



Vapor phase alkylation of indole with methanol and dimethylcarbonate over Ni–Mn based ferros spinels

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ABSTRACT

Vapor-phase methylation of indole with methanol and dimethylcarbonate (DMC) was carried out over $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ ($x = 0, 0.25, 0.5, 0.75, 1.0$) type ferros spinel in a fixed-bed reactor. 3-Methylindole was found to be the major product. It was observed that systems possessing higher 'x' values were highly selective for 3-methylindole. A maximum yield of 54.6% with selectivity 88.3% of 3-methylindole was obtained when methanol was used as alkylating agent, while yield of 48.6% with selectivity 80.1% was obtained using DMC as alkylating agent over MnFe_2O_4 under optimized conditions. $\text{Ni}^{2+}/\text{Mn}^{2+}$ ionic distribution in the spinel lattice influences the acido-basic properties. Effect of alkylating agent and different reaction parameters are discussed.

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1. Introduction

Indole and its derivatives are extensively used in perfumery, in preparing tryptophan (an amino acid) and as an intermediate in the synthesis of anti-inflammatory agents, antibiotics, dyes and plant growth hormone like auxin. 3-Methylindole also known as skatole has been found to promote the dimerization of butadiene and have physiological action as an anti-diuretic, stimulant anti-hypertensive, muscular relaxant, respiratory inhibitor and heart stimulant [1–3]. Conventionally Friedel–Crafts alkylation reaction using homogeneous acid catalysts are used to produce alkylated aromatic compounds. Due to stringent environmental concern over the disposal of spent catalysts, it is difficult to continue with these catalysts. A variety of heterogeneous catalysts such as metal oxides, clays and zeolites have been studied due to their eco-friendly nature and their potential to replace the conventional Friedel–Crafts catalysts [4–6]. In this context it is worth mentioning that ferrites are excellent catalysts for many alkylation reactions due to their high acidity, thermal stability and eco-friendly nature.

Ferrites are well known for their electrical, magnetic and catalytic properties [7–12]. The general structure of ferrites with spinel structure is $\text{M}_{2+}^{\text{tet}}[\text{Fe}_{3+}^{\text{octa}}]_4\text{O}_4$. The introduction of third metal ion modifies the distribution of ions in the spinel structure. Varying the concentration of third metal ion can easily alter distribution of Fe^{3+} ion. The present study is based on $\text{Ni}_{1-x}\text{Mn}_x\text{Fe}_2\text{O}_4$ type ferrite system, which produce an alternate route to conventional Friedel–

Craft reactions and is found to be highly selective for alkylation of indole to produce 3-methylindole. During the experimental condition no N-alkylated product was detected.

2. Experimental

2.1. Catalyst preparation

2.1.1. Preparation of NiFe_2O_4 (NF-1)

A solution of 1.2 mol of NaOH in 150 mL of water was allowed to react with a solution of 0.075 mol of NiCl_2 in 50 mL of water. The resulting solution was added to a 5 L beaker containing 0.15 mol of $\text{FeCl}_3 \cdot 6\text{H}_2\text{O}$ in 2.5 L of 0.6 M HCl and stirred for 2 h. The resulting mixture was further heated for 0.5 h at 333 K. The mixture was allowed to settle and then reacted with 2 M NaOH till a permanent phenolphthalein color was obtained. The product was washed by repeated decantation with 2.5 L portions of water until the supernatant was free of Cl^- (about 15 washings were required), filtered through a sintered glass filter, dried in an oven at 393 K and calcined at 773 K for 16 h. Finally the product was sieved through a sieve of 6/10 mesh size.

2.1.2. Preparation of other catalysts

Preparation of MnFe_2O_4 (MF-5) was similar to that of NiFe_2O_4 (NF-1) described above, except that now 0.075 mol of MnCl_2 were used in place of NiCl_2 . Similarly, $\text{Ni}_{0.75}\text{Mn}_{0.25}\text{Fe}_2\text{O}_4$ (NMF-2), $\text{Ni}_{0.5}\text{Mn}_{0.5}\text{Fe}_2\text{O}_4$ (NMF-3) and $\text{Ni}_{0.25}\text{Mn}_{0.75}\text{Fe}_2\text{O}_4$ (NMF-4) were prepared by using 0.0562, 0.0375 and 0.0188 mol of NiCl_2 salt and 0.0188, 0.0375, and 0.0562 mol of MnCl_2 salt, respectively.

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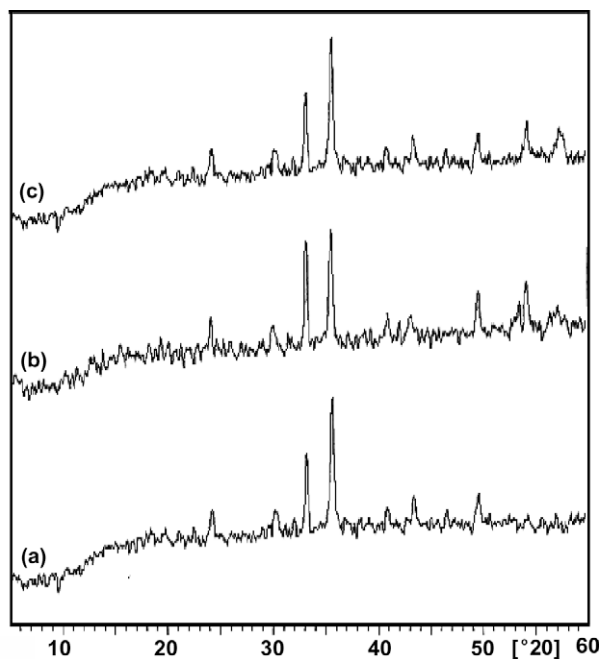


Fig. 1. X-ray diffractograms of (a) MF-5 (b) NF-1 (c) NMF-3.

