

An insight into the mechanism of selective mono-*N*-methylation of aniline on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$: a DRIFTS study

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Received 19 October 2004; received in revised form 6 January 2005; accepted 6 January 2005

Abstract

Mechanism of selective mono-*N*-methylation of aniline with methanol on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ catalysts was investigated in detail. The interaction of reactants (aniline, methanol and methanol:aniline) and possible products (*N*-methylaniline (NMA), *N,N*-dimethylaniline (DMA) and *o*-toluidine (OT)) on catalysts surface was studied by temperature-dependent in situ FTIR spectroscopy. Methanol adsorbs dissociatively over catalysts surface at 373 K as methoxy species and is oxidized to formate species at high temperature through dioxymethylene and/or formaldehyde as a surface intermediate species. On the other hand, adsorption of aniline:methanol mixtures shows that methanol oxidation was completely hindered in the presence of aniline. Aniline adsorbs on the Lewis acid sites at ≤ 373 K with phenyl ring oriented in a perpendicular manner to the catalyst surface; however, N–H bond scission occurs above 373 K. A comparison of adsorbed NMA and methanol:aniline (3:1) mixture on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ shows NMA forms from the reaction mixture at 473 K. However, maximum activity at 573 K in catalytic reaction studies suggests that desorption limits the methylation kinetics. FTIR study displays stable aniline and methyl species on ZnFe_2O_4 even at 573 K; however, no methyl species is detected on $\text{Cu}_{0.95}\text{Zn}_{0.05}\text{Fe}_2\text{O}_4$ at 473 K due to methanol reforming reaction and that limits the overall reaction and hence low catalytic activity. It is proposed that methanol is protonated on catalysts surface by the labile H^+ due to N–H bond scission. Co-adsorption of acidity probes with aniline and methanol indicates that aniline methylation takes place at single acid–base site. © 2005 Elsevier B.V. All rights reserved.

Keywords: $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$; Aniline; Methanol; *N*-Methylation; DRIFT; IR; Reaction mechanism; *N*-Methylaniline; Desorption limited

1. Introduction

Methylated anilines like *N*-methylaniline (NMA), *N,N*-dimethylaniline (DMA) and toluidines serve as important precursors for dyes, explosives and in pharmaceutical industries [1,2]. Several groups have reported vapor phase aniline methylation using methanol or dimethylcarbonate as methylating agent over a wide range of catalysts based on metal oxides [3–5], supported oxides [6], zeolites [7–9], aluminophosphates [10,11] and clays [12] and the influence of acid–base properties of the catalyst on activity and selec-

tivity was explored under a variety of experimental conditions. The conventional pre- and post-reaction investigations through physico-chemical characterization contribute to some understanding about the reaction. However, most often they do not adequately reflect the events that occur on the system under actual reaction conditions, like short-lived intermediates, surface complexes and the reaction mechanism. The in situ characterization techniques help to understand the interaction of adsorbed surface species on catalysts and highlight the chemical and orientation changes of the adsorbate, short-lived intermediates and surface complexes that formed during the reaction and ultimately lead to reaction mechanism. In addition, in situ techniques throw light on how catalytic conversion and product selectivity depend on structural and electronic prop-

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erties of the catalyst and the mode of catalyst deactivation [13,14].

Among the several in situ spectroscopic techniques available, FTIR is the most useful and valuable technique to study heterogeneous catalysis owing to its high sensitivity and the ability to be employed in practical catalytic reaction conditions. In the recent years, it has been used increasingly for in situ investigations to understand the catalytic reaction mechanism and reviewed in references [13,14]. In order to visualize the events that proceed during catalytic reaction conditions and to learn the mechanistic aspects of the reaction, in situ investigations have to be carried out on the working catalysts directly in the spectrometer [13]. To the best of our knowledge, no detailed reports on aniline methylation mechanism, using FTIR, are reported till date, even though a few reports of FTIR studies on interactions of amines over oxides [15,16], aluminium halides and GaCl_3 [17], alumina [18,19] and MCM-41 [20] are available. In this work, we report the main catalytic reaction results of aniline methylation reaction under optimized reaction conditions. A detailed investigation on adsorbed reactants and possible products on the $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x = 0.05, 0.5$ and 1) system was carried out by conducting temperature-dependent in situ FTIR study [21]. The enhanced selectivity towards NMA over DMA and *o*-toluidine (OT) was discussed. Shortcomings of the interaction of reactants with $\text{Cu}_{0.95}\text{Zn}_{0.05}\text{Fe}_2\text{O}_4$ and ZnFe_2O_4 surfaces were discussed in detail. This paper is a part of investigations in our laboratory to understand the alkylation of aromatic compounds on solid catalysts [21–28].

2. Experimental

Cu–Zn-containing ferros spinels were prepared by low temperature co-precipitation technique as reported earlier [21–28]. Briefly, an aqueous solution containing stoichiometric amounts of metal nitrates was added to a calculated amount of sodium hydroxide solution under continuous stirring. The final pH of the resulting mixture was adjusted to 9. The precipitate was filtered, washed several times, dried at 353 K for 36 h and calcined at 773 K for 8 h. The catalytic activity experiments were performed at atmospheric pressure in a fixed bed down-flow integral glass reactor placed inside a double zone vertical furnace (Geomechanique, France). 0.75 g of fresh catalyst with a particle size of 10 mesh was charged between the layers of inert porcelain beads acting as a pre-heater cum a vaporizer and activated under the flow of dry air for 8 h at 773 K before the reaction. The reactant mixture, methanol:aniline:water (3:1:1) was fed by a syringe infusion pump (Braun, Germany) at a desired weight hourly space velocity (WHSV) and products were collected by using a cold water circulating condenser fixed below the reactor. Agilent GC (Model 19091J-413) equipped with a flame ionization detector and an HP-5.5% phenyl methyl siloxane capillary column and GC–MS (Shimadzu GC-17A equipped with QP

5000 Mass spectrometer) were used to analyze the reaction products.

In situ FTIR spectra of the samples with various adsorbed molecules were recorded in diffuse reflectance infrared Fourier transform (DRIFT) technique on a Shimadzu (SSU8300) spectrometer equipped with MCT-A detector [21,22]. The calcined samples were placed in a Spectra-Tech made DRIFTS cell with a Zn–Se window (Model 0030-067) and heated in situ to 673 K for 3 h at a heating rate of 5 K/min in 99.99% pure N_2 stream (40 mL/min) and then the hydroxyl region of the spectra was measured. The sample was then cooled to 333 K and 10 μL of any compound or reaction mixture was introduced separately for 10 min in the N_2 flow. The temperature was ramped under N_2 flow and IR spectra were recorded at different temperatures between 333 and 623 K. 4 cm^{-1} resolution was attained after averaging over 500 scans. All the spectra presented here as the difference spectra between molecule(s) adsorbed on catalyst and calcined virgin catalyst.

