

Liquid-phase Friedel-Crafts acylation using $\text{Ni}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ spinel catalysts

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The liquid-phase Friedel-Crafts acylation of toluene using benzoyl chloride as benzoylating agent has been carried out over $\text{Ni}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8$ and 1.0) type systems under different reaction conditions. It is observed that the systems with high 'x' values are effective for the conversion of BOC and the selective formation of 4-MBP. Selectivity for 4-MBP over MnFe_2O_4 is more than 90% under the optimized reaction conditions. Sites of moderate acidity is effective in catalyzing the benzoylation reaction.

Studies of ferros spinels ($\text{M}^{\text{II}}\text{Fe}_2^{\text{III}}\text{O}_4$, where M^{II} is a bivalent cation) have received considerable attention in recent years owing to their versatile applicability in the theoretical, technological and catalytic fields¹⁻³. These spinel compounds have been conveniently tried as catalysts in some industrially important reactions such as oxidative dehydrogenation of butene to butadiene⁴, hydrodesulphurisation of petroleum crude⁵ and treatment of exhaust gas⁶. In contrast to the ferros spinels, the catalyst Fe_2O_3 loses its activity as it is reduced to FeO and metallic iron. Nickel based catalysts are active in some hydrogenation and dehalogenation reactions^{7,8}. Manganese ferros spinels have been extensively used as decomposition catalysts for alcohols⁹ and hydrogen peroxide¹⁰. Individual metal oxides lose their catalytical 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 these systems sustained activity for longer periods¹¹. It is known that mixed 3d transition metal oxides are more active than simple oxides¹². Thus mixed 3d transition metal oxides with spinel structure act as catalysts and they offer an advantage of increased catalytic activity.

The Friedel-Crafts acylation of aromatic compounds is industrially important to produce aromatic ketones, which are reactive intermediates for further use in fine chemistry¹³. The acylation reactions are performed well with the Lewis acids such as AlCl_3 , which require more than the stoichiometric amount with respect to the benzoylating agent. The high Lewis acidity of these homogeneous catalysts

results in several undesirable side reactions and also it lacks selectivity. Individual metal oxides such as Fe_2O_3 , NiO and MnO_2 gave low catalytic activity and they were not reusable. In an attempt to increase the stability of the structure and to generate moderate acid catalysts $\text{Ni}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8$ and 1.0) type systems were prepared. In this paper we report the selective benzoylation of toluene to 4-methyl benzophenone (4-MBP) using the above system as catalyst and benzoyl chloride as benzoylating agent. Moreover, the effects of reaction conditions, ie. the reaction temperature, catalyst composition, presence of moisture in the reaction mixture as well as in the catalyst and toluene/ benzoyl chloride (t/b) molar ratio, on the catalyst performance have also been studied. The systems $\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ and NiFe_2O_4 are found to be active for the effective conversion of BOC to the selective formation of 4-MBP.

Materials and Methods

Catalyst preparation

The various spinel compositions viz. MnFe_2O_4 (M), $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ (MN₁), $\text{Ni}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$ (MN₂), $\text{Ni}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ (MN₃), $\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ (MN₄) and NiFe_2O_4 (N) were prepared by a low temperature co-precipitation technique¹⁴. Calculated amounts of the nitrate salts were dissolved in doubly distilled water and the precipitation of the hydroxide was carried out at a controlled pH of 9-10 using 5.3 M NaOH. The precipitate was washed and filtered to remove excess alkali and nitrate ions. The compounds were dried in an oven at 353K for 36 h and then calcined at 773K

for 5 h. The stoichiometry was checked by the Inductively Coupled Plasma (ICP) analysis and was found to be in good agreement with the theoretical values and the results are given in the Table 1.

Catalyst characterisation

Structural analysis—The phase purity and crystallinity of the samples were ensured by X-ray diffraction analysis (RIGKU D/ MAX-C powder diffractometer with Cu K α radiation). The XRD patterns (Fig. 1) indicated the formation a single spinel phase. The DRIFT spectra of

all the samples typically show two strong IR bands γ_1 and γ_2 around 700 cm^{-1} and 500 cm^{-1} respectively (Fig. 2). The high frequency band at 700 cm^{-1} is due to the stretching vibration of the tetrahedral group and the lower frequency band at 500 cm^{-1} is due to the vibration of the octahedral M-O bond^{15,16}. The thermo gravimetric analysis revealed that ferrite samples are thermally stable in the temperature range of 423K-1073K without creating major weight loss. The BET and Langmuir surface areas and total pore volume of the catalysts (Table 1) were measured by nitrogen adsorption at liquid nitrogen temperature using Micrometrics Gemini Analyser.

