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Methylation of Aniline and Its Derivatives with Dimethyl Carbonate in the Presence of Binder-Free Micro-, Meso-, and Macroporous Zeolites KNaX, NaY, and HY

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Abstract—Aniline and its derivatives undergo methylation when treated with dimethyl carbonate in the presence of binder-free micro-, meso-, and macroporous zeolites KNaX, NaY, and HY leading to the formation of *N*-methyl- and *N,N*-dimethylanilines.

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N-Methylaniline, *N,N*-dimethylaniline, and their derivatives form an important class of nitrogen-containing compounds. They are used in manufacturing of drugs, dyes, and explosives. *N*-Methylaniline is an environmentally low hazardous antiknock agent for gasoline. An industriously significant method for *N*-methyl- and *N,N*-dimethylanilines production is the aniline methylation with alkyl halides and methanol. The disadvantage of this procedure is the low selectivity [1]. In most cases in the reaction of aniline with methanol along with *N*-alkylation also *N,N*-dialkylation occurs, and as well the alkylation in the ring takes place giving toluidines (yield 14–54%). These reactions proceed in the presence of vanadium, iron, and cobalt aluminum phosphates $MAlPO_4$ (M = V, Fe, Co, Cu) at high temperature (200–300°C) [2].

Dimethyl carbonate which is a “green chemistry” compound has been applied as methylation agent [3]. Carried out reactions involving dimethyl carbonate in the presence of K_2CO_3 promoted with 5% of poly-(ethylene glycol) PEG-6000 at 180°C. Under these conditions aromatic amines underwent the monomethylation by dimethyl carbonate, but their conversion did not exceed 50% [3]. Hydrotalcite $[Mg_6Al_2CO_3(OH_{16})\cdot 4H_2O]$ catalyzed the aniline methylation with dimethyl carbonate at 240–275°C over 2 h. Therewith the aniline conversion grew linearly with increasing temperature [4].

Zeolites NaY and KY are highly selective catalysts for aniline *N*-methylation with dimethyl carbonate. The reaction in their presence proceeds under relatively mild conditions (100°C, 2–3 h) and leads to the formation of *N*-methylaniline in 97% yield. The special feature of the method is the application of a double excess of the catalyst with respect to substrate. Analogous reaction with substituted anilines $XC_6H_4NH_2$ (X = *p*-CH_3, *o*-CH_3,*p*-OCH_3, *p*-NO_2, *p*-COOH) in the presence of NaY and KY proceeded very slowly, and the yields of *N*-methyl derivatives did not exceed 6% [5].

We established that zeolite catalysts prepared from crystalline aluminosilicates 0.72KNaX-BS (basic), NaY-BS (neutral), and 0.94HY-BS (acidic) are efficient for the methylation of aniline and its derivatives with dimethyl carbonate. Mechanically strong catalyst granules consist to 90–95% from slice crystals of zeolite faujasite X or Y and are binder-free. The porous structure of catalysts consists of micropores as well as meso- and macropores. The meso- and macropores provide an efficient diffusion of the reagents molecules to the catalytically active sites and backward to the surface of the granules. The concentration of active sites in binder-free catalysts is considerably higher than in catalysts with binders [6, 7]. The characteristics of the samples are compiled in Table 1.

Scheme 1.

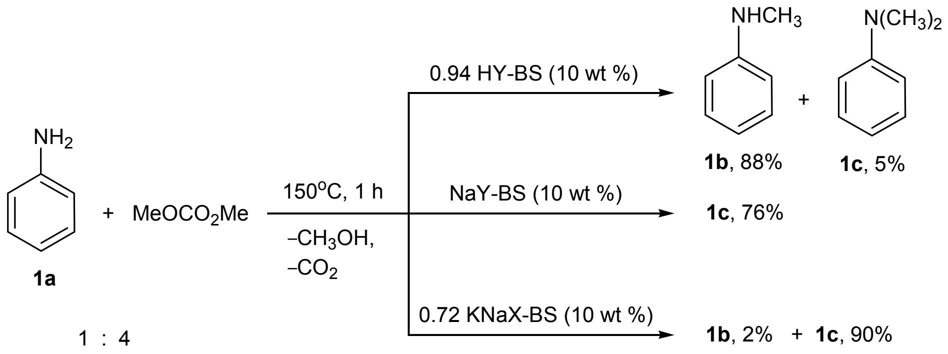


Table 1. Characteristics of samples of zeolite catalysts[a]