3. Results

3.1. Catalytic methylation of aniline

Aniline methylation using methanol as methylating agent was carried out on the $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ferros spinel system [21,28], where $x = 0.05, 0.25, 0.5, 0.75$ and 1 . Fig. 1a shows the time on stream (TOS) dependence of aniline conversion and NMA yield under optimum reaction conditions [21,28] of 3:1:1 molar ratio of methanol:aniline:water at 573 K with 3.58 h^{-1} weight hourly space velocity. It was found that NMA formed selectively (97%), with trace amounts of DMA and OT (not shown) on all catalyst compositions. Although catalysts with $x = 0.05, 0.25$ and 0.5 show comparable initial aniline conversion, only that with $x = 0.5$ shows stable catalytic activity at least up to 24 h; catalytic activity decreases at longer TOS (>4 h) on other catalyst compositions. Further, catalytic activity declines very fast with increasing TOS without water in the feed due to coke formation for all values of x . Fig. 1b shows temperature-dependent activity measurements at TOS = 8 h. High NMA yield with maximum aniline conversion was obtained at 573 K for all values of x (except $x = 1$). Above 573 K, formation of secondary products DMA and OT increases gradually. ZnFe_2O_4 shows poor activity over the entire temperature range studied, indicating that the role of Zn and Fe is negligible. Even though copper seems to be responsible for the total catalytic activity, aniline methylation was very low on pure CuO due to methanol reforming reaction (result not shown). However, a stable activity was achieved with 1:1 copper:zinc combination in $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$, hinting that there is some role for Zn ions. TOS-dependent studies indicate an increase in activity for systems with $x = 0.05$ to 0.5 and then a decrease with further increase in x . Therefore, to understand this catalytic behavior, a systematic in situ FTIR study on reactants

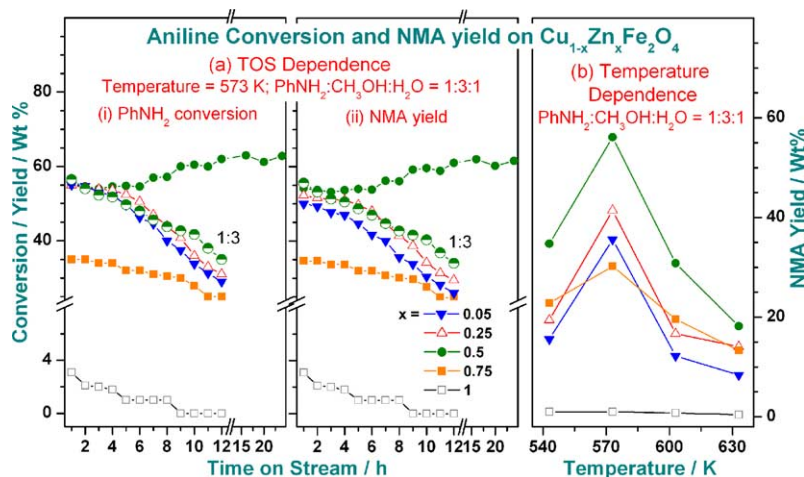


Fig. 1. Selective mono-*N*-methylation of aniline with $\text{MeOH}:\text{PhNH}_2:\text{H}_2\text{O}$ (3:1:1) on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$. (a) Time on stream and catalyst composition dependence of PhNH_2 conversion and NMA yield at 573 K. Data for methylation reaction with a feed that contains no water on the $x=0.5$ composition are also given for comparison. (b) Temperature dependence of NMA yield is given for all catalyst compositions.

and products on catalyst compositions $x=0.05, 0.5$ and 1 was carried out.

3.2. FTIR results

3.2.1. Adsorption of methanol

Fig. 2 shows the temperature-dependent FTIR spectra of methanol adsorbed on catalysts with $x=0.05, 0.5$ and 1 and their vibrational assignments are given in Table 1. At 373 K, methanol adsorbed dissociatively as a surface methoxy group with characteristic bands at 2924, 2895, 2814, 1440 and 1063 cm^{-1} [21,22,29,30]. The C–H asymmetric (ν_{as}) and symmetric (ν_{s}) stretching vibrations of methoxy species were observed at 2924 and 2895 cm^{-1} and overtone methyl bending (2δ) appeared at 2814 cm^{-1} . The presence of methoxy species during methanol adsorption was indicated by the C–O stretching mode at 1063 cm^{-1} , which appears at around 1035 cm^{-1} for liquid methanol. Another low frequency band

at 1440 cm^{-1} was due to the methyl group symmetric bending mode (δ_{s}). Since methanol undergoes oxidation on the present catalyst system, authentic spectra of formaldehyde and formic acid adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ are also given in Fig. 2 (and in Table 2 for comparison). Adsorbed formaldehyde and formic acid also show the formate species with unique features at 2956, 2876, 1570 and 1370 cm^{-1} . At 373 K, bands at 2938, 2850 and 1446 cm^{-1} were observed due to C–H asymmetric, symmetric and bending vibrations of adsorbed formaldehyde species, respectively, along with dioxymethylene [30] species features at 2870, 1300 and 1068 cm^{-1} . This dioxymethylene was believed to be a surface intermediate species during the oxidation of HCHO to HCOOH.

As the temperature increased to 473 K, there was a loss in intensity of a few bands with the formation of entirely new bands. However, such changes were prominent only in copper-containing systems ($x=0.05$ and 0.5)

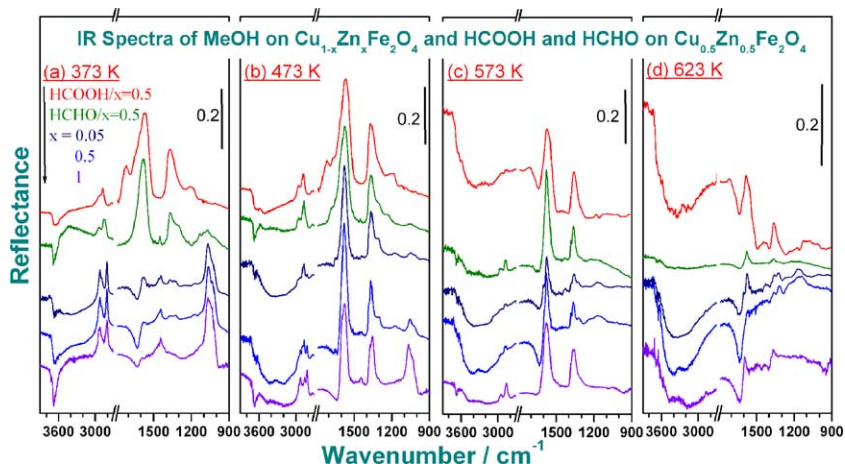


Fig. 2. Temperature-dependent FTIR spectra of methanol adsorbed on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for three selected catalyst compositions of $x=0.05, 0.5$ and 1 at (a) 373 K, (b) 473 K, (c) 573 K and (d) 623 K. IR spectra of HCOOH and HCHO adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at different temperatures are also shown for reference in top two traces.

Table 1
Vibration bands assignment of methanol on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ ($x=0.05, 0.5$ and 1) at various temperatures

Assignment	373 K			473 K			573 K		
	0.05	0.5	1	0.05	0.5	1	0.05	0.5	1
$\nu_{\text{as}}(\text{CO}_2^-) + \delta(\text{CH})$	–	–	–	2950	2954	–	–	–	2952
$2\delta(\text{CH})$	–	–	–	–	–	2946	–	–	–
$\nu_{\text{as}}(\text{CH})$	2923	2924	2926	2924	2924	2923	–	–	–
$\nu_{\text{s}}(\text{CH})$	2895	2895	2898	–	–	–	–	–	–
$\nu_{\text{s}}(\text{CH})$	–	–	–	2883	2885	–	2878	2878	2880
$\nu_{\text{s}}(\text{CH})$	–	–	–	2868	2867	2856	–	–	2861
$2\delta(\text{CH})$	2814	2814	2814	2814	2818	2817	–	–	–
$\nu_{\text{as}}(\text{CO}_2^-)$	1580	1573	–	1576	1578	1576	1576	1578	1578
$\delta(\text{CH})$	1441	1442	1443	–	–	–	–	–	–
$\nu_{\text{s}}(\text{CO}_2^-)$	1368	1368	–	1364	1366	1363	1364	1364	1363
$\tau(\text{CH}_2)$	–	–	–	1306	1300	–	–	–	–
$\Gamma(\text{CH}_2)$	–	–	–	1180	1171	–	1176	1171	–
$\nu(\text{CO})$	1068	1065	1067	–	–	1065	–	–	–

