquid phase Friedel-Craft's acylation of deactivated benzenes with benzoyl chloride giving corresponding ketones. Acidity of the catalysts in the weak and medium regions is mainly responsible for the good catalytic performance .

KEYWORDS : Cobalt-manganese ferrospinels, Friedel-Craft's benzoylation, Deactivated benzenes, Surface acidity.

INTRODUCTION:

Studies of ferrospinels ($M^{II} Fe_2^{III}O_4$, where M^{II} is a bivalent cation) have received considerable attention owing to their versatility in the theoretical, technological and catalytic fields[1]. These spinel compounds have been conveniently tried as catalysts in some industrially important reactions such as oxidative dehydrogenation of butane to butadiene and hydrodesulphurization of petroleum crude[2]. In contrast to the ferrospinels, the catalyst Fe_2O_3 loses its activity as it reduced to FeO and metallic iron. Individual metal oxides lose their catalytic activity rapidly owing to ageing and formation of coke over the catalyst surface. The spinel lattice imparts extra stability to the catalyst under various reaction conditions so that the system sustained activity for longer periods[3]. It is known that mixed 3*d* transition metal oxides are more active than simple oxides [4]. Thus mixed 3*d* transition metal oxides with spinel structure act as catalysts and they offer an advantage of increased catalytic activity.

Friedel-Craft's acylation reactions are fundamental and important processes in organic synthesis as well as in industrial chemistry[5,6]. These reactions can be carried out using homogeneous Lewis acids such as anhydrous metal halides as catalysts[7]. However, more than the stoichoimetry amount of the catalysts must be used which is destroyed at the end of the reaction with a significant production of undesirable wastes. In addition, drastic reaction conditions, disposal of the spent catalysts, high toxicity and tedious work-up procedures, which induce environment pollution especially in industrial scale processes, are involved. Due to the efficiency, life time and increasing demand for the cleaner processes prompted by stringent environmental laws, solid acids are preferred to their counter parts as they offer a number of advantages including easy recovery, regeneration and reuse of the catalyst.

using RIGAKU D/ MAX-C instrument with Cu Kα radiation.

The stoichiometry of the catalysts checked by inductively coupled plasma (ICP) analysis. The thermal stability of the samples was determined by TG analysis at a heating rate of 10˚C/min. The BET surface area and pore volume of the samples were measured by nitrogen adsorption at liquid nitrogen temperature using a Micrometrics Gemini Analyser.

Evaluation of surface acidity

The strength and distribution of acidity of the samples were determined by temperature programmed desorption (TPD) of ammonia. About 0.75 g of the samples were pelletised and activated at 500˚C for 2 h. To remove the surface impurities further, the pellets were activated in the reactor at 300˚C in a flow of nitrogen for half an hour.

After cooling to the room temperature, ammonia gas was injected into the reactor and was allowed to adsorb on the samples in a uniform manner. The physisorbed ammonia was desorbed by a run of nitrogen gas. The acid strength distribution was obtained from 100 to 600˚C in a flow of nitrogen in a number of steps. The ammonia evolved was trapped in dilute H_2SO_4 solution and was titrated with standard NaOH solution. The ammonia desorbed in the temperature range of 100°C –600°C is divided into three different temperature regions (°C) such as 100 -200°C, 201°C-400°C and 401°C-600°C and assigned as weak, medium and strong acid sites respectively.

Catalytic activity

The liquid phase acylation of activated benzenes (toluene, o-xylene and anisole), benzene and halo benzenes (fluorobenzene, chlorobenzene, bromobenzene) with benzoyl chloride as the benzoylzting agent was carried out in a 50 mL double necked round bottomed

ferrospinels increased the weak and medium acidity to some extent, but the total acidity and strong acidity is decreased to certain extent.

CATALYTIC ACTIVITY

Benzoylation of deactivated benzenes:

The acylation of benzenes and more particularly that of deactivated halobenzenes is rather difficult than the acylation of activated benzenes. The deactivated rings need more vigorous reagent/catalyst combinations and severe reaction conditions. The deactivated benzene chosen for study were benzene and halobenzenes such as fluporobenzene, chlorobenzene and bromobenzene. The product yield is comparable with the results obtained for hafium triflate and trifluromethane sulphonic acids[11]. The benzoylation of these substrates were carried out at their refluxing temperature for 90 minutes and the results are presented in Table 3.

