

# A novel electrochemical alkylation of aniline with methanol over Zn/Cu salts modified kaolin

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Received 4 November 2006; received in revised form 4 July 2007; accepted 4 July 2007  
Available online 10 July 2007

## Abstract

A novel liquid phase alkylation of aniline with methanol over Zn/Cu salts modified kaolin assisted with a pair of porous carbon electrode in slurry-bed reactor under constant current intensity, room temperature and atmospheric pressure was reported. The Zn/Cu salts modified kaolin catalysts were synthesized and characterized by infrared spectrometer (IR), powder X-ray diffraction (XRD) and scanning electron microscopy (SEM), which showed that the transition metals were completely supported on kaolin's structure and formed a pored one. The effect parameters, such as initial pH, electrolysis time, metal ratio with kaolin and salts composition in this electrochemical catalytic system, were studied. The procedure was inspected by ultraviolet–visible spectrum (UV–vis), and the product distribution was detected by gas chromatography/mass spectrometry (GC/MS). In addition, a possible reaction mechanism was also proposed.

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**Keywords:** Electrochemical; Catalyst; Alkylation; Slurry-bed reactor; Aniline

## 1. Introduction

Aniline alkylation was one of the most important industrial reactions due to the fact that many valuable bulk intermediate and fine chemicals can be prepared. Thus, alkylanilines formed the basic raw materials for synthesis of organic chemicals and chemical intermediates or additives in dyes, fuel oil, synthetic rubbers, explosives, herbicides, and pharmaceuticals [1–5]. The reaction involving the alkylation of aniline (PhNH<sub>2</sub>) with base alcohol (MeOH, EtOH) had been previously studied using several different kinds of catalysts such as zeolites [6,7], composites [8–15], and clays [4]. However, all of the reactions catalyzed by these materials were carried out at higher temperature (200–400 °C), higher pressure, longer procedure, moreover, the catalysts used for the alkylation of aniline must be calcined.

In this paper, we report a study of the alkylation of aniline using diversified Zn/Cu salts modified kaolin as catalyst in slurry-bed electrochemical reactor under mild condition. The effect of initial pH, electrolysis time, metal:kaolin ratio, and

salts composition on the electrochemical catalytic system were studied. The procedure was inspected by ultraviolet–visible spectrum (UV–vis), and the product distribution was detected by gas chromatography/mass spectrometry (GC/MS). A possible reaction mechanism was also proposed.

## 2. Experimental

### 2.1. Materials and instruments

All chemicals used in the experiment were analytically grade and without any further purification. Kaolin, provided by Shanghai Reagent Co., China, were composed of Al<sub>4</sub>[Si<sub>4</sub>O<sub>10</sub>](OH)<sub>8</sub> (surface area: 20 m<sup>2</sup>/g and pore volume: 0.5 cm<sup>3</sup>/g).

The electric power was supplied with regulated DC power supply, WYK302b, Xi'An, China. The current intensity and voltage ranged from 0 A to 2.5 A and 0 V to 35 V, respectively.

The procedure was inspected by ultraviolet–visible (UV–vis) 7504 spectrum apparatus made in Shanghai Xinmao Co. and the component and distribution of the products were checked by gas chromatography/mass spectrometry (GC(Agilent 6890)/MS (Hewlett-Packard 5973)). The infrared spectrometer (IR) of the catalyst was detected by Bruker Co., Germany. The crys-

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tallinity of the catalyst was determined by powder X-ray diffraction (XRD) D/Max-3c model (Rigaluc, Jp) using a scanning diffractometer of D/MAX-RA with Ni-filtered Cu K $\alpha$  radiation ( $\lambda = 1.5406 \text{ \AA}$ ). Solid morphology and average crystal size were determined by scanning electron microscopy (SEM, Quanta 200, Holland) and a gold film was sputtered onto the sample prior to observation (ISI DS-130).

