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Short communication

Cu layered double hydroxides as catalysts for *N*-methylation of p-anisidine: Influence of synthesis conditions



M.V. Bukhtiyarova*, A.L. Nuzhdin, A.V. Bukhtiyarov, T.Y. Kardash, A.V. Romanenko

Boreskov Institute of Catalysis SB RAS, 630090 Novosibirsk, Russia

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<i>Keywords</i> : Layered double hydroxides Base solution <i>N</i> -Methylation <i>p</i> -Anisidine conversion	Cu-containing layered double hydroxides were synthesized by co-precipitation method using base solution (NaOH and Na ₂ CO ₃) with different concentration of carbonate ions. The influence of the precipitating agent concentration on formation of hydrotalcite phase was investigated. Characterization of the surface of the obtained samples calcined at 450 °C and 650 °C was performed by x-ray photoelectron spectroscopy. Catalysts based on Cu-layered double hydroxides were investigated in N-methylation of <i>p</i> -anisidine by methanol obtaining N-methyl- <i>p</i> -anisidine using autoclave reactor. Effect of precipitating agent concentration during synthesis of the

Cu-layered double hydroxide on the catalyst performance was studied.

1. Introduction

N-methyl-para-anisidine (H_3 C-NH-C₆ H_4 -OCH₃) can be used as adding to gasoline due to its ability to increase the octane number. The presence of oxygen in the *N*-methyl-*p*-anisidine molecule allows one to increase the combustion of fuel and decrease the amount of CO and unburned hydrocarbons in the exhaust gases. According to patent [1], synthesis of *N*-methyl-*p*-anisidine in gas phase can be carried out by N-alkylation of *p*-anisidine by methanol in the presence of Cu-containing catalysts at the temperature range of 180–260 °C and atmospheric pressure.

Influence of the catalyst nature and the reaction conditions on catalytic activity in N-alkylation of amines were investigated in different research papers [2-7]. The homogeneous catalysts such as RuCl₃*nH₂O-P(OBu)₃ [2] or manganese-containing complexes [3] can be used for the reaction. Su and co-workers [4] used heterogeneous system of Al₂O₃-mordenite as catalyst. N-methylation was done in fixed-bed reactor at 270 °C, 10 bars and the methanol:amine ratio of 4:1. p-Anisidine was not used as a substrate in this paper. However, the high selectivity for N,N-dimethylamine was obtained. It means that the catalysts are not selective for N-methyl-p-anisidine which would be desirable reaction product. Recently, it was shown [5-7] that heterogeneous catalysts containing transition metals such as Pd, Ni and Cu can be used for N-alkylation of amines. Authors [5] demonstrated that secondary amines with yields of 54-88% can be obtained by alkylation of aniline by aliphatic or aromatic alcohols using Pd/C catalyst. p-Anisidine was alkylated by benzyl alcohol in the presence of sodium

formate, and yield of N-alkyl-p-anisidine was 74%. However, reaction temperature was not mentioned in [5]. Despite the fact that his catalyst is commercial one, it is possible to decrease the price of the process by using non-noble metals as active components for N-alkylation of amines. K. Shimizu [6] used Ni catalysts supported on different metal oxides, mainly θ -Al₂O₃ and γ -Al₂O₂ in N-alkylation of aniline at 144 °C without any additives such as base solution. High aniline conversions of 85-100% were obtained depending on alcohol and reaction time. It was shown that it is possible to obtain conversion > 99% depending on reaction conditions. Thus, the high conversion values can be caused by using high alcohol concentration, high catalyst amount or long reaction time. However, for comparison of the catalytic activity it is necessary to perform reaction at the same conditions. The Cu_{0.5}Zn_{0.5}Fe₂O₄ catalyst prepared by co-precipitation method was investigated in N-methylation of aromatic amines (aniline, o-toluidine, m-toluidine, p-toluidine and panisidine) at 300 °C for 10 h in fixed-bed reactor [7]. The p-anisidine conversions and N-methyl-p-anisidine selectivities were 32-35% and 94-96%, respectively, depending on reaction time. However, conversion continuously decreases with time-on-stream [7]. According to literature data, Cu-containing catalysts can be perspective for N-methylation of *p*-anisidine to *N*-methyl-*p*-anisidine.