Table 1—ICP analysis data, BET and Langmuir surface areas and total pore volumes of the system $\text{Ni}_x\text{Mn}_{1-x}\text{Fe}_2\text{O}_4$ ($x=0, 0.2, 0.4, 0.6, 0.8$ and 1.0) synthesized by co-precipitation technique

Composition (x)	ICP analysis data		Surface area (m^2/g)		Total pore volume (cm^3/g)
	Mn%	Ni%	BET	Langmuir	
0	23.78	--	153.3	221.2	0.2023
0.2	18.98	5.05	103.3	202.2	0.1899
0.4	14.16	10.06	97.4	173.3	0.1830
0.6	9.53	14.00	86.8	166.2	0.1730
0.8	4.67	20.07	74.5	155.8	0.1690
1.0	--	25.03	63.2	149.1	0.1386

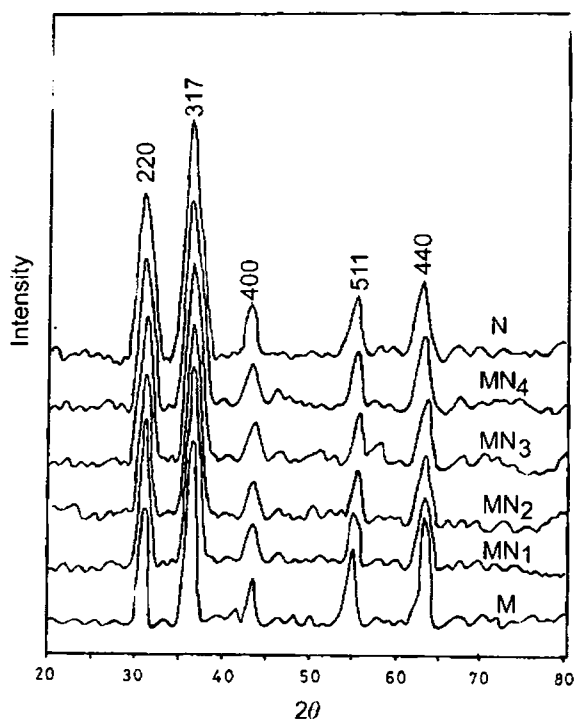


Fig. 1—Powder X-ray diffractogram of MnFe_2O_4 (M), $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ (MN₁), $\text{Ni}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$ (MN₂), $\text{Ni}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ (MN₃), $\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ (MN₄) and NiFe_2O_4 calcined at 500°C.

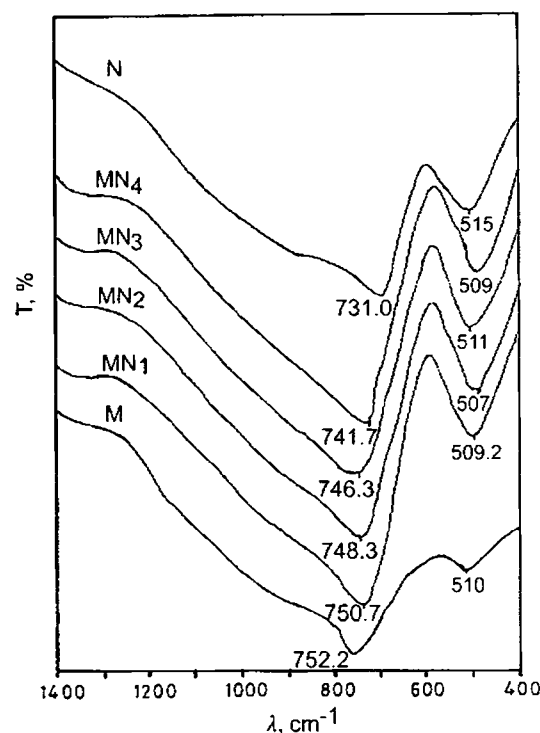


Fig. 2—Diffused reflectance infrared spectra of MnFe_2O_4 (M), $\text{Ni}_{0.2}\text{Mn}_{0.8}\text{Fe}_2\text{O}_4$ (MN₁), $\text{Ni}_{0.4}\text{Mn}_{0.6}\text{Fe}_2\text{O}_4$ (MN₂), $\text{Ni}_{0.6}\text{Mn}_{0.4}\text{Fe}_2\text{O}_4$ (MN₃), $\text{Ni}_{0.8}\text{Mn}_{0.2}\text{Fe}_2\text{O}_4$ (MN₄) and NiFe_2O_4 (N).

