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Side Chain Ethylation of Toluene with Ethanol over Hydrotalcite-Like Compounds[1]

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Abstract—Calcined Mg, Ni, Cu, Co, and Zn hydrotalcites (CHTs) tested for their catalytic performance in the side chain ethylation of toluene with ethanol at 300, 350, 400, and 450°C. The major products were propylbenzene, β-methylstyrene, *ortho*-, *para*-, and *meta*-ethyltoluene. MgAl-CHTs gave side chain alkylated propylbenzene, while over Co, Ni, Cu, and Zn-CHTs, side chain as well as nuclear alkylated products and ethyltoluene were observed.

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1. INTRODUCTION

Alkylation of aromatics with olefins and alcohols occurs at the aromatic ring over acid catalysts and at the side chain over basic catalysts [1]. It has been shown that selectivity towards side chain and nuclear alkylation depends critically on the nature of the catalyst and reaction environment [2, 3]. The alkylation of toluene using methanol over alkali exchanged and also over alkali impregnated HZSM-5 were studied [4]. The active sites were calculated to be weak Brønsted acid sites whose strength was rather reduced by alkali cations. As a result, the nuclear alkylation decreases in the order Li > Na > K > Rb > Cs. Huang and Ko [5] reported the methylation of ethylbenzene over X type zeolites that ring and side chain alkylation took place respectively on the acid and base zeolite such as HX and KX. The side chain alkylation and dealkylation proceed respectively via, carbanion and carbonium ion mechanism where as dehydrogenation occurs via, free radical mechanism [5].

Ethylation of toluene is an industrially important reaction as the polymer product, polymethylstyrene has more commercial importance than polystyrene as it possess high flash point, glass transition temperature and low specific gravity. The general terms hydrotalcite-like compounds or layered double hydroxides are widely used for the isomorphous and poly type compounds of hydrotalcites [6]. A broad spectrum of divalent and trivalent cations in different atomic compositions constitutes LDHs with HT-like network. Interlayer anions can be varied which allows the tailoring of desired catalytic properties with these materials [8]. A detailed description of synthesis, characterization and various applications of hydrotalcites have been reported elsewhere [7–10].

The basic zeolites studied for alkylation of toluene, showed greater selectivity for nuclear alkylation than the side chain alkylation [11]. By quantum chemical calculation [12], the basic sites make the carbon atom of the side chain more active than that of benzene ring; the role of acid sites is attributed to the adsorption and stabilization of toluene. The methyl group condenses with the carbonyl group adsorbed on acidic sites. In the present work, we investigate the side chain alkylation of toluene with ethanol over a series of mixed metal oxides derived from hydrotalcite-like precursor.

2. EXPERIMENTAL

2.1. Preparation of Catalysts

Co-precipitation at low supersatuaration and constant pH is the method most frequently used in the preparation of hydrotalcites [6]. They can be represented by the general formula $[M(II)_{1-x}M(III)_x(OH)_2]^{x+}[A^{n-}_{x/2}]mH_2O$, where M(II) = Mg, Ni, Cu, Zn, Co and M(III) = Al, Cr, Fe, with M(II)/M(III) atomic ratio of 3, 4, 5, 7, and 10. The aqueous solution of metal nitrates (70–100 ml) and a mixture of aqueous solution of NaOH (2–3 M) and Na_2CO_3 (0.2–0.35 M) were mixed at room temperature with vigorous stirring at the pH range 7–10. The resulting slurry is aged at 75°C for 30 min with vigorous stirring. The precipitate, filtered and washed with distilled water to eliminate the alkali metal and nitrate ions was dried at 110°C overnight. Calcination was carried out in the presence of air at 450°C for 12 h, and then cooled to room temperature.

