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Research Note

Spectroscopic witness from reactants to product: FTIR studies on selective mono-N-methylation of aniline on $Cu_{1-x}Zn_xFe_2O_4$

Munusamy Vijayaraj, Chinnakonda S. Gopinath *

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

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Abstract

An active N-methylation ferrospinel catalyst, $Cu_{1-x}Zn_xFe_2O_4$, is reported for the first time. A mechanistic approach to selective mono-N-methylation of aniline on $Cu_{1-x}Zn_xFe_2O_4$ is successfully explained by in situ temperature-dependent DRIFTS studies of reactants on the catalyst. Perpendicular orientation of aromatic rings of aniline, methyl group availability, an optimum metal–ion distribution on the catalyst surface, and a stable methyl group on Zn leads selectively to N-methylaniline (NMA) on $Cu_{0.5}Zn_{0.5}Fe_2O_4$. Desorption-limited kinetics is evident from NMA formation at low temperatures.

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1. Introduction

Product selectivity is a key issue in the production of several fine chemicals through catalytic means. Exclusive product selectivity often comes from the right combination of reactants and proper orientation for the right interaction among them on the right catalyst surface under less severe conditions. Despite the large industrial and economical stake involved, there are not many studies of the molecular origins of such effects [1]. This lack of detailed knowledge is due to severe experimental conditions used on real-world catalysts and the highly complex nature of the catalysts themselves. However, IR spectroscopy is an excellent tool under such nonambient conditions and provides very useful details of catalysis [1].

A key unresolved problem in many catalytic studies is the spectroscopic identification of intermediates and the possibility of examining in situ their occupation on catalyst surfaces under normal reaction conditions. To address this problem, it is necessary to employ real-world catalyst and reaction conditions, or conditions that are close to the above [1]. Here, we present the results of selective mono-N-methylation of aniline (SMNMA) on $Cu_{1-x}Zn_x$-Fe_2O_4, which is of scientific and industrial interest [2,3]. Adsorption of reactants and possible products was investigated by diffuse reflectance infrared Fourier transform spectroscopy (DRIFTS) from 373 to 623 K. It was possible to observe a dissociative adsorption and orientation of reactants on the catalyst surface, their conversion to product at low temperatures, and desorption-limited kinetics, all under conditions that are close to the reaction conditions. Cu^{2+} is the active center for the aniline N-methylation reaction and IR studies reveal that Zn^{2+} acts as the main methyl species source and evidence for the same is given.

2. Experimental

$Cu_{1-x}Zn_xFe_2O_4$ ($x = 0.05$, 0.25, 0.5, 0.75, and 1) samples were prepared by the coprecipitation technique described in Ref. [4]. The integrity of the catalysts was confirmed by X-ray diffraction, surface area, and thermal analysis [3]. X-ray diffraction (XRD) patterns of the catalysts were recorded using Cu$K\alpha$ radiation ($\lambda = 1.5405$ Å) with a Ni filter (Rigaku Geigerflex). XRD of fresh and spent catalysts indicates the cubic spinel phase at all compositions with a marginal increase in lattice parameter (a) from 8.35 Å at

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* Corresponding author. Fax: +91-20-2589-3761.
E-mail address: gopi@cata.ncl.res.in (C.S. Gopinath).