Surface properties – acidity/basicity

The strength and distribution of acidic sites were determined by temperature programmed desorption (TPD) of ammonia. About 0.75g of the samples were pelletised and activated at 773K. To remove the surface impurities, the pellets were activated in the reactor at 573K in a flow of nitrogen for half an hour. The acid strength distribution was obtained from temperature programmed desorption of ammonia from 373K to 873K in a flow of nitrogen in a number of steps. The ammonia evolved was trapped in H₂SO₄ solution and was titrated with standard NaOH solution.

Ammonia is an excellent probe molecule to determine the acid properties of the solid acid catalysts due to its strong basicity and small molecular size^{17,18}. Though ammonia can titrate acid of any strength, it is not possible to discriminate between Bronsted and Lewis acidity¹⁹. The amount of ammonia desorbed in weak (373-473 K), medium (474- 673 K) and strong (674- 873 K) regions are shown in Table 2. For all the samples the amount of ammonia desorbed was increased from the weak, medium to strong acid region. Ammonia lacks selectivity in discriminating Bronsted and Lewis acid sites, the stronger acid region can be a Lewis acid sites or a strong Bronsted site. From the Table 2, it is seen that the acidity shows a decreasing trend with progressive substitution of Mn ions by Ni²⁺ in all the acidic regions.

The evaluation of the Lewis basicity of the systems by the adsorption of the electron acceptors (EA) having different electron affinity values has been well established²⁰⁻²². 7, 7, 8, 8-Tetracyanoquinodimethane (TCNQ), 2, 3, 5, 6-tetra-chloro-4-benzoquinone (chloranil) and *p*-dinitrobenzene (PDNB) with electron affinity values 2.84, 2.40 and 1.77 eV respectively in acetonitrile as solvent were employed for the present study. The catalysts were activated at

773K and were placed in an airtight cylindrical glass vessel. A 10 ml solution of the EA in the acetonitrile solution was added. The solution was stirred for 4h at room temperature. The amount of electron acceptor adsorbed was determined by means of UV-vis spectrophotometry by noting the absorbance of the solution of electron acceptor before and after adsorption at the λ_{max} of electron acceptor.

A strong electron acceptor (TCNQ) can accept electrons from both strong and weak donor sites, where as weak EA (PDNB) can adsorb only at strong donor sites. Negligible adsorption of PDNB in all the systems indicates the absence of very strong basic sites. The difference between the limiting amounts of TCNQ and chloranil adsorbed can give a measure of the number of weak donor sites. The limiting amounts of TCNQ and chloranil adsorbed for the systems are presented in the Table 3. From this Table, it can be seen that the basicity follows the order M<MN1<MN2<MN3<MN4<N, showing an increasing trend with progressive substitution of Mn²⁺ or Mn³⁺ by Ni²⁺. From the results on acidity measurements by the TPD of ammonia and adsorption of EA, it can be noted that the decrease in acidity is associated with a concomitant increase in the basicity. Jacob *et al.* have reported that major influence in the activity of the spinels comes from the octahedral ions as they are more exposed on the surface as revealed by the XPS and LEIS measurements²³. From the acidity and basicity values it can be inferred that either Ni²⁺ or Mn²⁺ in the octahedral sites are responsible for the basicity of the systems and either Mn³⁺ ions or Fe³⁺ ions in the octahedral sites are responsible for the acidity of the systems. Mn²⁺ or Fe³⁺ ions in the tetrahedral sites are less accessible.

Catalytic activity

The liquid phase acylation of toluene was carried out in a 50 mL double necked round bottom flask

Table 2—The NH₃ desorbed at weak (373-473 K), medium (474- 673 K) and strong (674 -873 K) regions of the system Ni_xMn_{1-x}Fe₂O₄ (x=0, 0.2, 0.4, 0.6, 0.8 and 1.0)

Composition (x)	NH ₃ desorbed (mmol / m ²)			Total
	373-473 K	474-673 K	674-873 K	
0	0.0385	0.0387	0.0438	0.1210
0.2	0.0370	0.0373	0.0400	0.1143
0.4	0.0353	0.0372	0.0388	0.1113
0.6	0.0349	0.0367	0.0382	0.1098
0.8	0.0332	0.0343	0.0372	0.1047
1.0	0.0331	0.0338	0.0361	0.1030