## 2.2. Preparation of the catalyst

Took the catalyst of  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin} = 2.5/2.5/10$  (wt.%) as an example, the catalyst was prepared as follows: adding 25 g  $\text{Zn}(\text{Ac})_2$ , 25 g  $\text{Cu}(\text{Ac})_2$  and 20 g  $\text{Na}_3\text{PO}_4$  into 150 ml distilled water (pH 7.1), 10 ml  $\text{H}_3\text{PO}_4$  was added to dissolve the metal salt, then the solution pH was adjusted with NaOH to a neutral conditions. 100 g kaolin was impregnated into the solution with stirring in a water bath at  $50^\circ\text{C}$  for 4 h. Then, the solution was aging at room temperature for 48 h, filtrated, washed, the deposit was dried at  $100^\circ\text{C}$  for 2 h to obtain the catalyst.

The other catalysts were prepared the same way, which merely required change the quantity and breed of the salts.

## 2.3. Experimental set-up

Fig. 1 shows the schematic diagram of the slurry-bed reactor for the electrochemical catalytic alkylation. The experiment was conducted by batch process in an undivided cell of 0.5 l at room temperature under 2.0 A current intensity. The reaction cell was airproofed to prevent the volatilization of methanol and cooled by the cooling water in a trough to maintain the room temperature condition. The anode and cathode both were the porous graphite plate and positioned vertically and paralleled to each other with a constant inter gap of 1.0 cm. Twenty grams of catalyst of metal salts modified kaolin and 10 g assisted catalyst of KF were packed around the working electrode, forming a multi-phase electrochemical alkylation slurry-bed. The solution was constantly stirred at 200 rpm using a magnetic stirrer in order to maintain uniform concentration of the electrolyte solution.

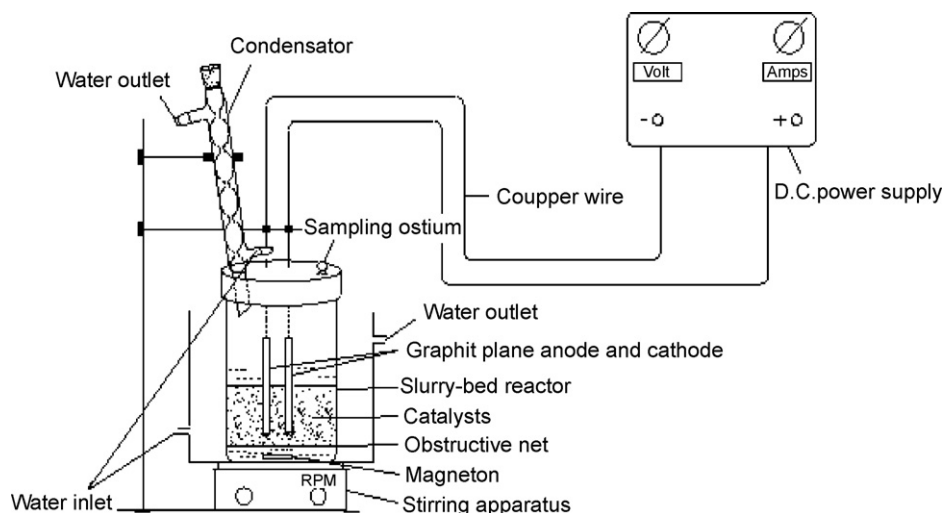


Fig. 1. Slurry-bed reactor for the electrochemical catalytic alkylation.

Table 1  
The solvent-supporting electrolyte system

Number	Original electrolyte (pH)	Catalyst	Ratio (wt.%)
1	7	$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	0.25/0.25/10
2	9	$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	0.25/0.25/10
3	11	$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	0.25/0.25/10
4	7	$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	2.5/2.5/10
5	9	$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	2.5/2.5/10
6	11	$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	2.5/2.5/10
7	7	$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	0.25/0.25/10
8	9	$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	0.25/0.25/10
9	11	$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	0.25/0.25/10
10	7	$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	2.5/2.5/10
11	9	$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	2.5/2.5/10
12	11	$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	2.5/2.5/10
13	7	$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	0.25/0.25/10
14	9	$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	0.25/0.25/10
15	11	$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	0.25/0.25/10
16	7	$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	2.5/2.5/10
17	9	$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	2.5/2.5/10
18	11	$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	2.5/2.5/10

