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# On the "Active spacer and stabilizer" role of Zn in $Cu_{1-x}Zn_xFe_2O_4$ in the selective mono-N-methylation of aniline: XPS and catalysis study

Munusamy Vijayaraj, Chinnakonda S. Gopinath *

*Catalysis Division, National Chemical Laboratory, Dr. Homi Bhabha Road, Pune 411 008, India*

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**Abstract**

A systematic catalytic methylation study on ferrospinel materials led to the selective production of N-methylaniline (NMA) with $Cu_{1-x}Zn_xFe_2O_4$. Aniline methylation was carried out on $Cu_{1-x}Zn_xFe_2O_4$ with a feed composition of $CH_3OH:PhNH_2:H_2O = 3:1:1$ at 513–633 K. NMA was formed selectively on all of the catalyst compositions, with trace amounts of secondary products under most of the conditions. $Cu_{0.5}Zn_{0.5}Fe_2O_4$ composition showed high catalytic activity and stability up to 100 h. Although the $Cu^{2+}$ was responsible for methylation activity, $Zn^{2+}$ enhanced the overall stability of the catalyst system. XPS investigations revealed that the degree of $Cu^{2+}$ reduction decreased dramatically from $x = 0.05/0.25$ to $0.5/0.75$ on spent catalysts. TPR studies indicated that the reducibility of $Cu^{2+}$ decreased from fully reducible at 523 K with Cu-rich compositions to partially reducible at 573 K on $x = 0.5$. Stable activity observed on $Cu_{0.5}Zn_{0.5}Fe_2O_4$ can be attributed to the highly heterogeneous distribution of metal ions. This heterogeneous distribution indicates an important role of zinc, likely as an "active spacer cum stabilizer" that hinders the reduction of active $Cu^{2+}$ and contributes to prolonged activity.

*Keywords:* Ferrite; N-Methylation; Aniline; N-Methylaniline; XPS; TPR; Spacer; Stabilizer; Surface distribution

## 1. Introduction

N-Alkyl anilines are the basic raw materials for the production of dyes, synthetic rubber, explosives, herbicides, additives, antioxidants, and pharmaceuticals [1–6]. In general, the conventional route for producing any alkyl aromatics using mineral acids or Friedel–Craft-type catalysts [7,8] is economically cheap but highly non-environmental friendly due to the disposal problems of acid wastes and other problems, such as reactor corrosion. The liquid-phase aniline alkylation process carried out under pressure in the presence of various acids [7,8] or on K-exchanged zeolite-Y [9] is tedious, due to difficulties in separating the catalyst and product mixture.

Vapor-phase methylation of aniline over environmentally safe solid acid catalysts has been studied in the last few decades. Several types of solid catalysts based on oxides and supported oxides [10–12], zeolites [4,13–16] and microporous aluminophosphates [2,5,17,18] have been tested for aniline methylation, leading to N-methylaniline (NMA), N,N-dimethylaniline (DMA), and *o*-toludine (OT). Owing to the numerous uses of these anilines, the demand for the active and selective catalyst to a particular product has been grown over the period of time. Selective synthesis of NMA is difficult due to the presence of two chemically equivalent protons in amino group, which most often leads to dimethylation, and the process conditions cannot be changed beyond a limit for a high selectivity to NMA [12,19]. Ko et al. [12] studied the methylation of aniline with methanol at 698 K over alumina to give both NMA and DMA; the corresponding activation energies were $62.7 \pm 2.1$ and $48.3 \pm 2.9\ \text{kJ mol}^{-1}$, respectively. It is obvious that NMA reacts faster than aniline and facilitates the consecutive methylation to DMA that leads to poor product selectivity or highly selective DMA production. Elangovan et al. [19] reported aniline methylation over AFI- and AEL-type molecular sieves at 623–673 K, where NMA, DMA, and N-methyl toluidines (NMT) were formed. The influence of different reaction parameters on the product distribution has also been analyzed. Rao et al. [20] tested aniline methy-

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* Corresponding author. Fax: +91 20 2590 2633.
*E-mail address:* cs.gopinath@ncl.res.in (C.S. Gopinath).

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lation with DMC to compare the selectivity between NMA and DMA on zeolites such as EMT, faujasite, and alkaline loaded zeolite-$\beta$ in the temperature range of 453–503 K and achieved 75% dimethylation selectivity. Bautista et al. [2,5,18] extensively studied the N-methylation of aniline over aluminum and chromium phosphates and observed a pseudo-first-order kinetic dependence with respect to aniline concentration. Their study of the effect of surface acidity on aniline alkylation by pyridine and 2,6-dimethyl pyridine adsorption experiments revealed that weak to moderate acid sites seem to be responsible for the reaction [2,5,18].