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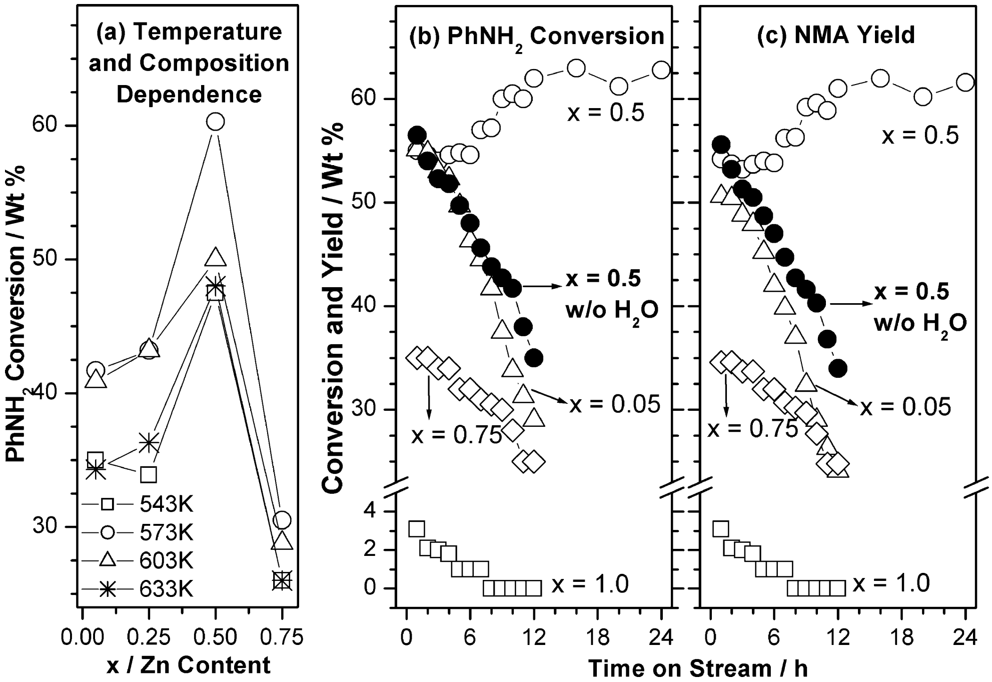

Fig. 1. Selective mono-*N*-methylation of aniline with MeOH:PhNH$_2$:H$_2$O (3:1:1) on Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$. (a) Temperature and catalyst composition dependence of PhNH$_2$ conversion at TOS = 8 h; (b and c) TOS dependence of PhNH$_2$ conversion and NMA yield at 573 K. Results without H$_2$O are shown as solid circles.

$x = 0$ to 8.41 Å at $x = 1$. The BET surface areas of the catalysts were determined using a Quantachrome NOVA-1200 adsorption unit at 77 K. Surface areas of fresh catalysts are in the range of 28 to 49 m^2/g with a high surface area for $x = 0.5$ composition. Vapor-phase aniline methylation was carried out, in a setup similar to that described in Ref. [4] between 473 and 633 K and the product analysis was performed with GC and GC-MS.

The FTIR spectra were recorded by the DRIFTS method on a Shimadzu 8300 spectrometer equipped with a MCT-A detector. Catalyst on a sample holder was placed in Spectra-Tech-made DRIFTS cell with a ZnSe window (Model 0030-067). Water circulation of the ZnSe window keeps the temperature close to room temperature even at a catalyst temperature of 573 K. The DRIFTS cell is equipped with an inlet and an outlet to introduce the probe molecules in a nitrogen stream. First, the sample was heated in situ to 673 K at a heating rate of 5 K/min in N$_2$ stream (40 ml/min and 99.99% pure). The sample was kept at 673 K for 3 h and then the hydroxyl region of the spectra was measured. Except for the above, no other IR bands are observed between 3500 and 900 cm^{-1} on the catalysts. The sample was then cooled to 333 K and 10 µl of any compound or mixture was injected and adsorbed in a N$_2$ stream. The temperature was ramped in a N$_2$ flow and IR spectra were recorded between 333 and 623 K. A resolution of 4 cm^{-1} was attained after averaging of 500 scans for the spectra reported. All spectra presented here are the difference spectra between molecule(s) adsorbed and pure catalyst.