Layered double hydroxides (LDHs) can be used as catalysts for N-alkylation of amines [8]. The LDHs, known as hydrotalcite-like compounds, can be represented by general formula: $[M_{1-x}^{2+}M_x^{3+}(OH)_2]^{x+}[A^{n-}]_{x/n} \cdot mH_2O$ [9]. The hydrotalcite Mg₆Al₂(OH)₁₆CO₃·4H₂O structure results from stacking brucite-like layers Mg(OH)₂ containing a positive charge due to partial substitution

* Corresponding author.

E-mail address: mvb@catalysis.ru (M.V. Bukhtiyarova).

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of Mg^{2+} by Al^{3+} . The positive charge is compensated by anions (OHand CO_3^{2-}) which are located in the interlamellar spaces. The pure hydrotalcite phase can be obtained when 0.2 < x < 0.33, where x is a ratio of $M^{3+}/(M^{2+} + M^{3+})$, resulting in the M^{2+}/M^{3+} ratios of 2–4 [9]. These systems are perspective catalysts since Cu^{2+} and Al^{3+} ions can be used as divalent and trivalent metal, respectively. The common synthesis method of LDH materials is co-precipitation of metal nitrates by mixture of NaOH and Na₂CO₃ [10]. Works devoted to studying such systems in *N*-methylation of amines are practically absent in the literature.

Previously we demonstrated [11] that the Cu²⁺/Al³⁺ molar ratio in CuAl-LDHs has influence on the catalytic activity in *N*-methylation of *p*anisidine. It was shown that the best catalytic performance is obtained over the CuAl sample with the Cu²⁺/Al³⁺ molar ratio of 1 calcined at 450 °C. This paper is devoted to the investigation of effect of the base concentration used for the synthesis of LDH material on the phase composition and Cu surface state. Besides, the catalytic activity of the mixed metal oxides on the base of CuAl-LDH in *N*-methylation of *p*anisidine by methanol in "one-pot" synthesis was studied.

2. Experimental part

2.1. Synthesis of CuAl-layered double hydroxide

The layered double hydroxides with the Cu^{2+}/Al^{3+} molar ratio of 1:1 were synthesized by co-precipitation method at constant pH 9.0 \pm 0.1 and temperature of 70 °C by the base solution of NaOH and Na₂CO₃. There are several opinions about base concentrations which should be used during synthesis of layered double hydroxides. S. Miyata et al. [12] used base solution with the $[CO_3^{2-}]/[Al^{3+}]$ ratio of 0.7 closed to stoichiometric value while most papers [13,14] are dedicated to usage of the higher concentration of carbonate-ions: $[CO_3^{2^-}]/[Al^{3^+}] = 2.0$. The concentration of carbonate-ions should be sufficient for the formation of pure carbonate form of hydrotalcite phase [15]. The authors of the work have chosen the following concentration of carbonate ions: $[CO_3^{2^-}]/[Al^{3^+}] = 0.5, 0.86$ and 1.0. Materials were denoted as CuAl-LDH-1, CuAl-LDH-2, CuAl-LDH-3, respectively. Hydroxide concentration for all samples was $[OH^{-}] = 1.6([Al^{3+}] + [Cu^{2+}])$, that is sufficient for the formation of the layered double hydroxide [16]. The aging was performed at 70 °C for 4 h. After aging the precipitate was filtered and washed with hot water (51). The precipitate was dried at 110 °C for 14 h and calcined at 450 °C for 4 h. The samples were denoted as CuAl-x (where is x = 1, 2and 3). After drying the CuAl-LDH-2 sample was also calcined at 650 °C for 4 h (CuAl-2-650).

2.2. Characterization of the catalysts

Chemical analysis of the samples was done by atomic-absorption method [17].

X-ray patterns were obtained by Bruker D8 (CuK α -radiation, $2\theta = 5-70^{\circ}$ with step of 0.05°, the accumulation time is 3 s). The multichannel LynxEye detector was used for the signal detection. Phase analysis was done by comparison of interlayer distances d_i and intensities I_i of corresponding reflexes with theoretical values from ICDD PDF-2 database.