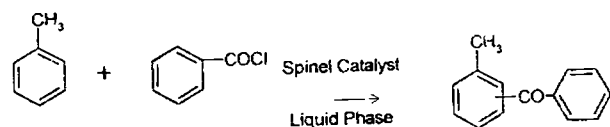
Table 3—Limiting amount of electron acceptor (EA) for the system $Ni_xMn_{1-x}Fe_2O_4$ ($x=0, 0.2, 0.4, 0.6, 0.8$ and 1.0)

Composition (x)	Electron acceptor adsorbed (10^{-4} mmol / m^2)		
	TCNQ	Chloranil	TCNQ-Chloranil
0	10.71	2.6	8.11
0.2	20.81	6.41	14.39
0.4	22.47	7.0	15.47
0.6	23.13	7.58	15.52
0.8	23.97	7.92	16.05
1.0	25.52	8.91	16.61

equipped with a reflux condenser in an oil bath. About 0.1 g of the catalyst was taken and prior to each experiment it was activated at 773K for 2 h. Toluene and benzoyl chloride were taken according to the molar ratio specified in the experiment. The effect of reaction conditions such as reaction temperature, catalyst composition, presence of moisture in the reaction mixture as well as in the catalyst and toluene/benzoyl chloride molar ratio (t/b) on the catalytic performance have been studied.

Results and Discussion

The acylation reaction of toluene with benzoyl chloride as the benzoylating agent leads mainly to two types of products estimated by GC and identified as 2-methylbenzophenone (2-MBP) and 4-methyl benzophenone (4-MBP) by GC-MS. Trace amounts of 3-methyl benzophenone (3-MBP) was also observed. Dibenzoylated products arising from the secondary reaction of the monobenzoylated product was not observed in any of the system at any reaction conditions. The reaction scheme for the acylation of toluene with benzoyl chloride using $Ni_xMn_{(1-x)}Fe_2O_4$ systems can be represented as Scheme 1.



Scheme 1

The catalytic activity and the nature of the products greatly depend on the composition of the catalyst and also on the reaction conditions. It can be mentioned that the conversion of BOC obtained using the system $Ni_xMn_{(1-x)}Fe_2O_4$ is comparable with the results obtained by using sulphated zirconia²⁴ and modified zeolite catalysts²⁵.

Effect of catalyst loading

The amount of the catalyst required for the reaction was optimized using $MnFe_2O_4$ as a catalyst and toluene/BOC molar ratio of 10 at 353 K for 20 minutes. It can be seen that as the amount of catalyst increases from 0.01g to 0.1g the percentage conversion of BOC increases from 18.23% upto 78.42%. After this, the conversion of BOC to the reaction products is found to be decreasing and remained more or less constant. This trend can be explained in terms of the fact that the increase in the catalyst amount restricts desorption of the acylated product from the catalyst surface. Therefore 0.1g was used in the subsequent experiments.

Effect of molar ratio

A series of experiments were done at 353K with different molar ratios of toluene/BOC over $MnFe_2O_4$. In all the cases 4-methyl benzophenone (4-MBP) and 2-methyl benzophenone (2-MBP) were found to be the main reaction products. At lower toluene/BOC molar ratios ($t/b=1/2.5$ and $1/5$) a significant amount of 3-methyl benzophenone (3-MBP) was also formed in the reaction mixture. Dibenzoylated products were not produced even at lower toluene/BOC molar ratios in any of the systems. An increase in the conversion of BOC was observed with the increase in the toluene/BOC molar ratio. This is probably due to the inhibiting effect of the acylated product which can be strongly adsorbed on the catalyst surface²⁶. The inhibiting effect would be less significant for mixtures richer in toluene, which helps to desorb the ketones formed. It is seen that the selectivity for the formation of 4-MBP remains constant beyond the toluene/BOC molar ratio of 10 ($t/b=10$).

Effect of reaction temperature

The conversion of BOC was found to increase with the increase in temperature. The increase in temperature also facilitates the selective formation of 4-MBP. There is a possibility of formation of the bulkier products when the reaction temperature is raised, since the higher reaction temperature favours the consecutive acylation, disproportionation, alkylation and decarboxylation. But no such products were seen even at 383 K.