3. Results and discussion

The present paper is a part of continuing efforts in our laboratory to understand the aromatic alkylation reactions in detail [4]. Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ was chosen from a thorough search for suitable catalysts from ferrospinel (AFe$_2$O$_4$, A = one or two transition-metal ions) materials. Detailed studies of SMNMA over a Cu$_{1-x}$Zn$_x$Fe$_2$O$_4$ ($x = 0.05$–1) system reveal an optimum reaction condition of 3:1:1 ratio of MeOH:PhNH$_2$:H$_2$O at 573 K [3]. Fig. 1a shows an aniline methylation reaction carried out under the above conditions and indicates pronounced catalyst composition and temperature dependence and maximum activity with $x = 0.5$ at 573 K. Results in Figs. 1b and 1c show 97% *N*-methylaniline (NMA) selectivity (trace amounts of *N*,*N*-dimethylaniline (DMA) and *C*-alkylated products are not shown) for all catalysts with a 3:1:1 feed. $x = 0.5$ shows high and stable catalytic activity at least up to 24 h. Though $x = 0.05$ and 0.5 shows the same initial activity, it decreases rapidly for 0.05. $x = 0.75$ shows intermediate activity in the first few hours of time on stream (TOS) and then decreases rapidly at high TOS. Low activity with ZnFe$_2$O$_4$ and the above $x = 0.75$ results indicate that the role of Zn and Fe is negligible. Further, catalytic activity declines very fast with increasing TOS without H$_2$O in the feed through coke formation for all x values.

Though Cu seems to be responsible for the total catalytic activity, the best activity achieved with $x = 0.5$ indicates the importance of a 1:1 bulk combination and distribution of Cu and Zn on the catalyst surface. The main

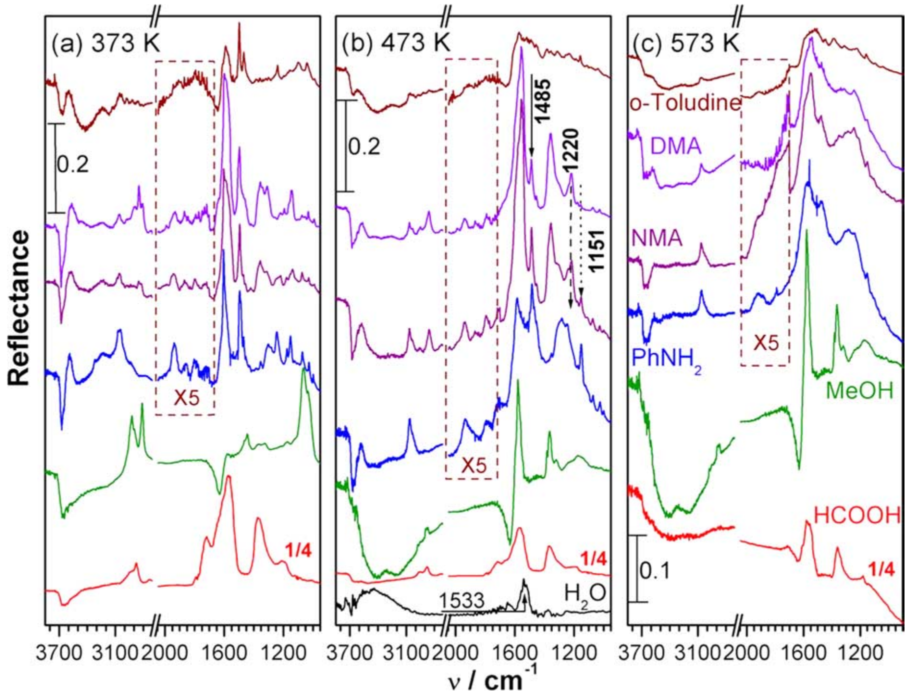

Fig. 2. FTIR spectra of standard compounds (reactants and possible products of aniline methylation with methanol) adsorbed on $Cu_{0.5}Zn_{0.5}Fe_2O_4$ between 373 and 573 K. H_2O adsorbed on $Cu_{0.5}Zn_{0.5}Fe_2O_4$ is shown only at 473 K. On all panels 2100–1700 cm^{-1} range for aromatic compounds is multiplied on y-axis for clarity.