The XPS measurements of the samples were performed on the photoelectron spectrometer build by SPECS (Germany) equipped with a PHOIBOS-150 hemispherical energy analyzer and AlK_{α} irradiation (h ν = 1486.6 eV, 150 W). The binding energy (BE) scale was pre-calibrated using the positions of the photoelectron of Au4f_{7/2} (BE = 84.0 eV) and Cu2p_{3/2} (BE = 932.67 eV) core level peaks. Residual gas pressure was better than 8 × 10⁻⁹. For the measurements the samples were supported onto the double-sided conducting copper scotch tape (Scotch 3 M©). Spectra analysis and peak fitting were performed with XPSPeak 4.1 software. Integrated line intensities were measured from area of the corresponding narrow regions (Al2p, C1s, O1s, Cu2p and Na1s). The relative amount of the elements on the sample surface and the ratio of their atomic concentrations were determined from the integrated intensities of the lines corrected by their respective atomic sensitivity factors [18].

2.3. Catalytic test

The catalytic properties of the samples were investigated in autoclave reactor Tinyclave Steel (Buchiglasuster, Switzerland) with volume of 15 ml. The reaction mixture contained *p*-anisidine (0.1 M), methanol and n-decane as internal standard in *o*-xylene (10 ml). The catalyst mass was 27 mg. Reaction was carried out at 180–200 °C and H₂ pressure of 4 bars for 5 h. The liquid samples were characterized by gas chromatograph (Agilent) with FID detector. The gas analysis was done by gas chromatograph Chromos-1000. The conversion of *p*-anisidine was determined by internal standard (*n*-decane) method.

3. Results and discussion

3.1. Catalyst characterization

For the samples calcined at 450 °C the concentrations of the main components (Cu and Al) obtained by chemical analysis are present in Table 1. These values are lower than the theoretical values. It can be caused by the incomplete removal of the interlayer anions such as OH^- and CO_3^{2-} during heat treatment of the samples at 450 °C. The Cu:Al ratios were calculated based on these concentrations. The calculated Cu:Al ratios are practically the same as the theoretical values indicating that the degree of precipitation of the two species were very similar. It means that the concentrations of the base solution are sufficient for the precipitation of the layered double hydroxides.

Chemical analysis data were confirmed by thermal analysis data. Non-isothermal temperature-programmed treatment of the CuAl-LDH-2 sample in the temperature range of 25–700 °C is accompanied by *endo*effects on DTA curves (Fig. 1). Thermal analysis was done only for one sample due to the similarity in chemical composition of all samples. The mass loss for the sample is 38.2 wt%. The first step at 60–200 °C is related to removal of physical adsorbed and interlayer water. The second step at 200–300 °C can be attributed to the dehydroxylation of brucitelike layers and decarbonization of interlayer carbonate ions that leads to the collapse of the layer structure [19]. It can be concluded that processes of dehydroxylation and decarbonization occur at temperatures lower than 500 °C. The further sample heating promotes slightly mass loss around 5.2 wt%. This step can be attributed to the decomposition of strongly bound high-temperature carbonate [20,21]. A

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Sample	Cu concentration, wt%		Al concentration, wt%		Cu:Al molar ratio	
	Theoretical	Calculated	Theoretical	Calculated	Theoretical	Calculated
CuAl-1 CuAl-2 CuAl-3	48.9	40.3 40.7 40.2	20.4	17.5 17.2 17.6	1:1	0.97 1.00 0.98



Fig. 1. Thermal analysis of air-dried CuAl-LDH-2 sample.

higher decomposition temperature of this carbonate species is an indicator for strong interaction across interface and grain boundaries which were formed during the first decomposition step. Carbonate ions can be present as monodentate or bidentate ligand in interlayer of hydrotalcite phase. Monodentate carbonate decomposes at lower temperature whereas bidentate carbonate is stable at higher temperatures [22]. Thus, the CuAl-LDH-1, CuAl-LDH-2, CuAl-LDH-3 samples were calcined at 450 °C due to the fact that dehydroxilation and decarbonization occur at temperature lower that 500 °C. The CuAl-LDH-2 sample was calcined at 650 °C to investigate influence of the calcination temperature on catalytic performance.