It is observed that deactivated benzenes reacted smoothly with benzoyl chloride in the presence of spinel systems to afford corresponding aromatic ketones in high yields. In all cases the reaction proceeded without any side reaction. If the atom bonded to the aromatic ring has one or more non-bonding valence shell electron pairs, as do halogens, electrons may flow into the aromatic ring by pi-pi conjugation (resonance) and the charge distribution in the ring is greatest at *ortho* and *para* to the substituent. Though the benzoylation of halobenzenes give *ortho* and *para* products, the present spinel systems lead only to para product with satisfactory product yield.

The step-wise incorporation of cobalt ions for manganese in $Co_xMn_{(1-x)}Fe_2O_4$ systems increased the catalytic activity. The increase in acidity in the weak and medium regions with the incorporation of cobalt ions

into manganese ferrospinels enhances the
In the course of our investigations to develop more efficient catalytic Friedel-Craft's acylatios, particularly for the deactivated benzenes, we found a series of spinel systems. In this article we report the synthesis and physico-chemical properties of the ferrospinel systems, $Co_xMn_{(1-x)}Fe_2O_4$(x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0). A detailed investigation of the spinel systems towards the Friedel-Craft's acylation of some de-activated benzenes is also performed. We found that the progressive substitution of cobalt into manganese ferrospinels accelerated the Friedel-Craft's acylation of deactivated benzenes dramatically.

EXPERIMENTAL
Catalyst preparation:
In the present study, various spinel compositions viz. $MnFe_2O_4$ (M), $Co_{0.2}Mn_{0.8}Fe_2O_4$ (CM-1), $Co_{0.4}Mn_{0.6}Fe_2O_4$ (CM-2), $Co_{0.6}Mn_{0.4}Fe_2O_4$ (CM-3), $Co_{0.8}Mn_{0.2}Fe_2O_4$ (CM-4) and $CoFe_2O_4$ (C) were prepared by a low temperature co-precipitation technique[8]. Initially, calculated amount of the corresponding nitrate salts were dissolved in doubly distilled water and precipitation of the hydroxide was carried out at a controlled pH of 9-10 using 5M NaOH solution at a room temperature with vigorous stirring. The precipitate was washed several times with doubly distilled water to remove excess nitrite ions and alkali. It was then filtered, washed dried in oven at 80˚C for 36 hrs., powdered, sieved to 100 mesh size and calcined at 500˚C for 5 hrs to achieve the spinel phase.

CHARACTERISATION
Structural analysis
The catalyst samples were activated at 500˚ C for 2 hrs before each characterization technique. The X-ray diffractograms of the samples were taken flask equipped with a reflux condenser in an oil bath with controlled temperature and stirring. About 0.1 g of the catalyst was taken and prior to each experiment it was activated at 500°C for 2 hrs. A mixture of aromatic substrate and benzoyl chloride were taken in the 10:1 molar ratio. The products were analysed by gas chromatography(Chemito GC 8610, flame ionized detector, SE 30 column) and were identified by GC-MS.

RESULTS & DISCUSSION
Structural analysis
The XRD data well ascertained the formation of single spinel phase and crystallinity of the ferrites. The space lattice was found to be cubic. The XRD patterns of the samples were found similar and X-ray diffractogram of $MnFe_2O_4$ is presented in figure 1. The stoichiometry of the samples prepared by low temperature co-precipitation technique was in good agreement with the theoretical values as evident from inductively coupled plasma analysis (Table 1). The ferrite samples prepared by lowtemperature co-precipitation technique possess high surface area (Table 1).