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Table 1. Chemical composition and lattice parameters of M (II) M (III) CO_3 HT

Catalysts	M(II)/M(III)[a]	Lattice parameters (Å)		Surface area (m^2/g)	
		a	*c*	uncalcined	calcined[b]
Mg/Al 3.0	2.71	3.049	23.301	99.5	168.0
Mg/Al 4.0	3.74	3.061	23.609	103.8	172.6
Mg/Al 5.0	4.69	3.092	23.801	88.7	154.8
Mg/Al 7.0	6.46	3.098	23.865	–	–
Mg/Al 10.0	8.91	3.108	23.858	–	–
Ni/Al 3.0	2.78	3.082	22.969	110.0	189.3
Cu/Al 3.0	2.72	3.058	22.867	119.6	206.4
Co/Al. 3.0	2.69	3.072	22.821	83.0	149.6
Zn/Al 3.0	2.90	3.064	22.769	69.8	106.5

Note: [a] ICPES result.
[b] BET method at 450°C

2.2. Characterization of Catalysts

The characterization of hydrotalcite-like compounds were carried out using ICPES (Model 3410 ARL) method was adopted to estimate the ratios of the M(II) and M(III) ions in hydrotalcite-like compounds and BET (Carlo-Erba model 1800) surface area measurements. Thermal behavior of HTlc was carried out in a Perkin Elmer thermal analyzer (TGA-DSC 7).

2.3. Catalytic Studies

The vapour phase alkylation of toluene with ethanol has been carried out in a fixed bed down flow continuous type quartz reactor of 8.0 mm I.D and 35 mm length in which a porcelain disc was sintered and sealed in the middle of the reactor to support the catalyst. The catalyst (1.5 g of powdered CHT, 450°C for 8 h) packed inside the reactor was supported by two glass wool plugs, which were surrounded by ceramic beads to fill the space. Before starting the experiment, the catalyst was activated at 450°C for 3 h in nitrogen flow (23 cm^3/min) and then brought to the reaction temperature. The alkylation reaction was carried out using a mixture of toluene and alkylating agent, ethanol, (molar ratio 1 : 1), introduced at the top of the reactor by means of syringe infusion pump (Electronic Corporation of India) in the absence of carrier gas. The liquid products are collected in cold traps, identified and estimated in a Hewlett Packard 5890A gas chromatograph with a 2-m 5% bentone column using a flame ionization detector.

3. RESULT AND DISCUSSION

3.1. Physico Chemical Properties

The important physico chemical characteristics of hydrotalcites are presented in Table 1. These results

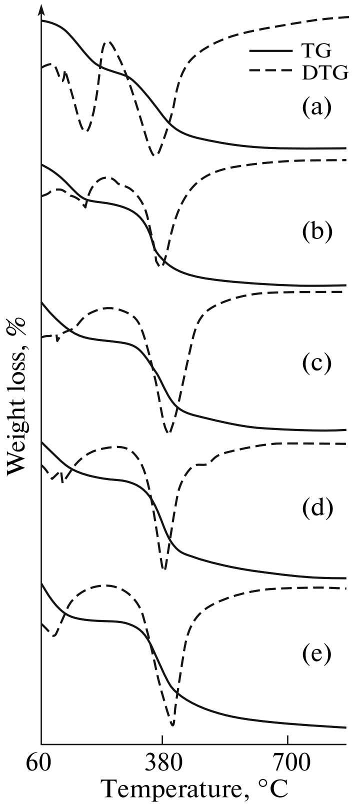

Fig. 1. TG and DTG curves of (a) Mg/Al 3.0, (b) Mg/Al 4.0, (c) Mg/Al 5.0, (d) Mg/Al 7.0, (e) Mg/Al 10.0.

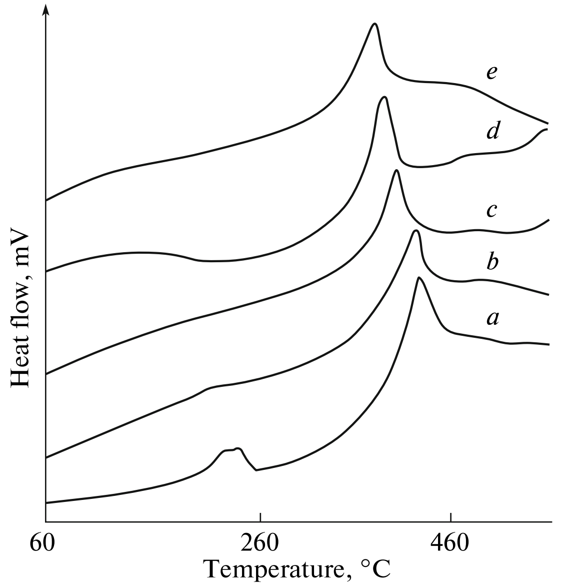

Fig. 2. DSC curves of *a*, Mg/Al 3.0; *b*, Mg/Al 4.0; *c*, Mg/Al 5.0; *d*, Mg/Al 7.0; *e*, Mg/Al 10.0.

enable one to know the exact '*x*' values. The appropriate lattice parameters required for a perfect HTlc formation were generally achieved by MgAl-HT for $x =$ 0.2 to 0.3. Instead of Mg^{2+} various M(II) ions (M = Co, Ni, Cu, and Zn) were used, keeping Al^{3+} constant.