where new bands at 2868, 1302 and 1171 cm^{-1} were attributed to dioxymethylene species [30] formed by oxidation of methoxy species. This dioxymethylene species was not seen on ZnFe_2O_4 , on which methoxy species were converted into formaldehyde [30], whose C–H stretching bands were observed at 2946 and 2856 cm^{-1} . Other bending modes were not visible as confirmed by adsorbed formaldehyde on the catalyst with $x=0.5$ (Fig. 2b). It is to be noted that a strong C–O stretching frequency ($\nu_{\text{C-O}}$) due to surface methoxy species at 1063 cm^{-1} was seen at $x=0.5$ and 1 even at 473 K. On the other hand, the $x=0.05$ system shows a very weak $\nu_{\text{C-O}}$ at 1063 cm^{-1} which indicates a fast methanol oxidation between 373 and 473 K. Further, on all catalyst compositions, a series of additional bands appeared at 2952, 2884, 1578 and 1364 cm^{-1} , which were ascribed to formate species. This was further confirmed from the IR features of adsorbed formic acid on $x=0.5$ system (Fig. 2). Few features of formate species (1578 and 1364 cm^{-1}) were seen ≥ 573 K due to surface bidentate carbonate formation [31] and no C–H signals were observed. These changes were also observed on HCHO/HCOOH adsorbed over the $x=0.5$ system. It was evident that methanol dissociates to methoxy species at 373 K and then converted to formate species which was completely oxidized to typical reformate products ≥ 473 K on all catalyst compositions.

Table 2
Vibration bands assignment of formaldehyde and formic acid on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ at various temperature

Assignment	373 K		473 K		573 K	
	HCOOH	HCHO	HCOOH	HCHO	HCOOH	HCHO
$\nu_{\text{as}}(\text{CO}_2^-) + \delta(\text{CH})$	2956	–	2956	2952	–	2960
$2\delta(\text{CH})$	–	2938	–	–	–	–
$\nu_{\text{s}}(\text{CH})$	2876	2850	2877	2870	–	2883
$\nu_{\text{as}}(\text{CO}_2^-)$	1570	1580	1566	1574	1573	1578
$\delta(\text{CH})$	–	1446	–	–	–	–
$\nu_{\text{s}}(\text{CO}_2^-)$	1370	1366	1368	1364	1360	1364
$\tau(\text{CH}_2)$	–	1300	–	1301	–	–
$\nu(\text{CO})$	–	1068	–	–	–	–

3.2.2. Adsorption of aniline

Fig. 3 shows the IR results of aniline adsorbed molecularly at 373 K on different catalyst compositions ($x=0.05, 0.5$ and 1). N–H asymmetric and symmetric stretching frequency appears at lower energy around 3320 and 3228 cm^{-1} compared to liquid aniline [35] at 3355 and 3290 cm^{-1} , respectively. This indicates that the N–H bond weakens on adsorption. A broad O–H stretching band between 3800 and 3500 cm^{-1} was observed due to the interaction of proton from polarized amino group with surface oxygen, thus forming surface hydroxyl groups. As NH_2 deformation band overlaps with phenyl ring stretching bands of aromatic amines [35] ($\nu_{\text{C=C}}$) around 1600 cm^{-1} , these bands were not resolved for adsorbed aniline in the present case. A series of low-intensity overtone bands observed at 1935, 1860, 1795 and 1725 cm^{-1} (out-of-plane aromatic C–H bending vibrations ($\nu_{\text{C-H}}$)) clearly indicate the perpendicular adsorption of aniline on the catalyst surfaces [32,33]. Bands at 1150, 1245 and 1290 cm^{-1} were ascribed to C–N stretching vibrations ($\nu_{\text{C-N}}$) and a pair of strong bands at 1495 and 1600 cm^{-1} were due to phenyl ring C=C stretching vibrations (ν_{13a}, ν_{16a}) [18,34]. These ring-stretching modes are accompanied with a shoulder at 1460 cm^{-1} (ν_{13b}). Aromatic C–H stretchings ($\nu_{\text{C-H}}$) were observed at 3070 and 3045 cm^{-1} . The bands that appear at the lower wave number side 1100–1000 cm^{-1} were due to aromatic C–H in-

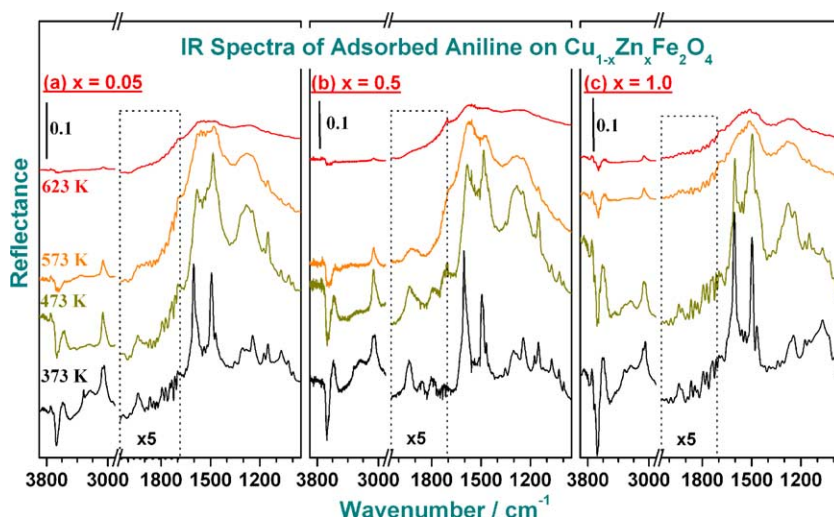


Fig. 3. Temperature-dependent FTIR spectra of aniline adsorbed on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for three selected catalyst compositions of (a) $x=0.05$, (b) $x=0.5$ and (c) $x=1.0$. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the out-of-plane C–H bending features clearly.

plane bending vibration ($\nu_{\text{C-H}}$). The above IR features for adsorbed aniline were observed on all catalyst compositions at 373 K, indicating similar modes of interaction.

On increasing the temperature to 473 K, $\nu_{\text{N-H}}$ bands at 3320 and 3228 cm^{-1} disappear as aniline chemisorbs very strongly on the surface and leads to complete N–H bond scission. This occurs on the catalysts with $x=0.05$ and 0.5 , whereas $\nu_{\text{N-H}}$ bands were clearly observed even at 473 K on pure ZnFe_2O_4 . The low-intensity $\nu_{\text{C-H}}$ vibrations start broadening and slowly disappearing with increasing temperature on those with $x=0.05$ and 1 , indicating a fairly parallel or tilted phenyl ring on the catalyst surface. However, $\nu_{\text{C-H}}$ was strong even at 573 K on the $x=0.5$ system, suggesting a perpendicular orientation of the phenyl ring. A red shift of about 15 cm^{-1} for ν_{16a} and 10 cm^{-1}

for ν_{13a} of C=C stretching vibrations was observed on the catalyst with $x=0.05$ and 0.5 , whereas no such shift was observed on ZnFe_2O_4 . The ring-stretching mode (ν_{13b}) at 1460 cm^{-1} merges with the ν_{13a} stretching mode and slightly shifts to higher frequency and appears as a shoulder. An overlap between $\nu_{\text{C-N}}$ bands at 1245 and 1290 cm^{-1} occurs with increasing temperature. Another $\nu_{\text{C-N}}$ at 1150 cm^{-1} of aniline appears very strong and indicates aniline was predominantly bound to the copper-containing catalyst surface. Nonetheless, this peak appears very weak in intensity along with aromatic C–H in-plane bending vibrations on ZnFe_2O_4 . A general decrease in intensity of all the peaks at 573 K indicates the desorption above 473 K. However, aromatic C–H and N–H stretching frequencies appeared on ZnFe_2O_4 at all temperature, indicating the molecular adsorption and desorption without any dissociation.

