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SELECTIVE METHYLATION OF PHENOL, ANILINE AND CATECHOL WITH DIMETHYL CARBONATE OVER CALCINED Mg-Al HYDROTALCITES

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ABSTRACT: Calcined Mg-Al hydrotalcites (Mg/Al=3) can be used as an efficient catalyst in the selective O-methylation of phenol and catechol and N-monomethylation of aniline employing dimethylcarbonate (DMC) as a methylating agent in vapor phase at 275°C.

Selective methylation reactions of phenol, catechol and aniline to anisole, guaiacol and N-methyl aniline respectively finds immense applications in the area of pharmaceuticals, drugs and fine chemicals.[1] Anisole is used as an additive in gasoline to boost octane, N-methylaniline is used as an intermediate in the synthesis of drugs and high energy materials and guaiacol is an important synthetic intermediate in the

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production of fine chemicals including flavorings, fragrances and pharmaceuticals. In our earlier report, we found that calcined Mg-Al hydrotalcites can be used in the selective monomethylation of aniline using methanol as an alkylating agent.[2] Velu et al. used the same catalyst for the selective C-alkylation of phenol to o-cresol and 2,6-xylenol.[3] Recently it has been demonstrated by different workers that dimethyl carbonate is a more efficient methylating agent than methanol. It is possible to carry out methylation reactions with DMC at a relatively lower temperature compared to methanol.[4-6]

Recently Fu and co-workers found that catalysts prepared by the modification of alumina with suitable alkali metal components can be conveniently used for the selective synthesis of guaiacol, veratrole and catechol carbonate from catechol and dimethyl carbonate under optimized conditions.[7-10] Their observations led to the conclusion that basic sites are the active centers for methylation. In this communication we report the methylation of phenol, catechol and aniline with DMC as an alkylating agent with an objective to explore the basic character of MgAl hydrotalcites to synthesize O-alkylated and N-alkylated products selectively.

Methylation of phenol with DMC was carried out in the temperature range 240-275 ^{0}C at various phenol/DMC molar ratios (Table 1). Anisole was obtained as the major product along with small amounts of o-cresol and 2,6-xylenol. No appreciable change in the selectivity of anisole is observed upon changing phenol/DMC ratio.

In the methylation of aniline, conversion increased linearly with rise in temperature (Table 2). A decrease in selectivity of N-methylaniline was observed at higher molar ratios with a concomitant increase in the selectivity of N,N-

Table 1 Methylation of phenol with DMC over calcined MgAl hydrotalcites

Reaction temperature ^{0}C	Phenol/DMC ratio	Phenol conversion %	Product selectivity %	
			Anisole	Others*
240	1:3	42	100	--
260	1:3	68	99.1	0.9
275	1:3	96	98.0	2.0
275	1:4	97	97.3	2.7
275	1:6	92	98.8	1.2

Reaction conditions: Feed rate 3 mL/h, Time on stream 2h, Reaction temperature 240-275 ^{0}C, Phenol/DMC mol ratio 1/3 to 1/6. * o-cresol and 2,6-xylenol.

Table 2 Methylation of aniline with DMC over calcined MgAl hydrotalcites

Reaction temperature ^{0}C	Aniline/DMC ratio	Aniline conversion %	Product selectivity %	
			N-methyl	N,N-dimethyl
240	1:3	48	100	--
260	1:3	71	98.1	1.9
275	1:3	92	96.0	4.0
275	1:4	94	88.0	12.0
275	1:6	91	87.0	13.0

Reaction conditions: Feed rate 3 mL/h, Time on stream 2h, Reaction temperature 240-275 ^{0}C, Aniline/DMC mol ratio 1/3 to 1/6.

Table 3 Methylation of catechol with DMC over calcined MgAl hydrotalcites

Reaction temperature ^{0}C	Catechol/DMC ratio	Catechol conversion %	Product selectivity %	
			Guaiacol	Veratrole
240	1:3	39	98.0	2.0
260	1:3	59	95.3	3.4
275	1:3	83	94.6	3.2
300	1:3	100	80.2	17.3
275	1:4	85	90.1	7.8
275	1:6	78	83.3	14.8

Reaction conditions: Feed rate 3 mL/h, Time on stream 2h, Reaction temperature 240-300 ^{0}C, catechol/DMC mol ratio 1/3 to 1/6.

dimethylaniline. It should be noted that no C-alkylated products were formed under the present reaction conditions.

The effect of temperature and catechol/DMC molar ratio on the catechol conversion and product selectivity is presented in table 3. In all cases only small amounts (<3%) of C-alkylated products were formed. At 275 ^{0}C, the guaiacol yield (conversion × selectivity /100) was 78.5 % (entry 3).

In conclusion, calcined MgAl hydrotalcite (Mg/Al=3) is an efficient catalyst for the selective methylation of phenol, aniline and catechol. Vapor phase reaction of catechol and DMC can be employed for the selective synthesis of guaiacol (o-methoxyphenol). The observed catalytic activity is attributed to the presence of co-ordinatively unsaturated O^{2-} ions acting as strong Lewis basic sites.[11]

Experimental

Preparation of Calcined MgAl hydrotalcite (Mg/Al=3)

Two separate solutions, one containing $Mg(NO_3)_2$. $6H_2O$ (115.38 g, 0.45 moles) and $Al(NO_3)_3$. $9H_2O$ (56.27 g, 0.15 moles) in 300 ml of distilled water and another containing NaOH (30 g, 0.75 moles) and Na_2CO_3 (15 g, 0.141 moles) in 200 ml of distilled water were prepared at room temperature. The metal nitrate solution was added to the second solution at a rate of 60 ml/h maintaining the pH 9-9.5. The resulting precipitate was kept at 338 K for 30 minutes with stirring and washed with distilled water many times until the pH of the filtrate became 7. The catalyst (Mg-Al hydrotalcite, atomic ratio=3) was filtered and dried at 383 K and calcined in air at 723 K for 6 h and stored in sealed ampoules.

Characterization of catalyst

The characterization of MgAl hydrotalcite was carried out using XRD, thermogravimetry and BET surface-area measurements.[12] The ICPES (Inductively coupled plasma emission spectrometry) method was adopted to estimate the ratios of the M^{II} and M^{III} ions in LDHs.

Reaction procedure

Alkylation reactions were carried out in vapor phase in a fixed bed down flow silica reactor. 2 g of the catalyst (as pellets 10-20 mesh) was loaded in the middle of the reactor fitted with a thermocouple for temperature measurements. The catalyst was activated in a stream of air at 723 K for 6 hours and brought down to the reaction temperature under nitrogen flow. The reaction mixture (phenol / aniline / catechol and DMC, 1:3 mol ratio) was introduced at the top of the reactor by means of an infusion pump. The products were collected in a water-cooled condenser and analyzed by a gas chromatograph fitted with a capillary column (HP-1) and flame ionization detector.

The identity of the products was established by the comparison of retention times of authentic samples and also by GC-MS and GC-IR.

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12 Typical XRD, IR, TGA and DTA substantiated the formation of hydrotalcites.

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