2.2. Apparatus and procedure

The vapor-phase alkylation reaction was carried out in a continuous fixed-bed glass reactor. 5.0 g of catalyst sieved through a 6/10 mesh size sieve, was placed in the middle of the reactor. The reactants were fed from the top of the reactor using a syringe pump (Perfusor, B. Braun). The products were collected from an ice-cold trap at the bottom of the reactor. Autochro GC 2003A gas chromatograph with flame ionization detector having SE-30 column was used to determine the composition of the product mixture. The conversions were given with respect to indole. The catalytic

activity data comparison is made between different catalysts at 3 h duration. A blank run without any catalyst indicated negligible thermal conversion.

2.3. Catalyst characterization, surface area, acidity measurement

Infrared absorption spectra for all the compositions are recorded on Shimadzu 8 000 FTIR series. The spectra consists of two significant bands first around 700 cm^{-1} and second around 500 cm^{-1} . Absorption bands observed within this limit reveal the formation of a single spinel structure having two sublattices: tetrahedral and octahedral. Absorption band around 700 cm^{-1} is attributed to the tetrahedral sites, whereas band observed around 500 cm^{-1} is assigned to octahedral sites [13]. The difference in the band position is because of the difference in the $\text{Fe}^{3+}\text{-O}^{2-}$ distance for tetrahedral and octahedral sites.

X-ray diffraction of NF-1, NMF-3 and MF-5 was recorded on a PW 1710 diffractometer equipped with a graphite crystal monochromator (for the diffracted beam) and a scintillation counter: Cu-K α radiation with wavelength 1.54 \AA was used in the 2θ range $5.015\text{--}66.875\text{ \AA}$ and are reproduced in Fig. 1. All the peaks in the pattern match well with the characteristic reflections of corresponding ferrites and this confirms the phase purity of samples.

Acidity of all the ferrite catalysts was measured by temperature programmed ammonia desorption ($\text{NH}_3\text{-TPD}$) method. 1.0 g of the catalyst was introduced in the tube. It was pre-heated to 673 K under a nitrogen flow for 2 h. The temperature of the catalyst is then brought down to 298 K and the catalyst at this temperature was exposed to ammonia for 2 h. After saturation, the sample was flushed with nitrogen for 1 h to desorb the loosely bound ammonia molecules from the catalyst surface. The temperature of the catalyst was then raised to 423 K and as a result physisorbed or weakly chemisorbed ammonia was desorbed. Ammonia desorbed in this temperature range corresponds to weak acidic sites. The catalyst temperature was then raised to 623 K and desorbed ammonia is estimated. The ammonia desorbed in this temperature range is considered to represent medium acidic sites. The desorption process was repeated by raising temperature to 723 K. Ammonia

Table 1
Compositional parameter 'x' acidity at different DMC temperatures, catalytic activity (indole conversion at temperature 598 K, WHSV 0.4 h^{-1} , molar ratio 6), and BET surface area (m^2/g) of ferrite catalysts.

X	Acidity (NH_3 uptake in mmol/g)			Total acidity	Catalytic activity		BET surface area (m^2/g)
	423–523 K	523–623 K	623–723 K		Indole conversion (%)		
					a	b	
0.0	0.38	0.34	0.36	1.08	46.9	49.6	73.25
0.25	0.39	0.34	0.37	1.10	49.6	50.2	67.26
0.50	0.40	0.35	0.38	1.13	54.3	55.3	60.34
0.75	0.42	0.36	0.40	1.18	58.1	57.3	50.17
1.0	0.43	0.37	0.42	1.22	61.8	60.7	43.73

a = With methanol, b = with DMC.

Table 2
Performance of various catalysts in the methylation of indole (at temperature 598 K, WHSV 0.4 h^{-1} , methanol or DMC to indole molar ratio 6).

Catalysts	Indole conversion (%)		3-Methylindole yield (%)		3-Methylindole selectivity (%)		Others ^a	
	With methanol	With DMC	With methanol	With DMC	With methanol	With DMC	With methanol	With DMC
NF-1	46.9	49.6	32.1	33.2	68.44	66.93	14.8	16.4
NMF-2	49.6	50.2	35.2	35.2	70.96	70.11	14.4	15.0
NMF-3	54.3	55.3	42.6	42.9	78.45	77.57	11.7	12.4
NMF-4	58.1	57.3	48.6	44.6	83.64	77.83	9.5	12.7
MF-5	61.8	60.7	54.6	48.6	88.34	80.06	7.2	12.1

^a 2-Methylindole, 2,3-dimethylindole and polymethylindoles.

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