focus of the present work is to understand the high activity of $x = 0.5$ and the mechanism of SMNMA. Fig. 2 shows the temperature-dependent FTIR study of $PhNH_2$, MeOH, H_2O, NMA, DMA, o-toluidine (OT), and HCOOH adsorbed on $x = 0.5$. MeOH adsorbed dissociatively at 373 K as surface OMe species with characteristic bands at 2924, 2814, and 1063 cm^{-1} [1,5–7]. The above bands disappear and new bands appear at 2952, 1579, and 1379 cm^{-1} due to formate species at $\geqslant 473$ K [1,5–7] and it is confirmed from a good correlation between the above spectra and the spectra of HCOOH adsorbed at $\geqslant 473$ K on $x = 0.5$. It is evident that MeOH alone on the catalyst gets oxidized to HCOOH above 373 K. H_2O shows OH_{str} and OH_{def} bands > 3300 and 1533 cm^{-1}, respectively.

$N–H_{str}$, aromatic $C{=}C_{str}$, $C–N_{str}$, and $C–H_{str}$ bands were observed at 3330–3220, 1610–1500, 1310–1100, and 3060 cm^{-1}, respectively, for aniline, NMA, DMA, and OT at 373 K on $x = 0.5$ (Fig. 2a) [2,8,9]. No $N–H_{str}$ band > 3350 cm^{-1} indicates a H^+ dissociation on adsorption. Dissociated protons interacting with oxygen and forming OH groups are evident from the broad OH_{str} band between 3800 and 3500 cm^{-1} and its intensity decreases with increasing temperature. It is to be noted that there are some inherent OH bands on the virgin catalyst surfaces. Bands characteristic of $C–H_{str}$ (Me) were observed around 2850 cm^{-1}. A definite intensity of overtone bands due to out-of-plane (aromatic) C–H bending was observed at 2050–1700 cm^{-1} indicates that the phenyl ring is fairly perpendicular to the surface except OT, and high intensity suggests a highly perpendicular orientation in aniline [8,9]. However, the above details change drastically at 473 K and the highlights are listed: (1) No $N–H_{str}$ bands are observed, indicating a dissociation of all H^+ in amino groups; (2) $C{=}C_{str}$ at 1600 cm^{-1} at 373 K moves to 1585 cm^{-1} for aniline and around 1560 cm^{-1} for other molecules; $C{=}C_{str}$ band intensity at 1485 cm^{-1} gradually decreases from aniline to NMA to DMA (solid arrow); (3) the intensity ratio of $C{=}C_{str}$ at 1485 to 1550–1585 cm^{-1} decreases from aniline to DMA, in contrast to the matching values at 373 K; (4) aliphatic and aromatic $C–N_{str}$ bands at 1320–1050 cm^{-1} decrease in intensity from aniline to DMA (dotted and dashed arrows); (5) aromatic $C–H_{str}$ around 3060 cm^{-1} decreases in intensity compared to methyl $C–H_{str}$ around 2850 cm^{-1} from NMA to DMA; (6) overtone band intensity also decreases from aniline to DMA; and (7) NMA and DMA show symmetric $C–H_{def}$ of the Me group at 1355 cm^{-1}. OT bands overlap to a large extent and were difficult to resolve. The above observations are attributed to a change in phenyl ring orientation to surface (perpendicular in $PhNH_2$) due to steric hindrance of a methylated amino group (more parallel in NMA and DMA); hence, the mode of interaction to catalyst surface also changes from N in $PhNH_2$ to phenyl ring in DMA. A general decrease in intensity of aromatics at 573 K indicates that the desorption sets in at > 473 K. Overtone band intensity also decreases in the same way as above.