Effect of moisture

In order to study the effect of moisture in the catalyst and in the reaction mixture, the catalyst was kept over water at room temperature in a desiccator for 48 hrs. and toluene was saturated with water at

room temperature. The reactions were carried out at 333 K for 1 hr. by taking toluene/BOC molar ratio of 10 in a double necked round bottom flask using about 0.1 g of moisture adsorbed MnFe_2O_4 as the catalyst. For comparison reaction was catalysed by moisture free MnFe_2O_4 . The reaction mixture was analysed after every 10 minutes (Table 4). In the presence of moisture, hydrolysis of benzoyl chloride was observed leading to benzoic acid as the major product in the initial stages of the reaction, but after some time the benzoylation reaction leads to the formation of 4-MBP. From data in Table 4, it can be seen that there exists an induction period for the benzoylation reaction which is the time required for replacing the adsorbed moisture by the reactants to start the catalytic reaction. From this observation it can be inferred that the Lewis acid sites are catalyzing the reaction and are initially blocked by the adsorbed moisture enhancing the hydrolysis of the benzoylating agent.

Effect of catalyst composition

The product distribution and selectivity pattern of toluene benzoylation over the system $\text{Ni}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ systems by taking toluene/BOC molar ratio of 10 at 353 K are shown in the Table 5. The catalytic activity and selectivity towards the 4-MBP follow the order $\text{N} \approx \text{MN}_4 > \text{MN}_3 > \text{MN}_2 > \text{MN}_1 > \text{M}$. The total acidity follows the reverse order. The contradictory observation can be due to the adsorption of the acylating product on the acid sites due to the higher polarity. Consequently, the adsorption of the toluene on the catalyst surface is restricted and the reaction rate is decreased. It is known that the stronger Lewis sites are provided by the octahedral ions, either Fe^{3+} in N or Fe^{3+} or Mn^{3+} and Mn^{2+} in the remaining systems. Though there exists Ni^{2+} in the octahedral sites, the presence of which is found to be decreasing the acidity values. Hence the conversion and selectivity towards the formation of 4-MBP can be

Table 4—Effect of moisture on the benzoylation of toluene over MnFe_2O_4 at 333 K and t/b molar ratio 10

Catalyst	Reaction temperature	T/ b molar ratio	Reaction time (minutes)	Conversion of BOC (%)	Product distribution	
					Hydrolydsis product	Benzoylated product
MnFe_2O_4 (adsorbed with moisture)	333 K	10	10	25.23	100	
			20	42.12	100	--
			30	53.51	100	--
			40	61.62	100	--
			50	70.61	90	10
			60	91.48	88.53	11.47
MnFe_2O_4	333 K	10	10	48.72	--	100
			20	53.48	--	100
			30	62.97	--	100
			40	71.67	--	100
			50	77.48	--	100
			60	80.96	--	100

Table 5—Performance of catalyst composition on toluene benzoylation over the system $\text{Ni}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ ($x=0,0.2, 0.4, 0.6, 0.8$ and 1.0) by taking toluene / BOC molar ratio 10 at 353 K

Catalyst	Conversion of BOC (%)	4-MBP selectivity	2-MBP selectivity	3-MBP selectivity
NiO	0.2	100	--	--
MnO_2	1.2	100	--	--
Fe_2O_3	72.87	33.64	33.76	32.6
M	78.42	82.72	14.42	2.86
MN_1	83.45	87.23	11.24	1.53
MN_2	87.91	88.12	10.42	1.42
MN_3	89.12	89.75	9.52	0.73
MN_4	94.68	93.39	7.49	--
N	95.01	92.93	6.91	--

due to the moderate acidity provided by the octahedral Fe^{3+} ions.

The commercially available individual metal oxides and the conventional homogenous catalyst such as AlCl_3 were also studied for comparison. With MnO_2 and NiO the conversion of BOC(%) was found to be very low. Fe_2O_3 gave 72.87 % conversion of BOC with very low selectivity. The homogenous catalyst AlCl_3 gave 78% which required large amount of the catalyst, but the selectivity was also low (Table 5).

The reusability of the system

All compositions of the system, $\text{Ni}_x\text{Mn}_{(1-x)}\text{Fe}_2\text{O}_4$ were found to be reusable. Though negligible, a decrease in the conversion of BOC was observed. This may be due to the trace amount of iron leaching during the reaction. In recycling the catalyst, the selectivity towards the formation of 4-MBP remained constant. After the completion of the reaction the catalyst was removed from the reaction mixture by filtration. It was washed thoroughly with acetone until free of reaction solution, calcined at 773K for 5 h. The spinel structure remained intact even after the reaction. This was confirmed from XRD patterns of the reused catalyst. The individual metal oxides NiO , MnO_2 and Fe_2O_3 were not found to be reusable.

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