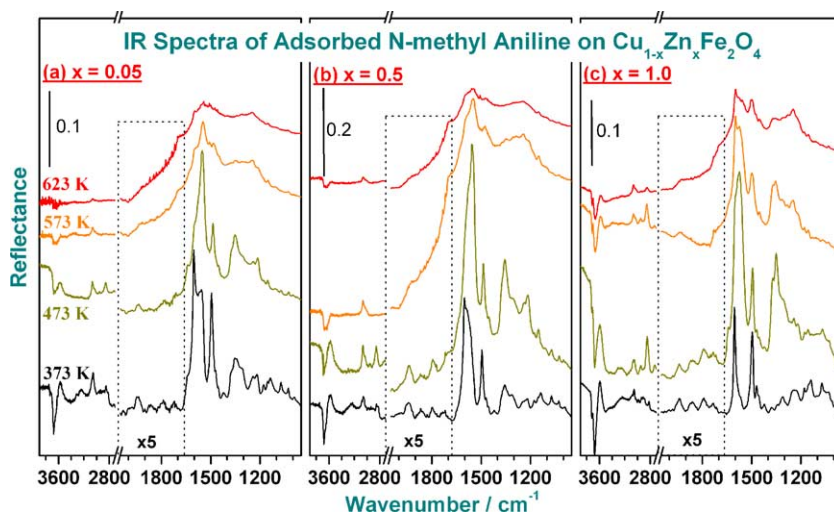


Fig. 4. Temperature-dependent FTIR spectra of NMA adsorbed on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ for three selected catalyst compositions of (a) $x=0.05$, (b) $x=0.5$ and (c) $x=1.0$. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the features clearly.

3.2.3. Adsorption of NMA, DMA and OT

Fig. 4a–c shows the IR spectra of NMA adsorbed at different temperatures on the catalysts with $x = 0.05, 0.5$ and 1 , respectively. The N–H stretching band (3230 cm^{-1}) appears very weak at 373 K . The $\nu_{\text{C–H}}$ bands were observed at $1935, 1860, 1795$ and 1725 cm^{-1} , indicating that the phenyl ring was perpendicular to the catalyst surface on all catalyst compositions. The $\nu_{\text{C–N}}$ band appeared at 1140 cm^{-1} (aliphatic) and $1220, 1240\text{ cm}^{-1}$ (aromatic). The aromatic $\nu_{\text{C=C}}$ bands appeared at 1595 cm^{-1} (ν_{16a}) and 1495 cm^{-1} (ν_{13a}) and the latter was accompanied with a shoulder at 1460 cm^{-1} (ν_{13b}). The methyl group symmetric bending (δ_s) band was observed at 1355 cm^{-1} . Asymmetric and symmetric stretching modes of the methyl group appear at 2850 and 2820 cm^{-1} , respectively. The aromatic C–H stretching band was observed at 3050 cm^{-1} . As the temperature increased to 473 K , $\nu_{\text{C=C}}$ shows red shift by 40 cm^{-1} in ν_{16a} and 10 cm^{-1} in ν_{13a} . These shifts were observed on copper-containing catalysts whereas ZnFe_2O_4 shows a red shift of 20 cm^{-1} in ν_{16a} . The $\nu_{\text{C–N}}$ band at 1140 cm^{-1} became weak and at the same time, the other two $\nu_{\text{C–N}}$ bands at 1220 and 1240 cm^{-1} became strong and overlap with each other. NMA desorption occurs above 473 K and spectral features at $\geq 573\text{ K}$ appeared broad on the catalysts with $x = 0.05$ and 0.5 , whereas ZnFe_2O_4 shows very sharp and clear bands. This suggests that NMA chemisorbs strongly on ZnFe_2O_4 even at high temperature.

Fig. 5 shows IR spectra of DMA adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ whose spectral features have definite similarities to NMA features except a few differences that are

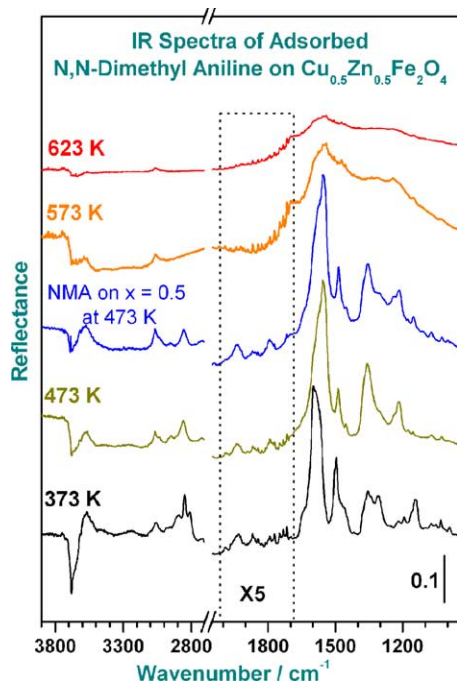


Fig. 5. Temperature-dependent FTIR spectra of *N,N*-dimethylaniline adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the features clearly. NMA adsorbed is also shown for comparison.

highlighted in the following. The aromatic $\nu_{\text{C–N}}$ band at 1240 cm^{-1} with high intensity for NMA was hardly seen for DMA. In contrast, the aliphatic $\nu_{\text{C–N}}$ band at 1140 cm^{-1} appeared very strong for DMA due to two methyl groups attached to nitrogen. The methyl group band (δ_s) at 1355 cm^{-1} was higher in intensity for DMA than NMA. The $\nu_{\text{C–H}}$ band for DMA was very weak compared to NMA and aniline, suggesting that the phenyl ring was either tilted or parallel to the catalyst surface. This is attributed to steric factors due to two methyl groups at nitrogen atom. The aromatic $\nu_{\text{C–H}}$ band appears around 3060 cm^{-1} and low in intensity compared to the methyl group $\nu_{\text{C–H}}$ band at 2850 cm^{-1} . Unlike NMA, an additional $\nu_{\text{C–H}}$ band at 2890 cm^{-1} was observed. At 473 K , $\nu_{\text{C=C}}$ bands were shifted to lower frequency by 40 cm^{-1} for ν_{16a} and 10 cm^{-1} for ν_{13a} . A noticeable decrease in the extinction coefficient (ϵ_{max}) of the ν_{13b} mode was observed compared to NMA. The $\nu_{\text{C–N}}$ band at 1140 cm^{-1} disappeared and that at 1220 cm^{-1} became strong; at this temperature, DMA resembles NMA in spectral features. However, the aromatic to aliphatic C–H stretching band intensity ratio is high for DMA compared to NMA (Fig. 5).