Representative FTIR spectra of $MeOH{:}PhNH_2$ (1, 3, and 5) mixtures adsorbed on $x = 0.05$, 0.5, and 1 between 373 and 573 K are shown in Fig. 3. There is a large overlap between OH_{str} and OH_{def} bands with NH_{str} and $C{=}C_{str}$ bands, respectively, and hence limited results are given for

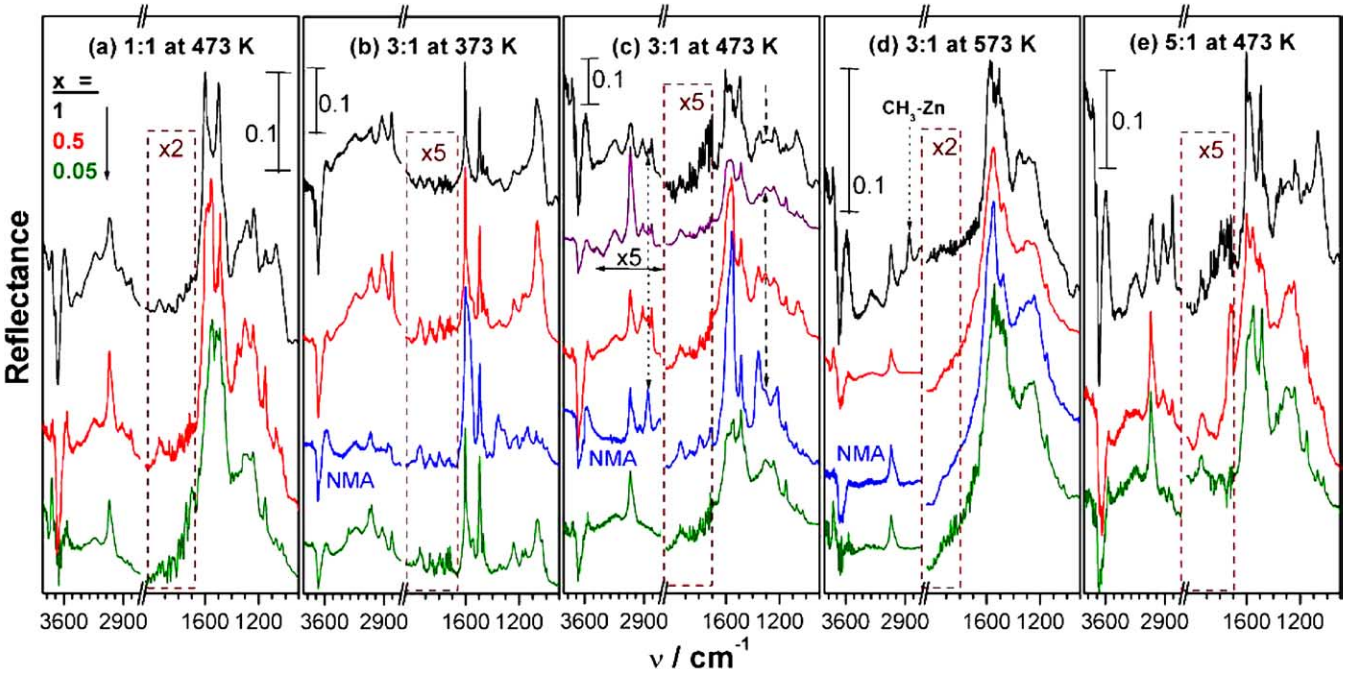

Fig. 3. Representative FTIR spectra of MeOH:PhNH$_2$ (1, 3, and 5) mixtures adsorbed on $Cu_{1-x}Zn_xFe_2O_4$ ($x = 0.05$, 0.5, and 1) between 373 and 573 K. NMA adsorbed on $x = 0.5$ (blue traces) is shown for reference. Purple trace is from MeOH:PhNH$_2$:H$_2$O (3:1:1) adsorbed on $x = 0.5$. On all panels 2100–1700 cm^{-1} range is multiplied on y-axis for clarity.

3:1:1 feed (Fig. 3c). The main points observed at 373 K are: (a) IR bands observed for all reactant ratios suggest a simple coadsorption of OMe and PhNH species with no major interaction among them (Fig. 3b); (b) only OMe and no sign of formate species indicate that the MeOH oxidation is hindered in coadsorption; (c) comparatively strong overtone bands for $x = 0.5$ indicate that the phenyl ring is highly perpendicular to the surface than in other cases.