## 2.4. Electrolysis procedures

The electrolysis was carried out in slurry-bed reactor without compartments. The solvent-supporting electrolyte system was formed as follows: 10 g KF and 50 ml aniline were added in 70 ml methanol with 20 g metal salts modified kaolin catalyst. The components of solvent-supporting electrolyte system are shown in Table 1. The resulting solutions were placed in the cells and electrolyzed at a current intensity of 2.0 A at room temperature. The reaction process and the conversion of starting material was investigated by UV–vis spectrum every 30 min as follows: transferring 0.01 ml solution by transfer-pipette accurately and diluting it to 20 ml in a volumetric flask, then the electronic spectra were observed at the range of 200–400 nm using methanol as blank. The current was interrupted at the moment of higher yield of the products.

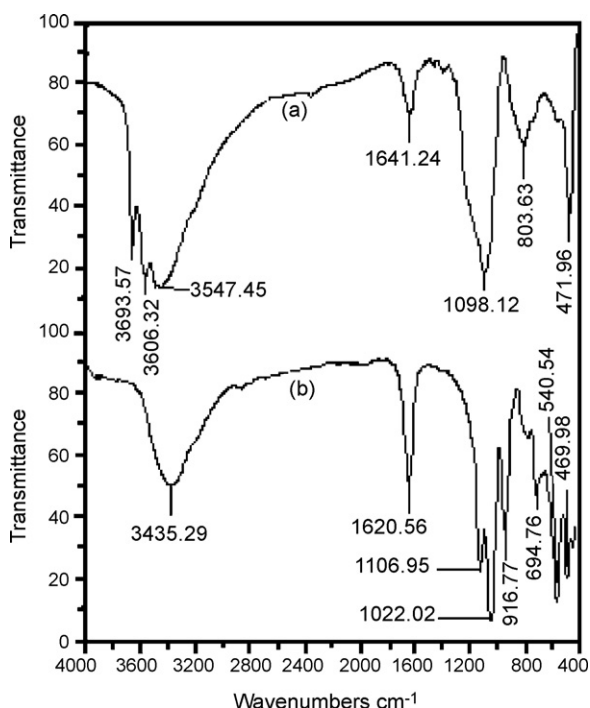


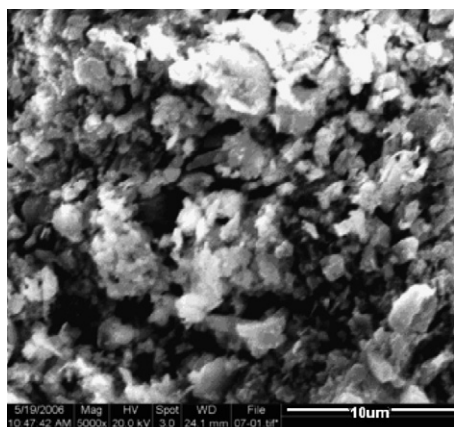
Fig. 2. Representative infrared spectrum of kaolin: (a) neat kaolin and (b) modified kaolin.

### 3. Results and discussion

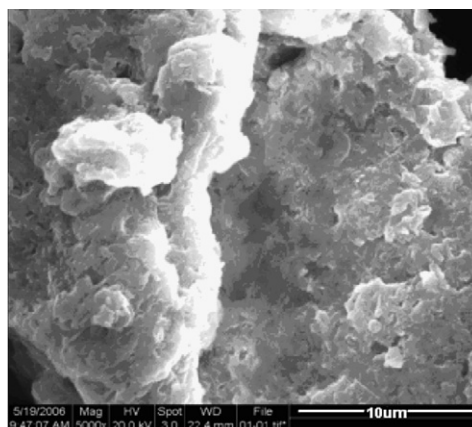
#### 3.1. Characterization of catalysts

##### 3.1.1. IR

The representative infrared spectrum of kaolin before and after modification is shown in Fig. 2. It could draw the conclusion that the bands at  $3693.57\text{ cm}^{-1}$ ,  $3606.32\text{ cm}^{-1}$ ,  $3547.45\text{ cm}^{-1}$  (Fig. 2a) assigned to the dissociative hydroxyl in neat kaolin has been shifted into  $3435.29\text{ cm}^{-1}$  for the binding form (Fig. 2b), and some new bands at  $1106.95\text{ cm}^{-1}$ ,  $1022.02\text{ cm}^{-1}$  and  $916.77\text{ cm}^{-1}$  can be attributed to the stretching vibration of the P=O, P-O, C-O, new bands appears at  $540.54\text{ cm}^{-1}$ ,  $469.98\text{ cm}^{-1}$  can be attributed to M-O (Fig. 2b), indicating the metal salt have been successfully modified on the kaolin.