Table 2. Decomposition of cyclohexanol over catalyst derived from CHTs and conventional oxides

Catalysts	Cyclohexanol, conversion, wt %	Product selectivity, wt %	
		cyclohexene	cyclo-hexanone
Mg /Al 3.0	37.6	14.3	85.7
Mg /Al 4.0	36.1	13.8	86.2
Mg /Al 5.0	34.0	10.9	89.1
Mg/Al 7.0	28.2	6.3	93.7
Mg/Al 10.0	21.4	1.3	98.7
Co/Al-3.0	39.3	34.1	65.9
Ni/Al-3.0	50.4	92.8	7.2
Cu/Al-3.0	52.2	95.6	4.4
Zn/Al-3.0	36.5	82.1	17.9
MgO	8.6	1.0	99.0
Al_2O_3	39.5	100	–
$MgO–Al_2O_3^*$	43.8	77.6	22.4

Note: Temperature: 300°C; Flow rate: 2 ml/h; Catalyst weight: 1.5 g; *Physical mixture of MgO and Al_2O_3.

3.1.1. Thermal analytical studies. The thermogravimetry (TG) and its differential curves (DTG) for the Mg/Al synthesized samples are shown in the Fig. 1. Two consecutive weight losses are recorded as expected for HTlcs with vaporizable interlayer anion [13]. The first weight loss in the temperature range (120–250°C) is attributed to the removal of physisorbed interlayer water molecules. The second endothermic weight loss occurring in the temperature range (250–450°C) is ascribed to the removal of structural water (from layer hydroxyl groups) and of CO_2 (from the interlayer carbonate anions) leading to the destruction of the layered structure [14]. This temperature range changes very little with the Mg/Al atomic ratio, both transformation temperatures *T*1 and *T*2 decrease with increase in Mg/Al atomic ratio. This can be attributed to the decrease in electrostatic attraction between the layer and interlayer owing to the lowering of electropositive nature of the brucite layer. The thermograms agree with the thermal results of various authors and characteristic thermal transitions are retained even up to atomic ratio variations [15, 16].

The DSC of these samples substantiates the TG results giving two endotherms in the same temperature range (Fig. 2). Although the DSC transformation temperatures *T*1 and *T*2 are slightly higher compared to that of TG transformation temperatures, the observed trend with respect to Mg/Al atomic ratio is similar in these experiments.

The thermal decompositions of M(II) Al-HT were studied by TG and DSC experiments. The TG and DSC curves of these compounds are given in Figs. 3 and 4, respectively. The transformation temperatures *T*1 and *T*2 in TG and DSC correlated well with each other. The thermograms of other compounds except CuAl-HTlc exhibit two stages of weight loss corresponding to dehydroxylation and decarboxylation. NiAl-HT showed considerable thermal stability (up to 300°C) while Cu, Co, and Zn containing samples exhibited poor thermal stability (less than 250°C). MgAl-HT exhibited a high thermal stability in comparison with other hydrotalcites. These observations would suggest that the amount of structural water associated with Mg is high in comparison with other hydrotalcites.

3.1.2. BET surface area measurement. Thermal decomposition of hydrotalcite precursors led to the formation of high surface area. Also creation of large surface area is an important characteristic need for catalysis. Surface areas of CHTs were significantly higher than in uncalcined HT samples [17]. The increase in surface area during calcination at 450°C can be attributed to the formation of mesopores due to expulsion of CO_2 and H_2O from the hydrotalcite precursors [18]. Mg/Al-4.0 CHT showed a maximum observed surface area. Due to variation in the radii of M (II) ions and M (III) ions substitution in the MgAl–