Interaction among the adsorbates is evident from enormous changes observed in the spectra recorded at $\geqslant 473$ K (Fig. 3c). Important points from the above results are: (1) $x = 0.5$ shows appreciable changes in band positions and intensity, including the appearance of N–C$_{str}$ and C–H$_{str}$ of N–CH$_3$ groups (dashed (1300 cm^{-1}) and dotted (2850 cm^{-1}) arrows, respectively), which corresponds to that of NMA and its formation close to 473 K. Similar results can be seen for a 3:1:1 feed, indicating that H$_2$O does not interfere in methylation. However, NMA desorption occurs above 473 K which is the limiting factor and a main reason for its spectroscopic observation. (2) On $x = 0.05$, no features correspond to NMA and weak or no MeOH features are seen at $\geqslant 473$ K (Figs. 3a, 3c, and 3e); however, it resembles that of adsorbed PhNH$_2$ at 473 K and suggests that the nonavailability of Me species is the limiting factor for the reaction. (3) OMe and N–H$_{str}$ bands were observed and no band at 1300 cm^{-1}, $\geqslant 473$ K on $x = 1$ suggests that there is no interaction among adsorbates; no overtone bands suggest that the phenyl ring is parallel to the surface, which is not preferred for N-methylation.

A very close similarity between NMA and MeOH:PhNH$_2$ (3:1) adsorbed on $x = 0.5$ at 573 K (Fig. 3d) further confirms the conversion of reactants to NMA. The low intensity of all the peaks at 573 K, compared to 473 K, suggests a desorption of NMA and aniline too. The Me group seen at 2852 cm^{-1} suggests its great stability on ZnFe$_2$O$_4$ and it is likely due to Zn–CH$_3$ species (Fig. 3d, dotted arrow). The possibility of N,N-dimethylation was tried with MeOH:PhNH$_2$ (5) (Fig. 3e) and was not successful as MeOH was converted to reformate products and/or HCOOH, under the present experimental conditions.

Surface atomic ratios $(Cu/(Fe + Zn))$ calculated from photoemission studies for $x = 0.05$, 0.5, and 0.75 are 1.04, 0.56, and 0.35, respectively, revealing a highly heterogeneous distribution of metal–ions on $x = 0.5$ and supporting our conclusions [3]. Additionally, the Zn/Fe ratio calculated on $x = 1$ is 1.06 indicating the surface domination by Zn^{2+} and hence the low catalytic activity. This factor further confirms that the stable methyl groups observed on ZnFe$_2$O$_4$ even at 573 K (Fig. 3d) is, likely to be entirely, due to CH$_3$–Zn species; therefore, the availability of methyl cation to SMNMA is hindered under optimum reaction conditions, which is a crucial step.

4. Conclusions

Catalytic aniline methylation on $Cu_{1-x}Zn_xFe_2O_4$ to selective N-methyl aniline is reported for the first time and mechanistic details are explored by IR spectroscopy. FTIR results are in good agreement to catalytic activity results of SMNMA on $Cu_{1-x}Zn_xFe_2O_4$. NMA detection at 473 K on $x = 0.5$ indicates a desorption-limited kinetics between 473 and 573 K. IR results indicate that the main conditions of aniline orientation and methyl species availability are very appropriate for $x = 0.5$ and suggests that the role of Zn + Fe could be a spacer to optimally distribute active Cu^{2+}. Stable MeOH-derived features on $ZnFe_2O_4$ suggest that Zn could be a methyl species source for SMNMA under actual reaction conditions on Cu in $x = 0.5$, where $x = 0.05$ shows no MeOH features. Efforts are in progress for long-term stability and to utilize the NMA formation at 473 K to desorb close to 473 K by modifying the acid–base properties of the catalyst. Detailed results on photoemission results [3] and IR analysis [10] are to be published.

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