(a)



(b)

Fig. 3. Representative SEM of kaolin (5000×): (a) neat kaolin and (b) modified kaolin.

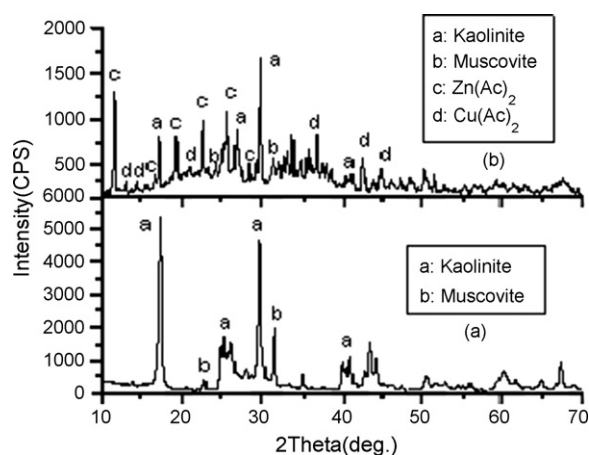


Fig. 4. Representative XRD patterns of kaolin: (a) neat kaolin and (b) modified kaolin.

##### 3.1.2. SEM

The morphology of Zn/Cu salts modified kaolin was examined by SEM and the representative photograph of  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}=2.5/2.5/10$  is shown in Fig. 3. It should be summarized that the previous disorder fragment of neat kaolin (Fig. 3a) was changed into the massive sandwich (Fig. 3b) after the modified process, which may be due to the interposition of Zn and Cu salts.

##### 3.1.3. XRD

The patterns of XRD for the neat kaolin and modified kaolin are displayed in Fig. 4. Two diffraction peaks which related to Kaolinite and Muscovite can be clearly observed in Fig. 4a, the presence of peaks as an attributive indicator of Kaolinite ( $2\theta=17.31^\circ$ ,  $25.28^\circ$ ,  $29.86^\circ$ ,  $39.86^\circ$ ) and of Muscovite ( $2\theta=22.88^\circ$ ,  $31.62^\circ$ ) could be detected. The intensity of the peaks characteristic of Kaolinite and Muscovite decreased after modification, meanwhile, the characteristic peaks for  $\text{Zn}(\text{Ac})_2$  and  $\text{Cu}(\text{Ac})_2$  appeared ( $\text{Zn}(\text{Ac})_2$ :  $2\theta=11.88^\circ$ ,  $16.84^\circ$ ,  $18.62^\circ$ ,  $23.14^\circ$ ,  $25.53^\circ$ ,  $28.26^\circ$ ;  $\text{Cu}(\text{Ac})_2$ :  $2\theta=13.46^\circ$ ,  $14.25^\circ$ ,  $20.18^\circ$ ,  $35.91^\circ$ ,  $44.82^\circ$ ), indicating that the kaolin had been modified by  $\text{Zn}(\text{Ac})_2$  and  $\text{Cu}(\text{Ac})_2$ .

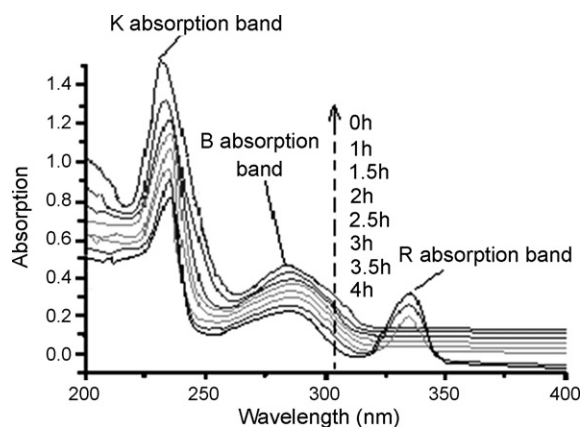


Fig. 5. Effect of time on alkylation with  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin} = 2.5/2.5/10$  (pH 9.0).