Fig. 6 shows OT spectral features adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. The $\nu_{\text{N–H}}$, aromatic ring $\nu_{\text{C=C}}$ and $\nu_{\text{C–N}}$ bands have a resemblance with aniline features, except an intensity difference in $\nu_{\text{C=C}}$; ν_{13a} vibration is stronger than ν_{16a} . Methyl group δ_s was very weak at 1380 cm^{-1} . The weak phenyl ring out-of-plane $\nu_{\text{C–H}}$ band at 1820 cm^{-1} suggests that the phenyl ring is somewhat perpendicular to the catalyst surface. The $\nu_{\text{C–H}}$ bands for methyl group and phenyl ring appeared at $2860, 2926$ and 2975 cm^{-1} and 3060 cm^{-1} ,

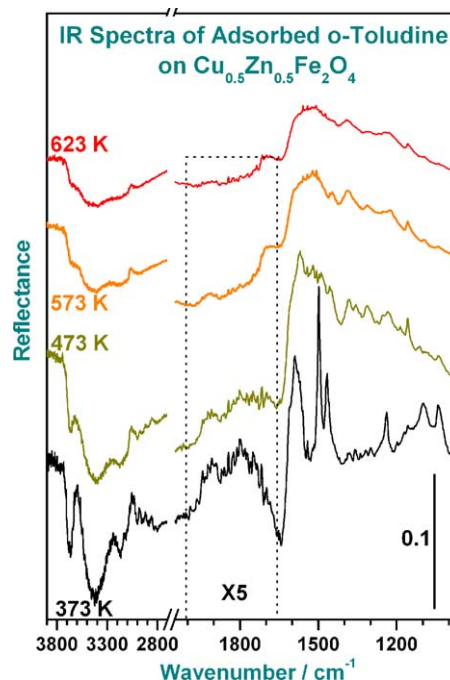


Fig. 6. Temperature-dependent FTIR spectra of *o*-toluidine adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the features clearly.

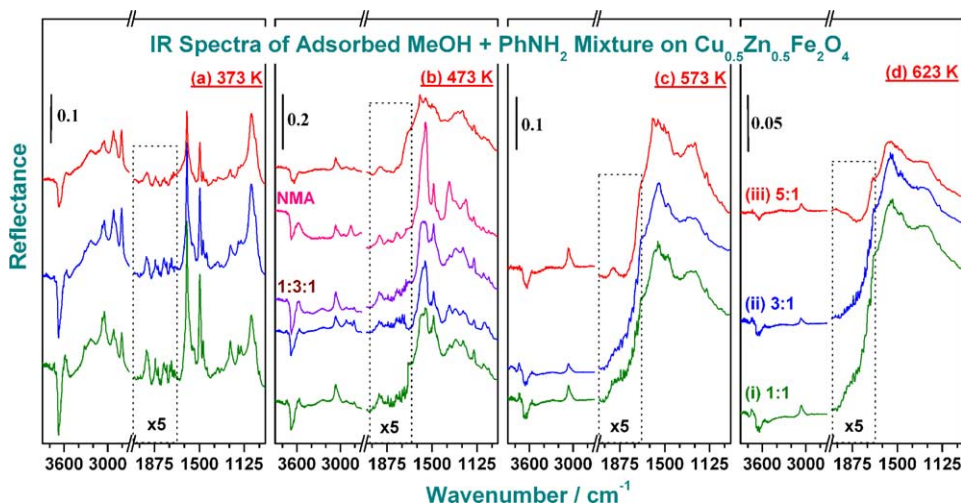


Fig. 7. Temperature- and feed composition-dependent FTIR spectra of methanol+aniline co-adsorbed on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ system. Three different methanol:aniline feed compositions, namely (i) 1:1, (ii) 3:1 and (iii) 5:1, are employed. 1:3:1 feed with water adsorbed at 473 K is shown for comparison. NMA adsorbed at 473 K is shown for reference. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the features clearly.

respectively. A general decrease in intensity of all bands $>473\text{ K}$ shows desorption of OT; further bands were difficult to be resolved due to broadening at high temperatures.

3.2.4. Adsorption of methanol:aniline reaction mixtures

Figs. 7–9 show adsorption of methanol:aniline reaction mixtures with three molar ratios (1:1, 3:1 and 5:1) at different temperatures (373–623 K) on the catalysts with $x=0.5$, 0.05 and 1, respectively. The bands observed at 373 K for all reactant ratios on all the catalyst compositions (Figs. 7a, 8a and 9a) indicate a simple co-adsorption of aniline and methanol with no significant interaction among them. Methanol was adsorbed dissociatively as sur-

face methoxy group on all catalysts composition whose spectral features match those of adsorbed methanol. It was evident from $\nu_{\text{C-H}}$ bands between 2050 and 1700 cm^{-1} that the phenyl ring orientation of aniline was perpendicular. However, significant spectral changes took place with respect to catalysts and reactants compositions $>373\text{ K}$ as given below.

No signals of formate species 2973 , 2884 , 1578 and 1365 cm^{-1} were observed above 373 K irrespective of catalysts composition and aniline:methanol feed ratio. This indicates methanol oxidation to formic acid was hindered in the presence of aniline. In contrast to IR features at 373 K , methoxy species $\nu_{\text{C-O}}$ (1063 cm^{-1}) and $\nu_{\text{C-H}}$ (2924 , 2895 and 2814 cm^{-1}) completely disappeared at 473 K on

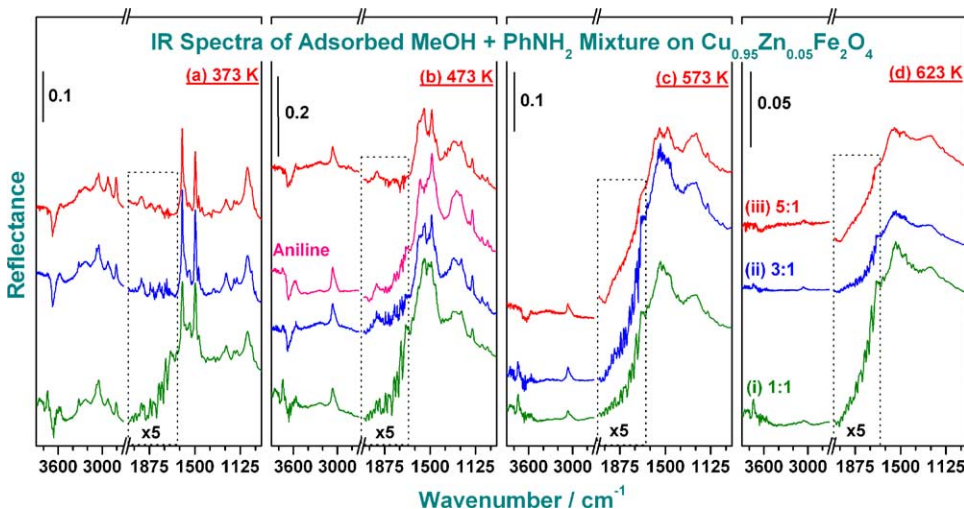


Fig. 8. Temperature- and feed composition-dependent FTIR spectra of methanol+aniline co-adsorbed on $\text{Cu}_{0.95}\text{Zn}_{0.05}\text{Fe}_2\text{O}_4$ system. Three different methanol:aniline feed compositions, namely (i) 1:1, (ii) 3:1 and (iii) 5:1, are employed. Aniline adsorbed at 473 K is shown for reference. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the features clearly.