Thermal analysis data were confirmed by XRD analysis. XRD was done for the CuAl-LDH-2 sample dried at 110 °C (Fig. 2a), calcined at 450 and 650 °C (Fig. 2b) and for the CuAl-1 and CuAl-3 samples (not presented). XRD pattern of the CuAl-LDH-2 sample dried at 110 °C shows the characteristic peaks corresponding to the (00l) crystallographic planes. This provides a clear evidence for the formation of the hydrotalcite phase [21]. The $2H_1$ trigonal prismatic structure of twolayered polytype is formed [23]. Calcination of the CuAl-LDH-2 sample at 450°C leads to destruction of the hydrotalcite phase and formation of oxide phase. XRD pattern (Fig. 2b) of the CuAl-2 sample shows the presence of broad peak at ~36° which can correspond to low-crystallized CuO that is in agreement with data of other research group [21,24]. The same phase is obtained for the CuAl-1 and CuAl-3 samples. Probably, it can be caused by incomplete removal of interlayer anions. Increase of calcination temperature of the CuAl-2 sample to 650 °C results in higher degree of crystallization of the CuO phase (Fig. 2b). More pronounced peaks appear at ~35.5, 39 and 48° which are characteristic peaks of tenorite CuO phase. The obtained results reveal that hydrotalcite phase gradually transforms to tenorite phase. As a result Cu²⁺ ions which are present in hydroxide structure turn into Cu^{2+} ions which are in oxide structure. This is confirmed by XPS data.

The surface copper state in the CuAl-LDH-2 sample dried at 110 °C, calcined at 450 and 650 °C was investigated by XPS. The lines corresponded to Al, C, O, and Cu are present in survey photoelectron spectra measured for the samples. Other elements were not obtained within the sensitivity of the XPS. The measured Cu2p XP spectra and CuLMM Auger spectra are shown on Fig. 3. Analysis of Cu2p lines (shape and position) measured for the sample dried at 110 °C shown that copper is presented only in one state with binding energy (BE) value near 935.5 eV which corresponds to the Cu in Cu²⁺ state in Cu(OH)₂ [18,25]. The shift of BE to lower values ~934.9 eV (which is more



Fig. 2. XRD of (a) CuAl-LDH-2 sample, (b) CuAl-2 and CuAl-2-650 samples.

typical for Cu^{2+} state in CuO) for samples calcined at 450 and 650°C means the partial decomposition of copper hydroxide and formation of CuO. XP spectra of the CuAl-1, CuAl-2 and CuAl-3 samples (not presented here) are practically the same: the binding energy is in the range of 935.4–935.5 eV. It means that all samples contain copper in Cu²⁺ state. The changes obtained in Auger spectra basically prove the suggestion concerning the CuO formation on the samples surface during calcination. For the samples dried at 110 °C there is a peak at 915.3 eV which is attributed to Cu²⁺ in copper hydroxide Cu(OH)₂ that is the evidence of the formation of layered double hydroxide. Increase of calcination temperature results in shifting the peak position to the higher binding energy. For the CuAl-2-650 sample the binding energy is 916.8 eV, which is characteristic for tenorite phase. However, the presence of Cu²⁺ in hydroxide structure cannot be excluded. The samples differ in the Cu:Al atomic ratio on the surface (Table 2).

Increase of the calcination temperature of the CuAl-LDH-2 sample results in decrease of the Cu:Al surface ratio. It can be caused by the decomposition of $Cu(OH)_2$ in a structure of layered double hydroxide with simultaneous formation of CuO particles on the sample surface.

3.2. Catalytic properties

Catalytic properties of the CuAl-1, CuAl-2, CuAl-2-650 and CuAl-3 samples were investigated in *N*-methylation of *p*-anisidine in autoclave reactor using *o*-xylene as solvent.



Fig. 3. XP and Auger spectra of the CuAl-LDH-2, CuAl-2 and CuAl-2-650 samples.

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Table 2

Atomic Cu:Al ratio on the sample surface and catalytic behavior of the samples depending on the calcination temperature and the concentration of carbonateions

Sample	Treatment temperature, °C	[CO ₃ ²⁻]/[Al ³⁺]	Cu:Al	Conversion of <i>p</i> - anisidine, %
CuAl-LDH-2 CuAl-1 CuAl-2 CuAl-3 CuAl-2-650	110 450	0.86 0.5 0.86 1.0 0.86	0.69 0.58 0.62 0.74 0.57	- 59 48 37 77

Reaction conditions: *p*-anisidine (0,10 M), *o*-xylene (10 ml), 1000 rpm, $\tau = 5$ h.



At the beginning, the search of optimal conditions for comparison of catalytic activity was done. For this purpose the CuAl-2 catalyst was used. F. Santoro and co-workers [26] showed that N-alkylation of aniline by different alcohols can be performed using reduced form of the Cu/Al₂O₃ catalyst. Therefore, N-methylation of p-anisidine was performed over the catalyst reduced in hydrogen atmosphere at 300 °C. Results of liquid phase synthesis of N-methyl-p-anisidine are presented in Table 3.