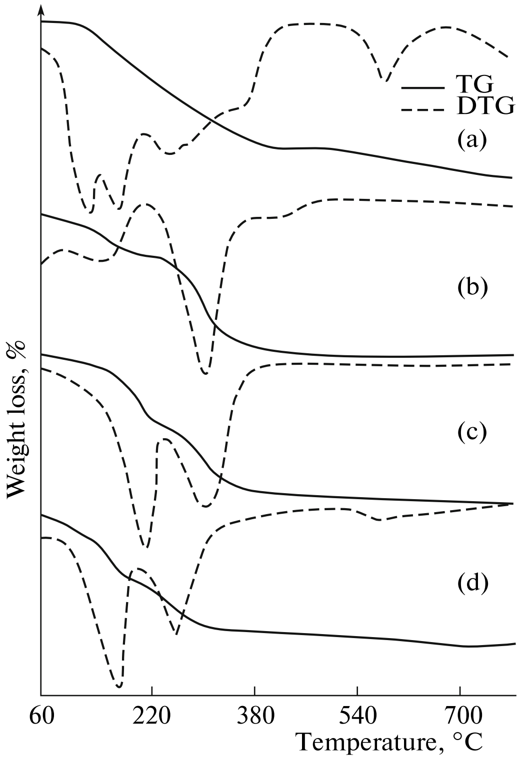

Fig. 3. TG and DTG curves of (a) Cu/Al 3.0, (b) Ni/Al 3.0, (c) Co/Al 3.0 and (d) Zn/Al 3.0.

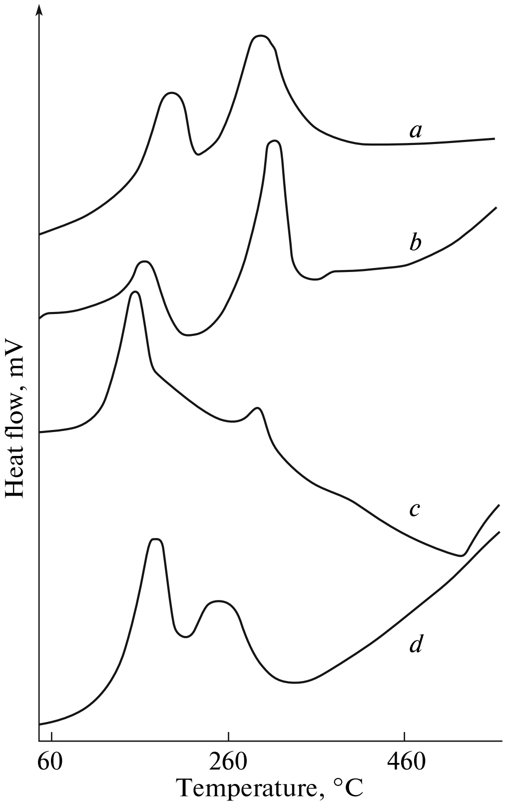

Fig. 4. DSC curves of *a*, Cu/Al 3.0; *b*, Ni/Al 3.0; *c*, Co/Al 3.0; and *d*, Zn/Al 3.0.

HT precursors there will be a lowering of surface area of CHTs (Table 1).

3.1.3. Acid–base properties. Catalytic conversion of cyclohexanol is often used as a model reaction to evaluate acidity, basicity and catalytic activity of the catalysts. It has been reported that the determination of acid-base properties of a catalyst by test reactions is superior to other conventional methods. This test reaction has been applied in order to evaluate the acid-base properties of some samples of hydrotalcite-like materials. The results of conversion of cyclohexanol over a series of MgAl-CHT are shown in Table 2. The catalytic activity of the catalyst is also monitored through the percentage extent of formation of cyclohexanone and cyclohexene. As expected, MgO showed exclusive selectivity for cyclohexanone indicating the presence of strong basic sites while Al_2O_3 showed 100% selectivity for cyclohexene. The physically mixed MgO–Al_2O_3 products possess approximately proportional amounts of cyclohexene and cyclohexanone which bears a close relation to the proportion of MgO–Al_2O_3 (~3.5 : 1). It has been observed that when Mg(II)–Al(III)–HTs were tested for cyclohexanol model reaction, although they possess both acidic and basic sites, ketones are formed predominantly than alkenes. This suggests that basicity dominates over the acidity in Mg(II)–Al(III)–HTs.