Surface acidity
Ammonia is frequently used as a probe molecule because of its small molecular size, stability and strong basic strength. Though ammonia cannot discriminate between Bronsted and Lewis acidity[9], TPD of ammonia can be used to characterize the strength and distribution of acidic sites and to obtain the quantitative amount of acid sites in a particular temperature range[10]. The amount of ammonia desorbed in weak (100°C -200°C), medium (201°C -400°C), and strong (401°C -600°C), acid regions are shown in table 2. The addition of cobalt ions into the pure manganese

formation of benzoylated products to a greater extent.

REUSABILITY OF THE CATALYSTS
All the prepared ferrospinels are found to be reusable after thoroughly washing with acetone and activating at 500°C for 5hrs. The spinel phase remained unimpaired even after the reaction. This was confirmed by comparing the peak positions and peak intensities of the fresh and used catalysts. The ferrospinels were tested for benzoylation reactions. There was negligible loss in activity even after repeated use for five times.

CONCLUSIONS
Cobalt manganese ferrospinels prepared by the low temperature co-precipitation technique provides homogeneous, fine and reproducible ferrite powders with high surface areas. All the peaks in the

XRD pattern matched well with the characteristic reflections of the ferrites. The successive incorporation of Co decreased the total acidity of $MnFe_2O_4$ as evident from the NH3-TPD studies, where as the weak plus medium acidity is improved by the progressive addition of Co ions. Liquid-phase benzoylation of deactivated bezenes proceeded efficiently over cobalt- manganese ferrospinels. The increase in weak plus medium acidity of the systems enables the formation of benzoylated product of deactivated benzenes to a greater extent. These catalysts were found to be reusable even after repeated use.

Figure. 1. XRD patterns of MnFe2O4

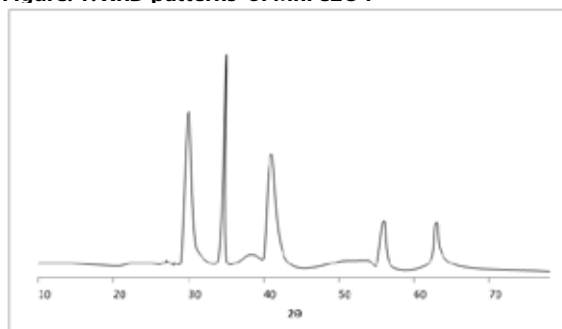**Table 1.**
ICP analysis data and surface areas of $Co_xMn_{(1-x)}Fe_2O_4$(x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)

Catalyst	ICP analysis data[a]		Surface area (m2/g)
	Mn%	Co%	
M	23.82 (23.82)	--	153.3
CM-1	18.99 (19.00)	5.08 (5.09)	112.95
CM-2	14.19 (14.19)	10.14 (10.15)	105.28
CM-3	9.43 (9.43)	15.16 (15.17)	97.23
CM-4	4.68 (4.69)	20.15 (20.16)	85.78
C	--	25.12 (25.12)	75.63

[a] Quantities in the parentheses indicate the theoretical value.

Table 2.
The acidity values from NH3-TPD studies carried out over CoxMn(1-x)Fe2O4(x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)

Catalyst	NH3 desorbed (10-3 mmol m-2)			
	Weak	Medium	Strong	Total
M	3.85	4.27	8.38	16.50
CM-1	3.86	4.70	7.80	16.36
CM-2	3.88	4.86	7.53	16.27
CM-3	3.90	4.90	7.33	16.13
CM-4	3.93	5.00	7.14	16.07
C	3.95	5.04	7.04	16.03

Table 3
Benzoylation of deactivated benzenes over CoxMn(1-x) Fe2O4(x = 0.0, 0.2, 0.4, 0.6, 0.8 and 1.0)

Catalyst	Product yield (%)			
	Benzene (Reaction temperature-80°C)	Fluorobenzene (Reaction temperature-80°C)	Chlorobenzene (Reaction temperature-80°C)	Bromobenzene (Reaction temperature-80°C)
M	62.57	50.22	55.79	58.32
CM-1	64.28	54.33	57.95	60.22
CM-2	68.13	57.12	59.08	63.92
CM-3	70.92	59.79	63.47	66.41

| CM-4 | 72.57 | 62.45 | 66.48 | 68.50 |
| C | 73.01 | 66.37 | 68.91 | 70.37 |

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