Sample	α_{Na}	Cr., %	M
0.72KNaX-BS	0.72	98	2.6
NaY-BS	–	100	5.2
0.94HY-BS	0.94	90	7.1

[a] α_{Na} is the degree of exchange of Na^+ cations for cations K^+ or H^+; Cr. is the degree of crystallinity of the sample; M is the molar ratio SiO_2/Al_2O_3 in the crystal lattice of zeolite; BS means binder-free.

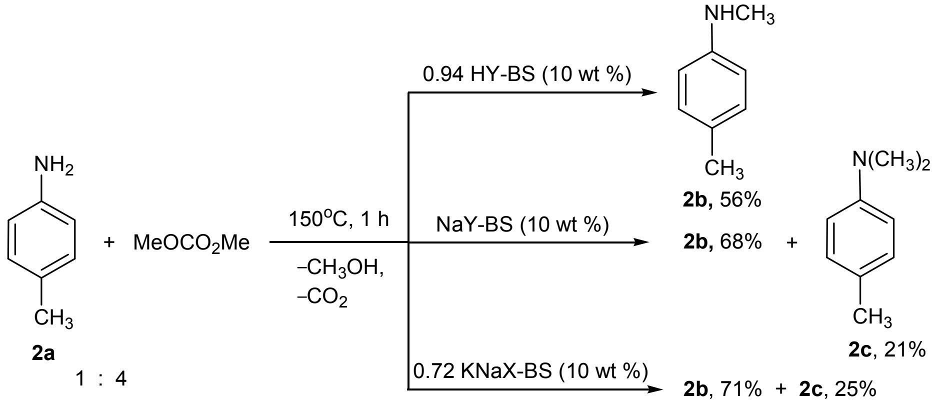
The anilines conversion and the direction of the reaction depend on the acid-base characteristics of the catalysts, their concentration, and the conditions of the process. The reaction of aniline **1a** with dimethyl carbonate, 1 : 4 (150°C, 1 h 5 wt % of acid catalyst 0.94HY-BS) resulted in the formation of *N*-methylaniline **1b** in 60% yield. At increasing the catalyst concentration to 10 wt % the aniline conversion grew to 72%, and the selectivity with respect to compound **1b** remained high. The increase of the reaction time to 4 h in both cases favors a total conversion of aniline and led to the formation of a mixture of *N*-methyl- (**1b**) and *N,N*-dimethyl- (**1c**) anilines. The similar reaction in the presence of the neutral (NaY-BS) and basic (KNaX-BS) catalysts notwithstanding their concentration and reaction time resulted in a selective formation of *N,N*-dimethylaniline **1c** (Scheme 1, Table 2).

The position of the methyl substituent in toluidine affects the reaction direction with dimethyl carbonate depending on the reaction conditions and the acid-base properties of catalysts. Dimethyl carbonate reacted with *p*-toluidine **2a** in the presence of 0.94 HY-BS

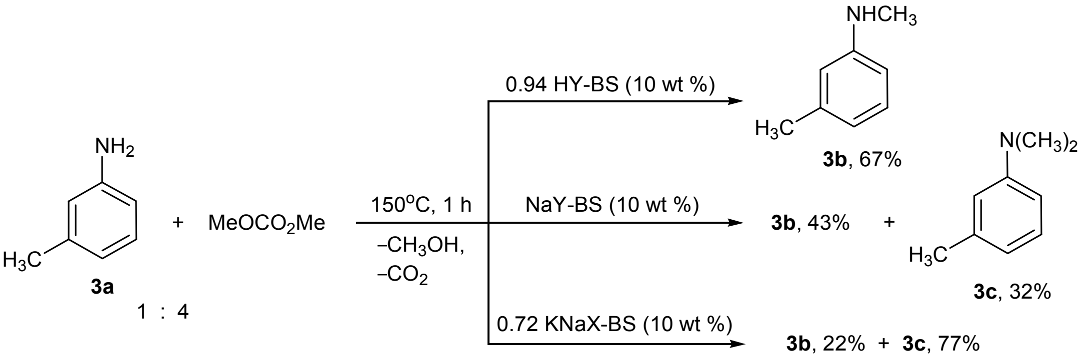
Table 2. Effect of reaction conditions and acid-base characteristics of the catalyst on aniline conversion and yield of *N*-methyl- (**1b**) and *N,N*-dimethyl- (**1c**) aniline