### 3.2. Analysis of the liquid products

#### 3.2.1. UV-vis spectrum

The course of the electrochemical catalytic alkylation was inspected by UV-vis spectrum. The effect of time on the alkylation with  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin} = 2.5/2.5/10$  at pH 9.0 detected by UV-vis absorption spectrophotometer show in Fig. 5. With the time prolong (0–4 h), the K absorption band and the B absorption band of the benzene ring bathochromic shifted from 231 nm to 237 nm and 284 nm to 287 nm, respectively; the R absorption band presented itself at 336 nm (3 h) and the height of the absorbed peak enlarged. The K and B absorption band of the benzene ring changed, maybe due to the interactions of the solvent and the components of the reaction system: the interaction between the amino of aniline and methyl group reduced the energy band of  $\pi \rightarrow \pi^*$  contrast to that of aniline, while hydrogen atom in the amino of the aniline was substituted by one or two methyl group, the conjugation between the methyl group and the amino in the benzene ring was strengthened, the energy needed by  $\pi \rightarrow \pi^*$  transition receded, the K and B absorption shifted to bathochromic. The R absorption band presented was likely to  $n \rightarrow \pi^*$  transition caused by the multi-benzene rings or by the isolated electron in nitrogen atom, when the two hydrogen atom in the amino of aniline was all substituted by methyl group or by the isolated electron in the oxygen atom of methoxyl ( $\text{CH}_3\text{O}-\text{CH}_2-\text{NHAr}$ ). The absorbed peak height enlarged, indicating that the reaction degree was proportioned directly to the reaction time and the content of alkylates.

The influence of the electrolyte initial pH and the catalyst proportion on the alkylation under the same reaction time of 4 h and the identical current intensity of 2.0 A were also studied. The representative picture of  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$  is shown in Fig. 6. It can be found that the K absorption band bathochromic shifted differently, the R absorbed peak height was decreased as follows ( $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$ ):

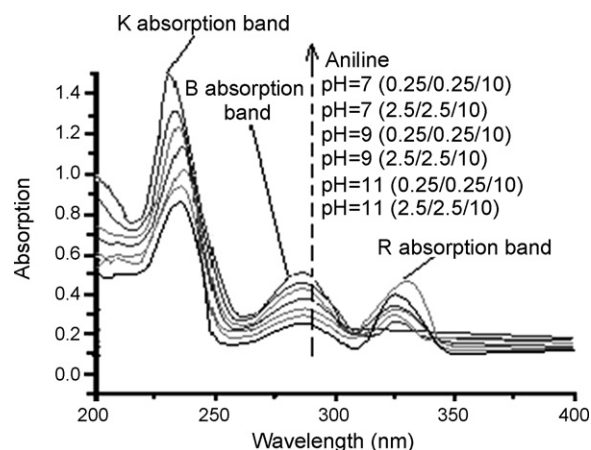
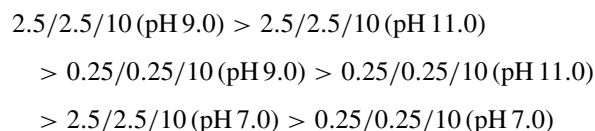
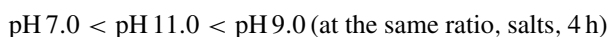


Fig. 6. Effect of the initial pH and the ratio of catalyst on alkylation (4 h).

These were related to the content of the alkylation products, which was further proved by GC/MS. It could be found that the big proportion catalyst was better than the small proportion catalyst, which could be explained that the more metal in the catalyst, the more active of the catalyst. It can also be found that the pH had a great impact on the reaction. The R absorbed peak height was increased as follows:



It can be assumed that, a certain quantity of  $\text{OH}^-$  could add to the electromotive force of the electrolyte and the adsorption of kaolin, thus increasing the alkylation extent, however, more  $\text{OH}^-$  restrained the creation of  $\text{H}^+$ , less  $\text{H}^+$  transformed to  $\text{H}_2$  and hold back the reaction.