Using hydrogen atmosphere of 4 bars for N-methylation allows one to observe consumption of *p*-anisidine (Table 3, line 1), although its conversion is only 6% at 180 °C. Temperature increase from 180 to 200 °C provides significant increase in *p*-anisidine conversion to 34% (Table 3, lines 1, 2). Rate of methanol conversion during reaction is much higher than rate of *p*-anisidine *N*-methylation. It can be related to simultaneous side reactions with formation of CH₄, CO₂, and CO. As it is known [27,28], several reactions involving methanol (methanol steam reforming and methanol decomposition) can occur over Cu-containing catalysts. The steam reforming takes place due to the water formation during N-methylation of p-anisidine. Water will react with methanol to produce CO₂ and H₂. Besides, interaction of CO with H₂ promotes formation of methane in trace amounts [27].

$$CH_3OH + H_2O \rightarrow CO_2 + 3H_2$$

 $CH_3OH \rightarrow CO + 2H_2$
 $CO + 3H_2 \rightarrow CH_4 + H_2O$
The formation of CH = CO = and CO is a

The formation of CH₄, CO₂, and CO is confirmed by the chromatograph analysis of gas phase obtained during N-methylation of p-anisidine.

It was observed that the catalyst which was reduced directly in reaction media (4 bar of H₂) at 200 °C reveals the same activity as the sample which was reduced prior to reaction in hydrogen atmosphere at 300 °C (Table 3, lines 3, 4). p-Anisidine conversion reaches ~32% in both cases. Thus, it can be assumed that reduction of Cu^{2+} ions to Cu^{0-} occurs in autoclave at reaction conditions: 200 $^\circ$ C and 4 bar and in H₂ atmosphere. Thus, it is not necessary to reduce the catalyst prior to the reaction.

Increase of methanol concentration from 0.15 to 0.65 M (Table 3, lines 4-6) promotes raise of *p*-anisidine conversion from 33 to 99.8% while selectivity to N-methyl-p-anisidine remains practically the same (99.9% vs. 97.5%). Influence of the catalyst amount on the catalytic activity was also investigated. Decrease of catalyst amount leads to decline in *p*-anisidine conversion from 99.8 to 34% (Table 3, lines 6–8). Using higher methanol concentration of 0.9 M promotes increase of panisidine conversion to 48% (Table 3, line 9). At the same time the selectivity to N-methyl-p-anisidine is 99.0-99.8%. It can be concluded that the catalyst amount and methanol concentration should be high enough to obtain high *p*-anisidine conversion. It was established that optimum hydrogen pressure for N-methylation of p-anisidine is 4 bars. Pressure decrease to 2 bars, probably, leads to incomplete reduction of ${\rm Cu}^{2+}$ in the catalyst that promotes decrease in catalytic activity from 48 to 31% (Table 3, lines 9, 10). Pressure increase to 6 bars results in

Table 3

Liquid-phase synthesis of *N*-methyl-*p*-anisidine over CuAl-2 catalyst.

No	[CH ₃ OH], M	Substrate:Cu	P, bar	T, °C	Conversion MeOH, %	Conversion, %	Selectivity, %
1 ^a	0.10	1.33	4 (H ₂)	180	n.d.	6	100
2 ^a	0.10	1.33	4 (H ₂)	200	84	16	99.9
3 ^a	0.15	1.33	4 (H ₂)	200	90	32	99.9
4	0.15	1.33	4 (H ₂)	200	88	33	99.9
5	0.40	1.33	4 (H ₂)	200	90	69	99.8
6	0.65	1.33	4 (H ₂)	200	85	99.8	97.5
7	0.65	2.66	4 (H ₂)	200	76	84	99.5
8	0.65	5	4 (H ₂)	200	68	34	99.8
9	0.90	5	4 (H ₂)	200	54	48	99.7
10	0.90	5	2 (H ₂)	200	73	31	99.9
11	0.90	5	6 (H ₂)	200	66	40	99.8

Reaction conditions: *p*-anisidine (0.10 M), *o*-xylene (10 ml), 1000 rpm, $\tau = 5$ h.