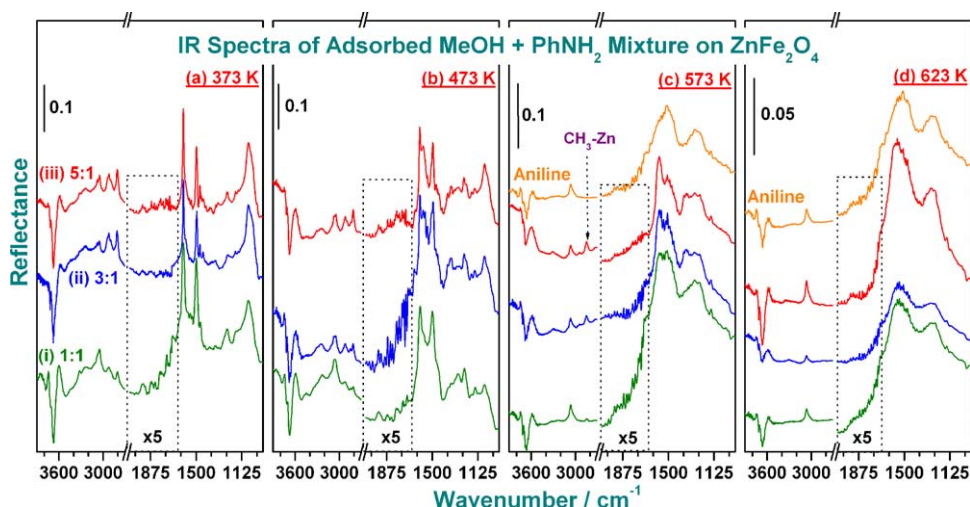


Fig. 9. Temperature- and feed composition-dependent FTIR spectra of methanol + aniline co-adsorbed on ZnFe_2O_4 system. Three different methanol:aniline feed compositions, namely (i) 1:1, (ii) 3:1 and (iii) 5:1, are employed. Aniline adsorbed on $x=1$ at 573 and 623 K is shown for reference. Note that the $2050\text{--}1700\text{ cm}^{-1}$ region is multiplied by a factor of 5 to show the features clearly.

the $x=0.05$ system for all the feed ratios, whereas on the $x=0.5$ system, intense $\nu_{\text{C-H}}$ and $\nu_{\text{C-O}}$ bands of methoxy species exist only for the 3:1 feed ratio. The $\nu_{\text{C-O}}$ and $\nu_{\text{C-H}}$ bands were seen very clearly on ZnFe_2O_4 at 473 K, depending on the methanol concentration; the higher the methanol:aniline molar ratio, the stronger the band intensity of methoxy species. At 573 K, the $\nu_{\text{C-H}}$ and $\nu_{\text{C-O}}$ bands completely disappeared on the $x=0.5$ system, whereas on the $x=1$ system, the $\nu_{\text{C-H}}$ band was still observed at 2852 cm^{-1} without $\nu_{\text{C-O}}$ band, indicating a stable $\text{CH}_3\text{-Zn}$ feature (Fig. 9c, dotted arrow). At 623 K, the $\nu_{\text{C-H}}$ band also disappears on the catalyst with $x=1$. The above observations clearly show that methanol was either utilized for methylation or oxidized to typical reformate products and a combination of both. However, it was highly dependent on catalysts composition, methanol:aniline ratio and reaction temperature.

On the $x=0.5$ system (Fig. 7), $\nu_{\text{C=C}}$ bands at 1600 and 1495 cm^{-1} at 373 K shift to 1558 and 1483 cm^{-1} at 473 K, respectively. The $\nu_{\text{C-H}}$ bands decreased in intensity and broadened at high temperature. A decrease in intensity of $\nu_{\text{C-N}}$ at 1150 cm^{-1} and a new peak at 1220 cm^{-1} coupled with a peak at 1240 cm^{-1} were observed. The above changes were observed for adsorbed NMA on the $x=0.5$ system at 473 K and given in Fig. 7b. Another new band at 1355 cm^{-1} matches well with the methyl group bending vibration observed for methylated anilines especially that of NMA and obviously $\nu_{\text{C-H}}$ of methyl groups was present at 2850 cm^{-1} . This highlights the formation of main product NMA at 473 K on catalyst surface. Neither catalytic aniline conversion nor NMA production was observed at 473 K (results not shown). This is in contrast to large (no) NMA production at 573 K (473 K) under catalytic reaction conditions (Fig. 1). Besides, 5:1 feed composition shows less intense and broadened aniline features at 473 K. At $\geq 573\text{ K}$, very broad bands

of phenyl ring stretching with clear aromatic C–H stretching were seen for all feed compositions. The 3:1:1 ratio of methanol:aniline:water at 473 K on the $x=0.5$ system shows the effect of water on methylation (Fig. 7b). The spectral features of aniline and methanol hardly show any change, suggesting that water did not take part directly in any of the reaction sequence that aniline and methanol follow. However, it just enhances the stability of the catalytic activity by removing the coke deposit on catalyst surface and enhances the catalyst lifetime as observed in the TOS studies (Fig. 1a) [26].

At Cu-rich composition, $x=0.05$, only aniline features without any methanol features were seen at 473 K and that was attributed to un-reacted aniline (Fig. 8). As indicated earlier, surface methoxy species were oxidized into reformate products and hence the disappearance of methanol derived features at 473 K (independent of methanol:aniline ratios). The $\nu_{\text{C=C}}$ bands of the phenyl ring at 1585 and 1485 cm^{-1} and the $\nu_{\text{C-N}}$ bands at 1150 and 1240 cm^{-1} were attributed to un-reacted aniline on the $x=0.05$ system. This is in good agreement with the spectra observed for adsorbed aniline on the catalyst with $x=0.05$ at 473 K (Fig. 8b). IR spectra recorded at $\geq 573\text{ K}$ closely resemble those of aniline on the $x=0.05$ system.

In contrast, on the catalyst with $x=1$, no new bands appeared at 473 K for adsorption of all methanol:aniline feed ratio. The spectra were ascribed to chemisorbed methanol:aniline mixture without any interaction among them even at 473 K irrespective of the feed ratio. No shift in $\nu_{\text{C=C}}$ and $\nu_{\text{C-N}}$ bands was observed as in the case of aniline on the $x=1$ system at 473 K. Above 473 K, although aniline N–H bond scission took place to some extent, there was hardly any change in aniline features. No bands due to any of the possible products were seen on the catalyst with $x=1$ at $>373\text{ K}$.

4. Discussion

4.1. Reactivity of methanol, formaldehyde and formic acid

Copper-containing systems ($x=0.05$ and 0.5) behave differently from ZnFe_2O_4 when methanol was the sole adsorbate. Although on all the catalyst compositions methanol was oxidized to formate species above 373 K, on copper-containing systems surface methoxy species was first converted to dioxymethylene species and then to formate species. In contrast to the above methanol decomposition, a different route through HCHO formation was observed and identified from the C–H stretching vibrations at 2946 and 2856 cm^{-1} on ZnFe_2O_4 . An intense $\nu_{\text{C}-\text{O}}$ band even at 473 K on ZnFe_2O_4 also suggests the presence of stable methoxy species. Above 373 K, methoxy species was oxidized to formate species, which was very pronounced on copper-rich compositions especially on the $x=0.05$ system.

It is to be noted that adsorbed HCHO over $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ was also oxidized to dioxymethylene species at 373 K. This indicates copper highly promotes the above oxidation and suggests that no stable formaldehyde could be identified over copper-containing systems above 373 K. In other words, faster oxidation of methoxy species to dioxymethylene, formate and then to reformate products leads to faster reduction of copper species and hence catalysts deactivation.