Except Mg/Al-3.0 CHT, all other CHTs showed more than 90% selectivity of cyclohexanone indicating that these compounds possesses predominantly basic sites. The higher selectivity of cyclohexene in the case of Mg/Al-3.0 CHT compared to other CHTs indicates the higher acidity of this catalyst which can be attributed to the dissolution of more amount of Al^{3+} in the MgO lattice introducing Lewis acidity. From these results it can be concluded that MgAl-CHT possesses predominantly basic sites whose basicity is slightly less than that of MgO but higher than that of pure Al_2O_3. Jianyi Shen et al. [19] also observed similar observation from microcalorimetric determination of heat of adsorption study. They found that Mg-Al mixed metal oxides obtained from hydrotalcites do not possess acid sites and base sites with differential heats higher than 120 and 150 kJ/mol respectively. The γ-Al_2O_3 possesses acid sites with differential heat from 60 to 160 kJ/mol, and MgO has base sites with differential heats as high as 170 kJ/mol. The results of decomposition of cyclohexanol over Co, Ni, Zn, and Cu containing HTs at 300°C are shown in the Table 2. CuAl-CHT and NiAl-CHT are most selective for cyclohexene (around 90%). Many authors have claimed that the selectivity to cyclohexene in the decomposition of cyclohexanol can be taken as a measure of acidic strength of catalyst [20–22]. Taking into account the selectivity to cyclohexene, the activity of

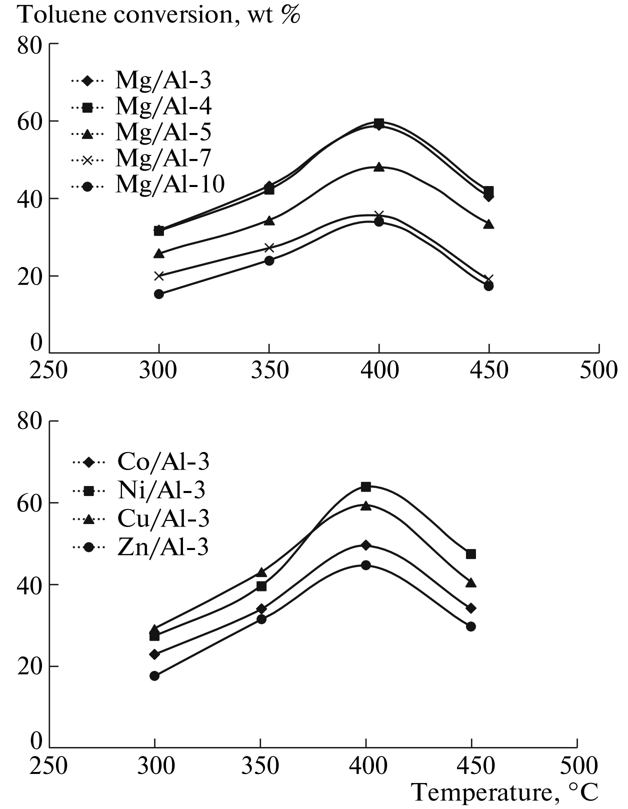

Fig. 5. Ethylation of toluene: the effect of temperature on toluene conversion.

the samples could be ordered as Cu > Ni > Zn > Co indicating that the acidity also decreases in the same order.

Table 3. Ethylation of toluene: the effect of CHTs on product distribution

Catalysts	Toluene conversion, wt %	Product yield, mole %		
		propyl benzene	β-methyl styrene	ethyl toluene
Mg/Al-3.0	31.8	19.2	7.5	3.6
Mg/Al-4.0	31.2	18.5	9.3	2.9
Mg/Al-5.0	25.6	13.8	9.1	–
Mg/Al-7.0	19.7	10.8	7.9	–
Mg/Al-10.0	15.2	6.7	8.2	–
Co/Al-3.0	22.8	12.8	–	9.9
Ni/Al-3.0	27.5	11.0	–	15.4
Cu/Al-3.0	29.3	12.2	–	11.6
Zn/Al-3.0	17.5	13.4	–	3.1

Note: Temperature: 300°C; Toluene : Ethanol = 1 : 1; Catalyst weight: 1.5 g; Flow rate: 2 ml/h.