Catalyst	Catalyst concentration, wt %	Reaction conditions	Aniline conversion, %	Yield of reaction products, %	
				1b	**1c**
0.94 HY-BS	5	150°C, 1 h	60	60	–
	5	150°C, 4 h	77	43	34
	10	150°C, 1 h	93	88	5
	10	150°C, 4 h	99	71	28
NaY-BS	5	150°C, 1 h	63	–	63
	10	150°C, 1 h	76	–	76
0.72KNaX-BS	5	150°C, 1 h	96	5	91
	10	150°C, 1 h	92	2	90

Scheme 2.



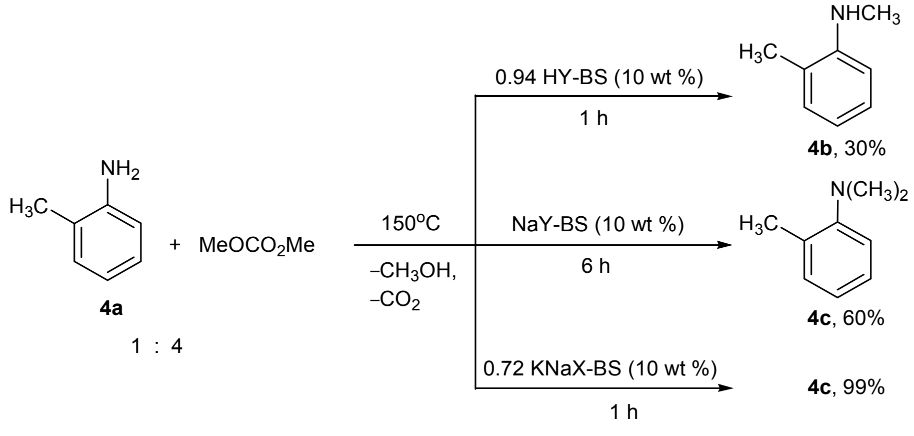
Scheme 3.



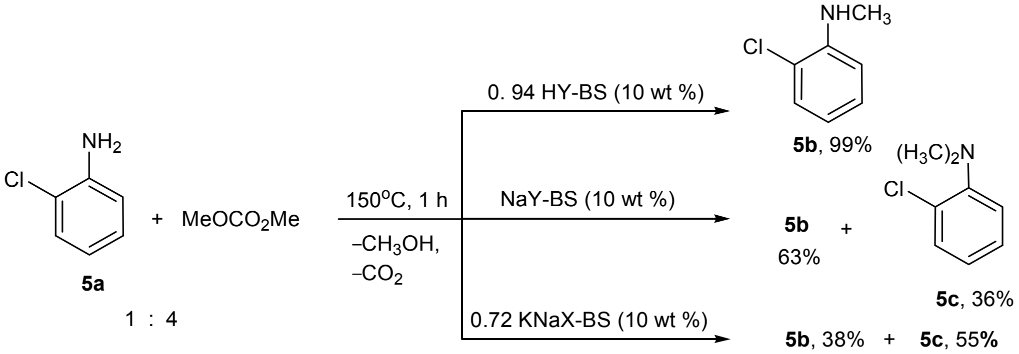
giving *N*,4-dimethylaniline **2b** with a high selectivity regardless the catalyst concentration (5–10 wt %) and the process duration (1–4 h). In the presence of NaY-BS and 0.72KNaX-BS a mixture formed of *N*,4-dimethyl- (**2b**) and *N,N*,4-trimethyl- (**2c**) aniline with the former prevailing. At increasing the temperature to 200°C (1 h) in the presence of 0.72KNaX-BS (10 wt %) compound **2b** formed exclusively in a quantitative yield (Scheme 2).

m-Toluidine **3a** reacted with dimethyl carbonate in the presence of 0.94HY-BS (10 wt %) affording *N*,3-dimethylaniline **3b** with a high selectivity. In the presence of catalyst 0.72 KNaX-BS a mixture formed of *N*,3-dimethylaniline **3b** and *N,N*,3-trimethylaniline **3c** with the prevalence in the reaction mixture of compound **3c**. At increasing the temperature to 200°C (1 h) in the presence of 0.72KNaX-BS (10 wt %) compound **3c** was the main reaction product (Scheme 3).