Our earlier characterization studies on alkylation of phenol and aniline on $Cu_{1-x}Co_xFe_2O_4$ [21–24] and $Cu_{1-x}Zn_xFe_2O_4$ [25,26] using XPS and in situ FTIR, respectively, led to an understanding of the electronic, structural, and mechanistic aspects of the alkylation reactions. Our earlier work on spinels at National Chemical Laboratory [21–27] revealed the potential catalysts for various alkylations. A thorough search for the selective catalytic production of N-monomethylation of aniline was carried out with $A_{0.5}A'_{0.5}Fe_2O_4$ systems, where A = Fe, Cu, Zn and A′ = Fe, Co, Ni, Cu, and Zn. Vapor-phase mono-N-methylation of aniline with methanol on $Cu_{1-x}Zn_xFe_2O_4$ is reported here. X-ray photoelectron spectroscopy (XPS), X-ray induced Auger electron spectroscopy (XAES), X-ray diffraction (XRD), and temperature-programmed reduction (TPR) investigations were carried out to evaluate the electronic and structural properties of the $Cu_{1-x}Zn_xFe_2O_4$ system and the interaction between the metal ions.

## 2. Experimental

### 2.1. Catalyst synthesis and characterization

Catalysts were prepared by adopting a low-temperature pH-controlled co-precipitation method, as reported previously [21–27]. The chemical compositions of calcined samples were determined by inductively coupled plasma spectrometry (ICPS) using a Perkin-Elmer PE 1000 device. XRD patterns of the powder samples were recorded using a Rigaku Geigerflex instrument using Cu-$K_\alpha$ radiation (1.5405 Å) with a Ni filter to verify the phase purity and obtain the unit cell parameter ($a$, Å) and crystallite size. The crystallite size of the samples was calculated using Scherrer's equation [21,28]. The BET surface area and the pore volume ($V_p$) of the catalysts were determined by $N_2$ adsorption–desorption at 77 K using a Quanta chrome NOVA-1200 adsorption unit. All of the above characterization results are given in Table 1. TPR experiments were carried out with a Micromeritic Autochem 2910 catalyst characterization system equipped with a thermal conductivity detector. Calcined catalysts were activated in Ar flow at 773 K for 1 h. After cooling to ambient temperature, the argon flow was replaced by a 5% $H_2$/Ar mixture. The catalysts were heated to 1073 K at a heating rate of 5 K/min. A flow rate of 30 mL/min was maintained throughout the experiments for all catalysts.

X-Ray photoelectron spectra were acquired on a VG Microtech Multilab ESCA 3000 spectrometer using a non-monochromatized Mg $K_\alpha$ X-ray source (1253.6 eV) on in situ scraped fresh catalyst pellets and powder samples of spent catalysts [21,29–31]. Selected spectra were recorded with an Al-$K_\alpha$ X-ray source (1486.6 eV) also to eliminate the overlap between different Auger and core levels. Base pressure in the analysis chamber was maintained in the range of $3–6 \times 10^{-10}$ Torr. The error in the reported BE values is ±0.1 eV.

### 2.2. Catalytic activity measurements

Vapor-phase methylation of aniline was carried out at atmospheric pressure in a fixed-bed, vertical-downflow glass reactor placed inside a double-zone furnace (Geomechanique, France). The 0.75-g sample of freshly calcined catalyst with 10 mesh particle size was charged each time in the center of the reactor in such a way that the catalyst was sandwiched between layers of inert porcelain beads. The upper portion of the reactor system served as a vaporizer cum preheater. The exact temperature of the catalyst bed was monitored with a K-type thermocouple placed at the center of the catalyst bed. The reactant mixture (methanol + aniline + water) was fed using a syringe pump (Braun, Germany) at a desired space velocity. Reaction products were collected from a condenser fixed below the reactor and analyzed using a gas chromatography (Agilent 19091J-413) with a HP-5.5% phenyl methyl siloxane capillary column equipped with a flame ionization detector and/or gas chromatography–mass spectroscopy (Shimadzu GC-17A equipped with a QP 5000 mass spectrometer).

## 3. Results

### 3.1. Effect of various metal ions toward N-methylation

Fig. 1 shows the aniline conversion and NMA yield on $A_{0.5}A'_{0.5}Fe_2O_4$ (A = Fe, Zn, Cu and A′ = Fe, Co, Ni, Cu, and Zn) at 573 K with a $CH_3OH$:$PhNH_2$ ratio of 3:1. NMA formed selectively on all of the systems; however, aniline conversion declined on all of the systems with TOS due to catalyst

Table 1
Chemical analysis, XRD parameters, and surface area of $Cu_{1-x}Zn_xFe_2O_4$

| $x$ | Metal concentration (wt%) | | | Crystallite size fresh (spent) (nm) | Lattice constant fresh (spent) $a$ (Å) | $S_{BET}$ fresh (spent) ($m^2/g$) |
|---|---|---|---|---|---|---|
| | Cu | Zn | Fe | | | |
| 0.05 | 22.94 | 1.19 | 57.65 | 10.0 (23.4) | 8.3459 (8.3723) | 23.0 (16.0) |
| 0.25 | 21.65 | 5.51 | 54.43 | 15.9 (19.5) | 8.4090 (8.3946) | 45.2 (34.0) |
| 0.5 | 15.02 | 10.40 | 50.70 | 10.7 (12.1) | 8.4052 (8.4133) | 49.3 (41.0) |
| 0.75 | 6.82 | 16.70 | 50.04 | 11.7 (19.5) | 8.4150 (8.4153) | 42.0 (22.0) |
| 1 | – | 24.22 | 49.56 | 13.0 (16.0) | 8.4180 (8.4117) | 35.0 (28.0) |