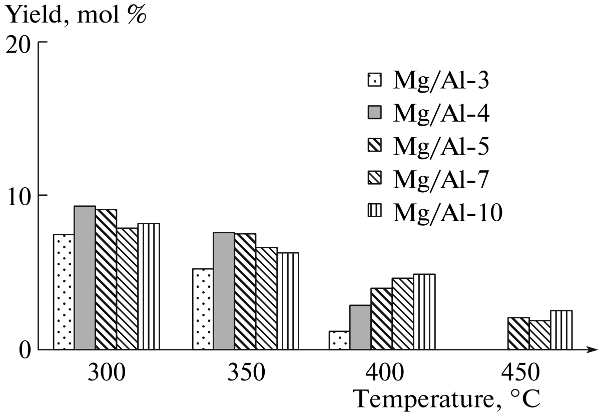

Fig. 6. Ethylation of toluene: the effect of temperature on the yield of β-methylstyrene.

3.2. Ethylation of Toluene

Ethylation of toluene with ethanol was carried out over Mg/Al, Ni/Al, Cu/Al, Co/Al, and Zn/Al calcined hydrotalcites from 300–450°C in steps of 50°C with toluene to ethanol feed ratio 1 : 1. The nuclear and side chain alkylated products of toluene (propylbenzene, β-methylstyrene, *o*, *p*, and *m*-ethyltoluene), and also the products of the side reactions of ethanol (ethane and diethyl ether) were formed.

Conversion of toluene increases with increase in temperature from 300 to 400°C as shown in Fig. 5. Yield of side chain alkylated products namely propylbenzene and β-methylstyrene (Table 3) is exclusive over MgAl–CHTs, while substitution of Mg^{2+} by other divalent metal ions shows higher nuclear alkylated product namely ethyltoluene (Table 3). Among the MgAl–CHT series, it is to be noted that Mg/Al 3.0 CHT is more active than other mole ratios and gives more of propylbenzene. Divalent substitution gives lesser yield of propylbenzene than MgAl-CHT. Formation of ethyltoluene by nuclear alkylation is higher over the series of divalent metal substitution.

3.3. Effect of Temperature

The effect of temperature on product selectivity over MgAl–CHT resulted in higher selectivity to β-methylstyrene at low temperatures in Fig. 6. As the temperature increases, the selectivity to β-methylstyrene decreased with concomitant increase in selectivity for propylbenzene (Fig. 7) and ethyltoluene (Fig. 8). The selectivity for propylbenzene and ethyltoluene showed maximum at 400°C. On the other hand, substitution of Mg^{2+} by other divalent cations resulted in predominant nuclear alkylation even at low temperatures. β-methylstyrene, an intermediate for the formation of propylbenzene, is noticed over MgAl–CHTs. Moreover, substitution of Mg^{2+} by other divalent metal ions does not favour the selectivity of β-methylstyrene. On the other hand, substitution of

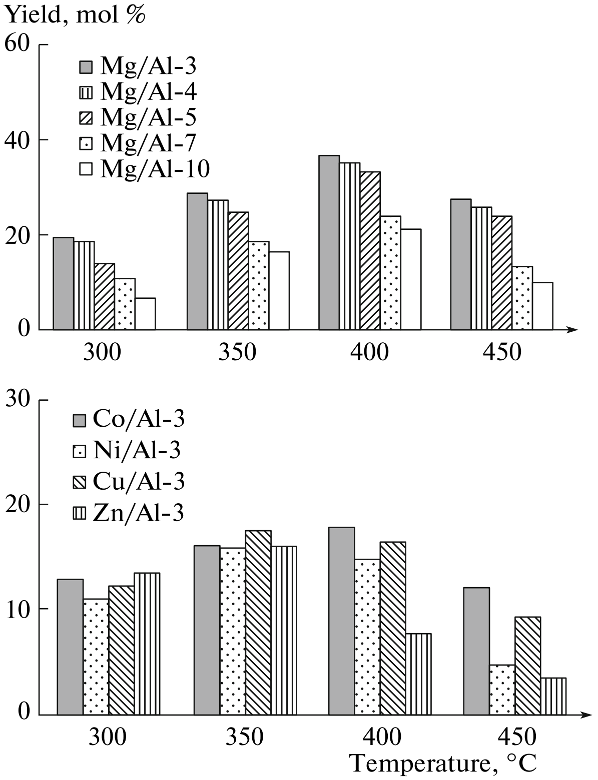

Fig. 7. Ethylation of toluene: the effect of temperature on the yield of propyl benzene.