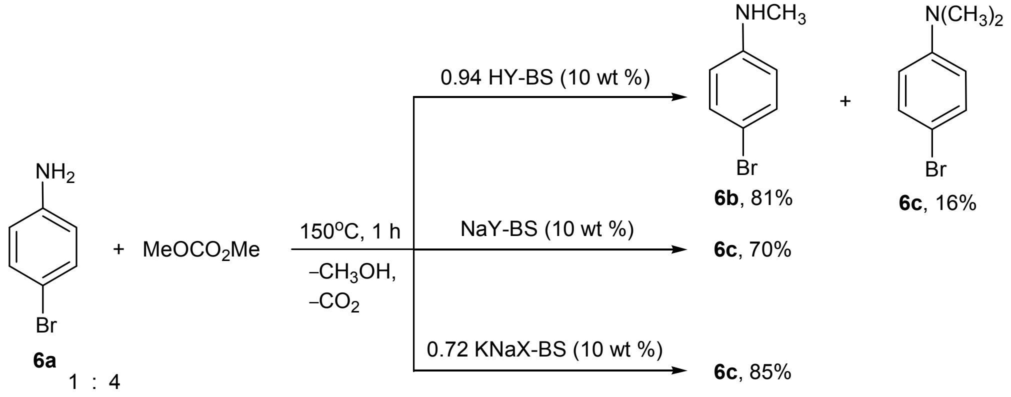
Scheme 4.



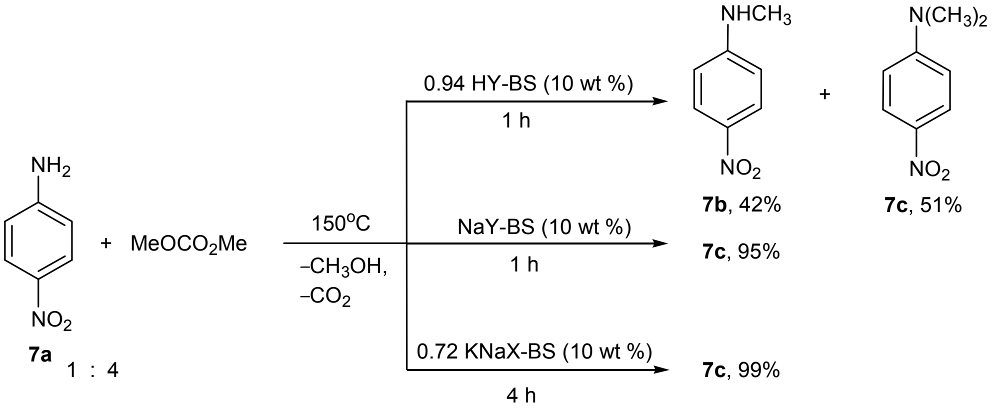
Scheme 5.



Scheme 6.



Scheme 7.



The reaction of *o*-toluidine **4a** with dimethyl carbonate in the presence of the acid form of the catalyst 0.94HY-BS (5–10 wt %) within 1 h proceeded to a low conversion (25–30%) with the formation of *N*,2-dimethylaniline **4b**. At increasing the process duration to 6 h at the incomplete conversion of the initial substrate (60%) selectively formed compound **4c**. In the presence of neutral catalyst NaY-BS (5 wt %) the reaction occurred to the conversion of 5–10%. At increasing the catalyst concentration to 10 wt % after 1 h the conversion of compound **4a** was 30%. After 4 h the conversion of *o*-toluidine **4a** completed affording compounds **4b** and **4c** in a ratio 1 : 4. In the presence of 0.72KNaX-BS regardless of the catalyst concentration and the reaction duration at the complete conversion of *o*-toluidine **4a** *N*,*N*,2-trimethylaniline **4c** formed in a quantitative yield (Scheme 4).