At $x=0.05$, methyl or methoxy species features disappeared below 473 K and reformate products appeared between 373 and 573 K and this could be the reason for its fast deactivation during reaction conditions compared to other Cu-containing compositions. Further, methyl group signals were seen clearly over ZnFe_2O_4 even above 473 K, indicating a strong chemisorption of methanol-derived species. Hence, a 1:1 copper and zinc combination on the $x=0.5$ system catalyzes minimum methanol oxidation and maximum methyl species availability for methylation. This reveals that Zn is important for the aniline methylation reaction by slowing down the methanol oxidation reaction and acts as a spacer for better distribution of Cu.

4.2. Reactivity of anilines and methylated anilines

Aniline and methylated anilines, NMA, DMA and OT adsorbed onto the catalyst system as a coordinated species. The nitrogen atom of aniline coordinates to the cationic sites, which act as Lewis acid center, and thereby N–H bond is weakened. Thus, weakened N–H bond was polarized further and the proton from polarized NH_2 group interacts with surface oxygen to form surface –OH. This is evident from a broad O–H stretching band between 3800 and 3500 cm^{-1} whose intensity decreases with increasing temperature [21]. This N–H bond polarization affects $\nu_{\text{C}-\text{N}}$ of aniline as evident from a sharp and strong band at 1150 cm^{-1} (intensity increases with temperature) along with the bands at 1245 and 1290 cm^{-1} .

The phenyl ring perpendicular to the catalyst surface was identified from the low-intensity $\nu_{\text{C}-\text{H}}$ bands and it is free from interaction with the catalyst surface; hence, phenyl ring C–H bands can freely undergo out of plane bending vibrations [32,33]. However, parallel orientation of adsorbed OT shows no well-defined $\nu_{\text{C}-\text{H}}$ and supports the above statement. The complete N–H bond scission occurs above 373 K as it was seen from the disappearance of N–H stretching band between 3320 and 3230 cm^{-1} at 473 K for copper-containing systems. However, at 473 K, the $\nu_{\text{N}-\text{H}}$ band was strong on ZnFe_2O_4 , which supports poor catalytic activity and suggests that N–H bond scission could be the rate-limiting step for methylation.

NMA adsorption on catalyst surface followed a similar trend as aniline adsorption. However, $\nu_{\text{C}-\text{N}}$ and $\nu_{\text{C}=\text{C}}$ have notable differences; aliphatic $\nu_{\text{C}-\text{N}}$ appears at 1140 cm^{-1} with aromatic $\nu_{\text{C}-\text{N}}$ at 1220 and 1240 cm^{-1} , among which the 1140 cm^{-1} band disappeared above 473 K. Further, the phenyl ring was perpendicular to the catalyst surface and its orientation was comparable to that of aniline, clearly showing that the NMA orientation was stabilized in a perpendicular fashion on the catalyst surface as evident from $\nu_{\text{C}-\text{H}}$ between 2050 and 1700 cm^{-1} . These bands were relatively strong on the $x=0.5$ system. This suggests that extent of phenyl ring perpendicularity of NMA was high on the $x=0.5$ system, despite a methyl group at the N center.

DMA adsorption bands were obviously similar to NMA adsorption band features; however, the intensity is different. Less intense $\nu_{\text{C}-\text{H}}$ bands were observed, suggesting that the phenyl ring in DMA was tilted towards or parallel to the catalyst surface. OT shows very weak interaction with the catalyst surface compared to aniline, NMA and DMA. The adsorption bands have similarities to those of aniline, except the high intensity ratio of ν_{13a}/ν_{16a} . A general decrease in intensity of all the bands at 473 K was ascribed to the weak interaction of OT with the catalyst surface and hence a faster desorption.

4.3. Reactivity of methanol: aniline mixtures on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

IR spectra due to methanol:aniline mixtures show no significant interaction at 373 K and spectral changes took place at higher temperature depending on reaction conditions. Methanol oxidation to formate species was hindered in the presence of aniline, which was in contrast to the interaction of methanol alone on the catalyst surface. This may be due to the protonation process that hinders the formate species formation from methanol in the presence of aniline. In addition, the extent of methanol protonation depended on the ease of N–H bond scission that occurred >373 K at $x=0.05$ and 0.5 and ≥ 573 K at $x=1$.

On the $x=0.05$ system, no methanol-derived features were seen at 473 K, indicating that protonated methanol undergoes oxidation to form typical reformate products. Consequently, faster reduction of active Cu^{2+} to Cu^0 occurred

and hence methylation activity ceased irrespective of the methanol:aniline ratio. XPS analysis results also show an extensive reduction of Cu^{2+} to Cu^0 on spent catalysts [28]. Hence, aniline methylation was not effective at $x=0.05$; catalytic reaction results also show that the initial catalytic activity declines fast at higher TOS on the $x=0.05$ system (Fig. 1a).

On the $x=0.5$ system, methanol protonation was favored as aniline N–H bond scission took place between 373 and 473 K. Zn having strong tendency to stabilize the methyl species prevents them from further oxidation by Cu^{2+} and aids an efficient methylation. This synergistic performance of Cu–Zn varies considerably with methanol:aniline ratio; at the equimolar ratio (1:1), methyl cation availability is less and at a higher ratio (5:1), more methanol tends to dissociate to reformate products and led to Cu^{2+} reduction. An intermediate methanol:aniline ratio (3:1) shows a steady-state aniline conversion with no catalyst deactivation for longer reaction time as revealed from the catalytic studies (Fig. 1a) [21].

Aniline spectral features also change with respect to catalyst composition, methanol:aniline ratio and temperature. On the $x=0.5$ system, $\nu_{\text{C-H}}$ bands observed between 2050 and 1700 cm^{-1} irrespective of the feed ratio suggest that phenyl ring orientation is perpendicular at 373 K. N–H bond scission took place irrespective of the feed ratio, suggesting that aniline was preferentially bound to the catalysts surface. Like NMA, above 373 K, $\nu_{\text{C=C}}$ bands of aniline at 1600 and 1495 cm^{-1} shift to 1560 and 1485 cm^{-1} , respectively, for 1:1 and 3:1 feed compositions. Aniline $\nu_{\text{C-N}}$ bands at 1245 and 1290 cm^{-1} were accompanied with a new band at 1220 cm^{-1} that matches well with that of $\nu_{\text{C-N}}$ of NMA. Another $\nu_{\text{C-N}}$ originating from chemisorbed aniline at 1150 cm^{-1} above 373 K became weak. This indicates strongly interacting aniline was methylated to NMA irrespective of the feed ratio. Methyl group vibrations at 1355 cm^{-1} (δ_s), 2820 cm^{-1} (ν_s) and 2850 cm^{-1} (ν_{as}) appear very strong for the 3:1 methanol:aniline ratio compared to other two feed ratios and suggests that the 3:1 ratio could be optimum for effective aniline methylation to NMA.

No interaction between methanol and aniline was clear from the spectral features at 473 K for all feed ratios on ZnFe_2O_4 . The $\nu_{\text{C-H}}$ band of the phenyl ring was very weak compared to other two catalyst compositions, indicating that aniline orientation was comparatively tilted on ZnFe_2O_4 . The $\nu_{\text{C-N}}$ and $\nu_{\text{C=C}}$ bands show hardly any changes in band positions and intensities for all feed ratios at 473 K, unlike copper-containing catalysts. Above 573 K, the $\nu_{\text{C-N}}$, $\nu_{\text{C-H}}$ and $\nu_{\text{C=C}}$ bands of aniline broadened with their intensity decreased, indicating the onset of aniline desorption. However, the $\nu_{\text{C-H}}$ band at 2856 cm^{-1} appeared strong at 573 K, indicating the stability of methyl species (Fig. 9c) and there is hardly any interaction among reactants even at high temperature. Catalytic reaction results on ZnFe_2O_4 also show small amount of aniline methylation to NMA at any reaction temperature.