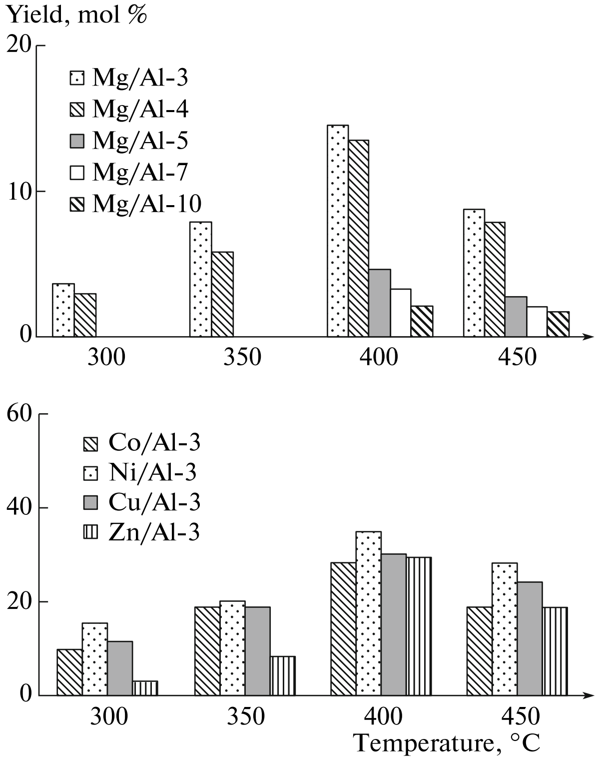

Fig. 8. Ethylation of toluene: the effect of temperature on the yield of ethyl toluene.

Table 4. Effect of temperature on isomer distribution of ethyl toluene

Catalysts	Temperature, °C	Product yield, mole %		
		o-ethyl toluene	*m*-ethyl toluene	*p*-ethyl toluene
Mg/Al-3.0	300	2.8	–	0.8
	350	3.6	1.0	3.2
	400	5.2	2.6	6.7
	450	4.5	2.2	2.0
Co/Al-3.0	300	3.6	1.5	4.8
	350	4.4	4.0	10.2
	400	4.0	8.4	15.6
	450	3.0	7.2	8.4
Ni/Al-3.0	300	4.5	3.0	7.9
	350	4.2	4.2	10.8
	400	3.8	13.6	17.4
	450	3.3	11.7	13.1
Cu/Al-3.0	300	4.8	2.6	4.2
	350	4.6	3.5	10.5
	400	4.2	11.6	14.3
	450	3.6	12.8	13.6
Zn/Al-3.0	300	1.9	–	1.2
	350	2.2	1.2	5.4
	400	2.0	13.4	17.3
	450	1.2	13.9	7.0

Note: Toluene : Ethanol = 1 : 1; Catalyst weight: 1.5 g; Flow rate: 2 ml/h.

Mg^{2+} in the HT framework influences the nuclear alkylation to give ethyltoluene predominantly.

In Table 3, the toluene conversion and products selectivity are compared at constant temperature of 300°C. It can be seen that MgAl-CHT with Mg/Al 3.0 is most selective catalysts for both nuclear and side chain alkylated products, while other divalent ions metal substituted catalysts show selective nuclear alkylation to give ethyltoluene. The selectivity for ethyltoluene decreases in the order ZnAl > NiAl > CuAl > CoAl > MgAl. The isomer distribution in the alkylation of toluene with ethanol is given in the Table 4. MgAl-CHTs show higher o-ethyltoluene, while other divalent substitutions give p-ethyltoluene in excess at low temperature. It is clear that with increase in temperature (i.e., at 350 and 400°C) m-ethyltoluene increases with corresponding decrease in p- and o-isomer, but there is no significant change in o- ethyltoluene in MgAl–CHT.

4. CONCLUSIONS

From this investigation, it is concluded that the combined participation of acidic and basic sites of the hydrotalcite-like compounds are found to be crucial for both side chain and ring alkylation of toluene with ethanol. Among these calcined hydrotalcites, MgAl-CHTs gave propylbenzene by side chain alkylation; while over Cu, Ni, Co, and Zn-CHTs gave side chain as well as nuclear alkylated product such as ethyl toluene. Among studied hydrotalcites, Mg/Al-CHTs are better for side chain ethylation of toluene.

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