Very active reaction of dimethyl carbonate is observed with *o*-chloroaniline **5a**. The reaction selectivity depends on the nature of the applied catalyst: in the presence of 0.94HY-BS *N*-methyl-2-chloroaniline **5b** forms in a quantitative yield (Scheme 5). A peculiar behavior was observed in the reaction of dimethyl carbonate with *p*-bromoaniline **6a**. Whereas at the use of the acid catalyst 0.94HY-BS at any concentration of the catalyst and the reaction time a mixture was obtained of *N*-methyl- (**6b**) and *N,N*-dimethyl- (**6c**) derivatives, in the presence of NaY-BS and 0.72 KNaX-BS selectively formed *N,N*-dimethyl-4-bromoaniline **6c** (Scheme 6). Similarly the methylation with dimethyl carbonate proceeded with *p*-nitroaniline **7a**: at the use of 0.94HY-BS a mixture was obtained of mono-*N*- (**7b**) and *N,N*-dimethyl- (**7c**) derivatives, and in the presence of NaY-BS and 0.72 KNaX-BS compound **7c** formed selectively (Scheme 7).

Thus we have developed an effective method of the synthesis of *N*- and *N,N*-dimethyl aniline derivatives applying a reagent of the "green chemistry", dimethyl carbonate, with the use of binder-free micro-, meso-, and macroporous zeolite catalysts with basic (0.72KNaX), neutral (NaY), and acidic properties (0.94HY).

EXPERIMENTAL

^{1}H and ^{13}C NMR spectra were registered on a spectrometer Bruker Avance-400 (400.13 and 100.62 MHz respectively) in $CDCl_3$. Mass spectra were measured on an instrument Shimadzu GCMS-QP2010Plus, capillary column SPB-5, 30 m × 0.25 mm, carrier gas helium, ramp from 40 to 300°C (heating rate 8 deg/min), vaporizer temperature 280°C, ionizing electrons energy 70 eV. Elemental composition of the samples was determined on an analyzer Carlo Erba 1106.

The reaction progress was monitored and the purity of compounds obtained was checked by GLC on an instrument Shimadzu GC-9A, GC-2014, column 2 m × 3 mm, stationary phase silicone SE-30 (5%) on the carrier Chromaton N-AW-HMDS, ramp from 50 to 270°C (heating rate 8 deg/min), carrier gas helium (47 mL/min).

Binder-free zeolite catalysts 0.72KNaX-BS, NaY-BS, and 0.94HY-BS were prepared by procedures [6, 7].

Methylation of anilines with dimethyl carbonate. General procedure. Into a pressure microreactor of stainless steel of 17 mL capacity or into a glass ampule (20 mL) (results of the parallel runs were virtually identic) was charged 5–10 wt % of catalyst (0.94HY-BS, NaY-BS, 0.72KNaX-BS), 100 mmol of aniline or its derivative, and 400 mmol of dimethyl carbonate. The reactor was hermetically closed (the ampule was sealed), and was heated for 1–4 h at 150°C. After the end of the run the reactor was cooled to room temperature, opened, the reaction mixture was filtered through a bed of Al_2O_3. Dimethyl carbonate was distilled off, the residue was distilled at atmospheric pressure or in a vacuum, or crystallized from ethanol.

***N*-Methylaniline (1b).** Yield 88%, bp 196°C. ^{13}C NMR spectrum, δ, ppm: 30.53 ($NHCH_3$), 112.17 ($C^{2,6}$), 117.12 (C^4), 129.10 ($C^{3,5}$), 149.42 (C^1).

***N,N*-Dimethylaniline (1c).** Yield 90%, bp 194°C. ^{13}C NMR spectrum, δ, ppm: 40.53 (CH_3), 112.67 ($C^{2,6}$), 116.12 (C^4), 129.01 ($C^{3,5}$), 150.68 (C^1).