Fig. 7 shows the impact of different metal salts in the catalyst on the alkylation at the same pH 9.0, the same ratio of 2.5/2.5/10 and the same reaction time of 4 h. It can be found that the catalytic activity of the catalyst  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin} = 2.5/2.5/10$  was better than that of the other catalyst, and increased as follows:

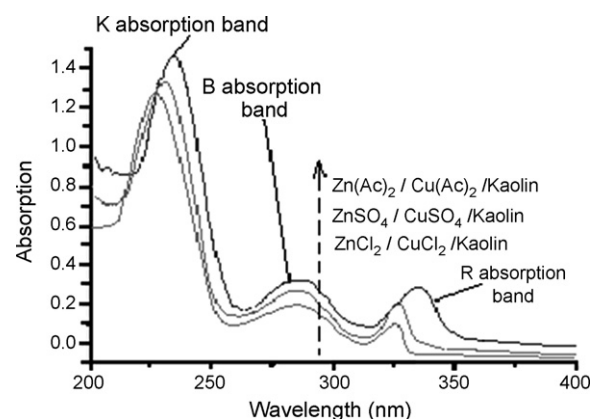
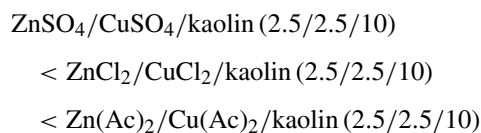


Fig. 7. Impact of metal salts on alkylation (pH 9.0, 4 h, 2.5/2.5/10).

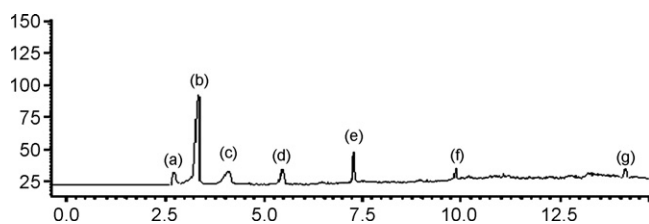


Fig. 8. GC of the products ( $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}=2.5/2.5/10$ , pH 9.0, 4 h). (a) *N*-Methyleaniline, (b) 2,6-dimethyl-*N*-methyleaniline, (c) *N*,2,6-trimethylaniline, (d) *N,N*,2,6-tetramethylaniline, (e) *N*-(methoxymethyl)aniline, (f) 2-fluoro-*N*-(methoxymethyl)aniline, and (g) *N*<sup>1</sup>-phenyl-*N*<sup>4</sup>-(4-(phenyl(*p*-tolyl)amino)phenyl)-*N*<sup>1</sup>-*p*-tolylbenzene-1,4-diamine.

These results were further proved by GC/MS and may be due to the peroxidic property of the acetate.

### 3.2.2. GC/MS

GC of the products is shown in Fig. 8 (the peak of the solvent was taken off). Table 2 compared the concentration of the products in different mediums and pH with the same reaction time of 4 h and the identical current intensity of 2.0 A. The yield of the alkylation products catalyzed by  $\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}=2.5/2.5/10$  can reach the highest of 51.09% at pH 9.0, which was in line with the results of UV–vis spectra:

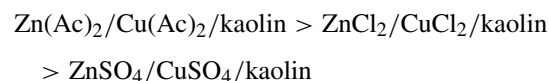


Table 2  
The electrolysis of aniline in various medium and different pH<sup>a</sup>