4.4. Mechanism of aniline methylation on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$

A possible reaction mechanism is suggested in the following: from IR results, it is clear that aniline molecule was activated through N–H bond polarization on Lewis acid sites, which led to N–H bond scission between 373 and 473 K on Cu-containing catalysts. This develops an unsaturated and electron-rich coordinatively bonded N atom on the catalysts surface. N–H bond scission leaves a labile H^+ on the surface that protonates methanol and leads to electrophilic $\text{CH}_3^{\delta+}$. Thus, electron-rich N was preferentially attacked by the $\text{CH}_3^{\delta+}$ group. In addition, perpendicular orientation of aniline on all Cu-containing catalysts composition was facile for product formation. Some supporting evidence for the above mechanism is given in the following section.

To support the above proposed aniline methylation mechanism, IR experiments with aniline and methanol adsorbed sequentially before or after pyridine adsorption on catalyst were carried out [22]. Aniline and methanol protonation is highly unlikely on the virgin catalyst surface, since the surface –OH group is incapable of protonating even strong bases like pyridine (absence of pyridinium ion band or Bronsted acid sites) [27]. Hence, Lewis acid–base pair sites are the most probable sites for adsorption of aniline and methanol. Since aniline is more basic than methanol, Lewis acid–base pair sites are covered by aniline and that enhances aniline N–H bond scission. N–H bond scission on acid–base pair sites generates labile H^+ on the surface. This freshly formed surface H^+ group has a tendency to protonate methanol molecules leading to $\text{CH}_3^{\delta+}$ cations. Proton from N–H bond scission of adsorbed aniline changes the course of methanol interaction through protonation. Methanol molecules are directed to adsorb on H^+ released from aniline and hence the active center for N-methylation is likely to be single acid–base pair site.

The above-suggested aniline single methylation mechanism was verified by three different experiments shown in Fig. 10a–c. Sequential adsorption of reactants with acidity probe molecules like pyridine was carried out at different temperatures on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$. Fig. 10a shows the sequential adsorption of aniline, pyridine and methanol at 373 K. Aniline and pyridine features coexisted after pyridine exposure to aniline adsorbed catalyst surface. However, methanol features were hardly seen with subsequent methanol adsorption. Fig. 10b shows the co-adsorption of a 1:1 ratio of aniline and pyridine at various temperatures. The catalyst surface was clearly dominated by pyridine features at 373 K. However, due to broad features of the bands at 1495 and 1600 cm^{-1} , aniline bands were unresolved from pyridine bands. At 473 K, a broadening of the 1600 cm^{-1} peak up to 1540 cm^{-1} clearly shows pyridinium ion formation [27,36]. This supports the mechanism consisting of the N–H bond dissociation, methanol protonation and subsequent aniline methylation. The above result also indicates that the pyridine and aniline equally compete for the adsorption sites when adsorbed sequentially, but pyridine is

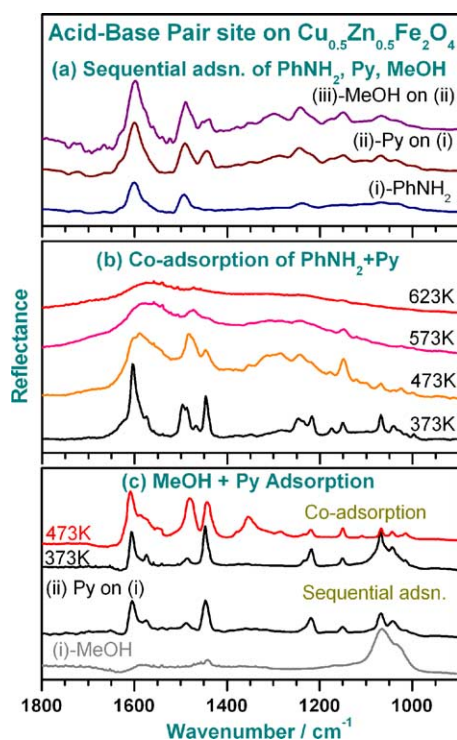


Fig. 10. FTIR spectra recorded on $\text{Cu}_{0.5}\text{Zn}_{0.5}\text{Fe}_2\text{O}_4$ for competitive adsorption of reactants: (a) sequential adsorption of aniline, pyridine and then methanol at 373 K; (b) temperature dependence of co-adsorption of 1:1 ratio of aniline and pyridine and (c) sequential adsorption of methanol and pyridine at 373 K and co-adsorption of methanol and pyridine at 373 and 473 K.

preferentially adsorbed in the case of co-adsorption, since it is more basic than aniline. Fig. 10c shows both the sequential and the co-adsorption of methanol and pyridine. Sequential adsorption of methanol and pyridine at 373 K clearly demonstrates that initially adsorbed methanol was fully displaced by pyridine. Co-adsorption of 1:1 methanol:pyridine mixtures shows spectra dominated by pyridine ≤ 473 K. These results demonstrate that the weakly acidic methanol can be displaced easily by strongly adsorbing pyridine. The weak methanol features in Figs. 7–9 (methanol:aniline) and Fig. 10c (methanol:pyridine) clearly support the aniline methylation mechanism and justify the strong domination of aniline on the catalyst surface. The above results also indicate that despite a high methanol content in the aniline methylation feed (3:1, methanol:aniline), it may be close to a 1:1 ratio of methanol:aniline on the catalyst surface and also supports the reaction stoichiometry. Larger amount of methanol in the reaction mixture was necessary due to weak interaction of methanol on the catalyst surface.

5. Conclusions

FTIR study of adsorbed reactants and products of aniline methylation on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ is described in the present work. FTIR adsorption of methanol on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ in-

dicates a dissociative chemisorption of methanol as methoxy species on catalyst surface at 373 K. As the temperature increases, oxidation of methoxy species to formate species via formaldehyde and dioxymethylene is observed and above 573 K, complete oxidation takes place to CO , CO_2 and H_2 . Methoxy and formate species are comparatively reactive on Cu-containing samples due to the presence of easily reducible Cu^{2+} ions.

Adsorption of aniline on $\text{Cu}_{1-x}\text{Zn}_x\text{Fe}_2\text{O}_4$ indicates its molecular adsorption through the N atom on an acid–base pair site. However, N–H bond breaks and aniline chemisorbed very strongly above 373 K. Chemisorbed aniline molecules are on the Lewis acid sites with the phenyl ring perpendicular to the plane of the catalyst surface. The phenyl ring of aniline and NMA also interacts in a very similar manner, supported by the out-of-plane C–H bending vibrations observed. However, for DMA and *o*-toluidine, very weak or no C–H bending vibrations are seen, indicating that they interact in a parallel manner to the plane of the oxide. Also, it is found that NMA formation from the reaction mixture at 473 K on the catalyst surface and its desorption above 473 K indicate a desorption-limited kinetics. High catalytic activity observed on $x=0.5$ is apparently due to well-separated Cu^{2+} sites by Zn and suggests that Zn acts as a spacer.

It is found that the methylation of aniline is initiated by the protonation of methanol with the aid of a Lewis acid–base pair. The protonation of methanol occurs on the oxides by accepting protons released from the adsorbed aniline to form the *N*-methylated products. Thus, the active center for the methylation is an acid–base pair site. This mechanism is further supported by the IR studies of competitive adsorption of reactants with pyridine as an acidity probe molecule.

Acknowledgements

We thank Dr. Veda Ramaswamy for providing the GC facility. MV and BM thank the Council of Scientific and Industrial Research (CSIR), New Delhi, for research fellowship.

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