***N*,4-Dimethylaniline (2b).** Yield 71%, bp 110°C (30 mmHg). ^{13}C NMR spectrum, δ, ppm: 20.59 (CH_3), 31.24 ($NHCH_3$), 112.89 ($C^{2,6}$), 129.76 ($C^{3,5}$), 130.18 (C^4), 147.58 (C^1).

***N,N*,4-Trimethylaniline (2c).** Yield 25%, bp 128°C (60 mmHg). ^{13}C NMR spectrum, δ, ppm: 20.72 (CH_3), 41.23 (NCH_3), 113.53 ($C^{2,6}$), 126.45 (C^4), 130.01 ($C^{3,5}$), 149.19 (C^1).

***N*,3-Dimethylaniline (3b).** Yield 67%, bp 119°C (50 mmHg). ^{13}C NMR spectrum, δ, ppm: 21.33 (CH_3), 30.33 ($NHCH_3$), 109.30 (C^6), 111.37(C^2), 118.95 (C^4), 128.76 (C^5), 138.31 (C^3), 149.18 (C^1).

***N,N*,3-Trimethylaniline (3c).** Yield 77%, bp 130°C (50 mmHg). ^{13}C NMR spectrum, δ, ppm: 21.10 (CH_3), 40.27 (NCH_3), 109.66 (C^6), 112.87 (C^2), 115.57 (C^4), 128.67 (C^5), 138.64 (C^3), 150.50 (C^1).

***N*,2-Dimethylaniline (4b).** Yield 30%, bp 115°C (40 mmHg). ^{13}C NMR spectrum, δ, ppm: 17.37 (CH_3), 30.80 ($NHCH_3$), 109.17 (C^6), 116.89 (C^4), 121.94 (C^2), 127.00 (C^5), 129.95 (C^3), 144.64 (C^1).

***N,N*,2-Trimethylaniline (4c).** Yield 99%, bp 102°C (30 mmHg). ^{13}C NMR spectrum, δ, ppm: 17.42 (CH_3), 44.27 (NCH_3), 118.63 (C^6), 122.33 (C^4), 127.25 (C^5), 129.95 (C^3), 130.48 (C^2), 147.30 (C^1).

***N*-Methyl-2-chloroaniline (5b).** Yield 99%, bp 208–210°C. ^{13}C NMR spectrum, δ, ppm: 31.29 ($NHCH_3$), 116.64 (C^6), 119.07 (C^4), 121.17 (C^2), 128.00 (C^5), 129.30 (C^3), 142.42 (C^1).

***N,N*-Dimethyl-2-chloroaniline (5c).** Yield 55%, bp 221°C. ^{13}C NMR spectrum, δ, ppm: 48.30 (CH_3), 118.2 (C^6), 121.7 (C^2), 125.34 (C^4), 127.70 (C^3), 129.10 (C^5), 150.7 (C^1).

4-Bromo-*N*-methylaniline (6b). Yield 81%, bp 107–109°C (12 mmHg). ^{13}C NMR spectrum, δ, ppm: 30.45 ($NHCH_3$), 120.79 (C^4), 123.96 ($C^{2,6}$), 130.52 ($C^{3,5}$), 152.88 (C^1).

4-Bromo-*N*,*N*-dimethylaniline (6c). Yield 85%, mp 52–55°C. ^{13}C NMR spectrum, δ, ppm: 40.23 (NCH_3), 113.83 (C^4), 125.55 ($C^{2,6}$), 132.00 ($C^{3,5}$), 149.59 (C^1).

***N*-Methyl-4-nitroaniline (7b).** Yield 42%, mp 149–151°C. ^{13}C NMR spectrum, δ, ppm: 30.52 ($NHCH_3$), 112.29 ($C^{2,6}$), 126.76 ($C^{3,5}$), 136.18 (C^4), 156.08 (C^1).

***N*,*N*-Dimethyl-4-nitroaniline (7c).** Yield 99%, mp 163–166°C. ^{13}C NMR spectrum, δ, ppm: 40.23 (NCH_3), 110.53 ($C^{2,6}$), 126.10 ($C^{3,5}$), 136.31 (C^4), 154.19 (C^1).

Structural investigations were carried out in the Center of joint usage "Agidel" at the Institute of Petrochemistry and Catalysis, Russian Academy of Sciences.

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