Catalyst	Original electrolyte (pH)	Ratio (wt.%)	Product concentration (mass%) <sup>b</sup>							Total alkylates (%)
			(a)	(b)	(c)	(d)	(e)	(f)	(g)	
$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	7	0.25/0.25/10	2.21	22.56	12.37	3.23	1.43	0.32	0.41	40.37
$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	7	0.25/0.25/10	1.86	19.64	9.85	2.34	0.81	0.48	0.56	33.69
$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	7	0.25/0.25/10	1.55	16.62	8.66	2.07	0.79	0.53	0.34	28.90
$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	7	2.5/2.5/10	3.04	23.87	13.68	3.4	0.92	0.35	0.51	45.77
$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	7	2.5/2.5/10	1.96	20.69	10.31	2.43	0.67	0.32	0.47	35.39
$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	7	2.5/2.5/10	1.66	17.27	9.32	2.27	0.77	0.51	0.54	30.52
$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	9	0.25/0.25/10	3.11	25.83	14.66	3.79	0.98	0.29	0.38	47.39
$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	9	0.25/0.25/10	2.16	22.35	10.84	2.77	0.72	0.43	0.49	38.12
$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	9	0.25/0.25/10	1.72	18.89	9.74	2.52	0.69	0.42	0.58	32.87
$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	9	2.5/2.5/10	3.88	27.72	15.31	4.18	0.83	0.43	0.54	51.09
$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	9	2.5/2.5/10	2.49	24.39	11.26	2.86	0.61	0.38	0.46	41.00
$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	9	2.5/2.5/10	1.81	19.91	10.67	2.68	0.65	0.32	0.59	35.07
$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	11	0.25/0.25/10	2.67	23.94	13.53	3.41	0.96	0.37	0.42	43.55
$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	11	0.25/0.25/10	1.93	20.78	10.02	2.46	0.75	0.46	0.41	35.19
$\text{Zn}(\text{Ac})_2/\text{Cu}(\text{Ac})_2/\text{kaolin}$	11	0.25/0.25/10	1.63	17.55	9.03	2.24	0.62	0.47	0.52	30.45
$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	11	2.5/2.5/10	3.29	25.64	14.32	3.86	0.74	0.52	0.36	47.11
$\text{ZnCl}_2/\text{CuCl}_2/\text{kaolin}$	11	2.5/2.5/10	2.06	21.77	10.74	2.53	0.76	0.44	0.49	37.1
$\text{ZnSO}_4/\text{CuSO}_4/\text{kaolin}$	11	2.5/2.5/10	1.73	18.43	9.97	2.39	0.58	0.42	0.53	32.52

*N*-Methyleaniline (a): 105 $M^+$ (100), 91(62), 77(35), 65(14), 51(7), 39(6), 29(4), 15(1); 2,6-dimethyl-*N*-methyleaniline (b): 133 $M^+$ (63), 105(100), 91(58), 77(45), 65(19), 51(9), 39(6), 29(14); *N*,2,6-trimethylaniline (c): 135 $M^+$ (99), 121(51), 105(44), 93(36), 77(31), 65(7), 43(12), 39(7); *N,N*,2,6-tetramethylaniline (d): 149 $M^+$ (52), 119(100), 105(88), 91(39), 77(64), 65(32), 51(24), 39(32); *N*-(methoxymethyl) aniline (e): 137 $M^+$ (100), 106(49), 92(53), 77(5), 65(4), 51(2), 39(1); 2-fluoro-*N*-(methoxymethyl)aniline (f): 157 $M^+$ (99), 137(23), 91(56), 77(26), 65(11), 51(13), 39(19); *N*<sup>1</sup>-phenyl-*N*<sup>4</sup>-(4-(phenyl(*p*-tolyl)amino)phenyl)-*N*<sup>1</sup>-*p*-tolylbenzene-1,4-diamine (g): 531 $M^+$ (27), 273(34), 77(100), 63(22), 51(17), 39(5).

<sup>a</sup> Reaction conditions: current intensity, 2.0 A; reaction temperature, 298 K; reaction time, 4 h.

<sup>b</sup> GC/MS spectrum, 70 eV,  $M/e$  (relative intensity).

## Large proportion catalysts > Small proportion catalysts

These results also indicated that this method for alkylation was feasible and convenient, although the yield of alkylates was lower (<52%) than that of chemical alkylation with a yield of 70–90% [2,3,7–11]. Another limitation was that this process afforded a mixture of different alkyanilines products rather than pure alkylation product, which should be further improved for the industrial application.