^a Catalysts were reduced in hydrogen flow at 300 °C in fixed-bed reactor for 2 h. Obtained sample was cooled down in hydrogen flow and placed in a Schlenk flask under nitrogen atmosphere.

decline of *p*-anisidine conversion to 40% (Table 3, line 11) that is caused by shifting reaction equilibrium to methanol on the step of methanol dehydrogenation to formaldehyde [29]. Based on the obtained results and previous papers [5,6,29], the plausible mechanism was proposed. The reaction begins with dehydrogenation of methanol by Cu sites to formaldehyde, which further reacts with *p*-anisidine to give corresponding imine. Finally, *N*-methyl-p-anisidine is obtained by hydrogenation of imine by surface hydrogen atoms of Cu hydride species. Taking into account XPS data, Cu⁰ species are responsible for the dehydrogenation and hydrogenation transfer steps.

Thus, it was shown that CuAl-2 sample can provide high selectivity of *N*-methyl-*p*-anisidine performing reaction in liquid phase with an excess of methanol in H₂ atmosphere. The optimal reaction conditions were obtained: temperature of 200 °C, pressure of 4 bars, methanol concentration of 0.9 M, *p*-anisidine concentration of 0.1 M, substrate:Cu ratio of 5 despite the fact that p-anisidine conversion of ~100% was achieved at other reaction conditions (Table 3, line 6). However, it is incorrect to compare the catalytic activity at conversion of 100%. Thus, the optimal conditions were used for the next experiments.

The effect of base solution concentration used for the synthesis of Cu-LDHs on catalytic properties in *N*-methylation of *p*-anisidine was investigated. Four samples were taken for this purpose: CuAl-1, CuAl-2, CuAl-3 and CuAl-2-650. The effect of calcination temperature of the CuAl-2 sample on the catalyst performance was also studied in the mentioned reaction. The p-anisidine conversion increases from 37 to 59% with decrease of the $[CO_3^{2-}]/[Al^{3+}]$ ratio from 0.5 to 1.0 (Table 2). The lower the Cu:Al surface ratio, the higher *p*-anisidine conversion. As it was mentioned before the decrease in the molar Cu:Al surface ratio can be caused by formation of the CuO particle on the sample surface. However, increase in the calcination temperature of the CuAl-2 sample to 650 °C leads to rise in the *p*-anisidine conversion from 48 to 77% while the molar Cu:Al surface ratio is the same as that for the CuAl-1 sample calcined at 450 °C (Table 2).

It means that the molar Cu:Al surface ratio is not the only parameter which determine the catalytic behavior of the catalysts on the base of Cu-layered double hydroxide. Other important factor can be formation of well-crystallized tenorite phase CuO which can be easily reduced to Cu⁰. As it was shown in [11], Cu⁰ is active component for the *N*-methylation reaction of *p*-anisidine. According to XRD data, the CuAl-LDHs calcined at 450 °C represent low-crystallized CuO phase. This phase can contain strongly bound high-temperature carbonate that can prevent low-crystallized CuO phase from complete reduction. On the other hand, well-crystallized tenorite phase is formed when the CuAl-2 sample is calcined at 650 °C. The reduction of this phase is easier. Thus, the higher conversion of *p*-anisidine can be reached by the calcincation of Cu-LDH at high temperature and using the lower concentration of carbonate ions in the base solution.

4. Conclusions

The catalytic properties of the samples on the base of Cu-layered double hydroxides in *N*-methylation of *p*-anisidine were investigated. Effect of the reaction conditions was also investigated. The CuAl-2 catalyst was chosen as a reference catalyst. It was shown that increase in reaction temperature promotes raising *p*-anisidine conversion. The pressure change leads to conversion decrease that can be caused by side reactions of methanol. Using lower amount of the catalyst does not improve catalytic activity. The optimum reaction conditions for performing *N*-methylation of p-anisidine are following: 200 °C, 4 bars, the substrate:Cu ratio of 5.

Varying synthesis conditions of the CuAl-LDH sample is possible decision to obtain more active catalyst for *N*-methylation of *p*-anisidine. Different sodium carbonate concentration in the base solution was used for the synthesis of LDHs. It was shown that p-anisidine conversion over Cu catalysts on the base of LDH increases in the same order as carbonate concentration decreases. Thus, lower concentration promotes better catalyst performance in *N*-methylation of *p*-anisidine. Besides, higher calcination temperature of CuAl-2 results in formation of well-crystallized tenorite phase CuO that facilitates higher p-anisidine conversion. CuAl-layered double hydroxides can be used as the catalysts in the *N*-methylation of other aniline derivatives.

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