### 3.3. Assumed mechanism

The assumed mechanism of the reaction was also proposed. The amino group ( $-\text{NH}_2$ ) bound to the aromatic ring exerts *ortho/para* orientation effect, because of the delocalization of the unshared pair of electrons over the amine group into the benzene ring. As a result, the *ortho* and *para* sites of the ring became most susceptible to the electrophilic substitution and the expected major product was the *ortho* and/or *para* C-alkylated aniline. Due to the adsorption of aniline on the surface of the catalyst, alkylation usually yielded *N*-alkylated products. The catalyst also plays a key role in releasing the electrophile from the alkylating agent, namely, alcohol. Alkylation with alcohols took place by generation of electrophiles from heterolysis of carbon–oxygen bonds. In the presence of hydrogen, *N*-alkylation of aniline took place by dehydrogenation of alcohol to carbonyl, followed by the formation of an imine which was finally hydrogenated to alkyaniline (Fig. 9) [1,3,10,13].

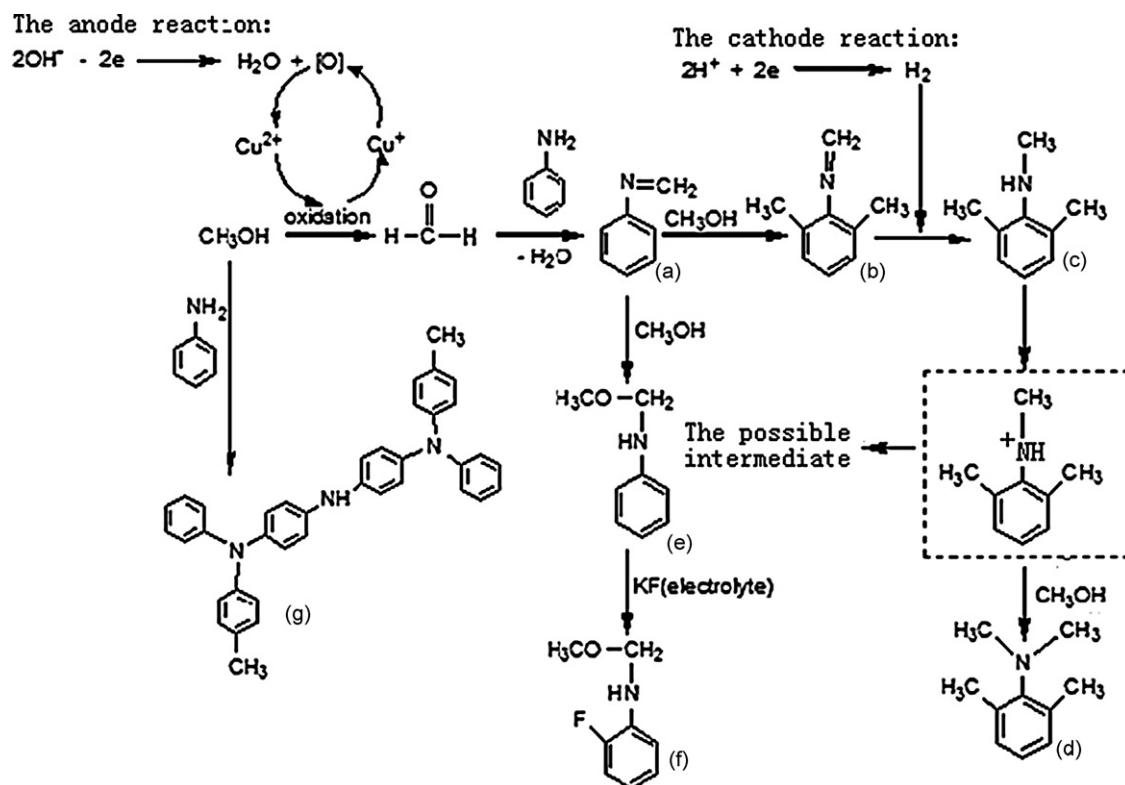


Fig. 9. Possible mechanism for the main reactions.

#### 4. Conclusion

With the aforesaid experiment executed in the single undivided slurry-bed cell, it can come to the view that this method was more effective than the traditional one using electrochemistry cooperated with metal salts modified kaolin as catalysts, which avoided the disadvantages yield from the traditional one, such as: higher temperature and pressure in reaction. Therefore, the said method was far better as it was safe and more convenient in the process of alkylation, for which is recommendable. However, this process afforded a mixture of different alkyanilines products rather than pure alkylation product, which should be further improved.

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