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HYDROXIDE CLAYS AS SOLID BASE CATALYSTS

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Heterogeneous base catalysts of a new type have been described. The features of organic syntheses carried out in the presence of clay catalysts are considered. Kinetic equations are obtained and the mechanisms of oxyethylation and aldol condensation are discussed.
Keywords: layered double hydroxide clays, base catalysts.

INTRODUCTION

There are a large number of important chemical processes, which are homogeneously catalysed, in particular polymerisation, oligomerisation, alkylation, hydrogenation and dehydrogenation, oxidation etc. At the same time, catalysts, with proven basic catalytic sites, capable to display the base properties in a wide range of pK_a, insoluble in the reaction mixture, stable to effects of temperature and substrates, are hardly known. The existing base catalysts [1], such as alkali and alkali-earth metals, their oxides and hydroxides and anion-exchange resins, are thermally and chemically unstable compounds and materials.

The search for heterogeneous base catalysts should be carried out among the substances of inorganic nature, especially, among inorganic anion exchangers [2]. To solve this problem there is the need to:

- understand the main reasons of occurrence of base-catalytic properties of solids
- investigate the parameters that influence basicity and activity of heterogeneous catalysts,
- develop the methods of control of concentration, strength and type of catalytic sites
- develop the methods of control of structure for creation of highly selective catalysts
- investigate the catalytic activity and selectivity in several organic reactions.

MATERIALS AND METHODS

Layered double hydroxide clays were selected as heterogeneous base catalysts in this work. The methods of catalyst preparation are described in a previous paper [2]. Alcohol oxyethylation and aldol condensation of acetone were investigated as model reactions.

All reagents were classified as "pure for analysis" and all solvents were distilled before use. Glass reactors equipped with a device for temperature control and stirrer were used. The acetone aldol condensation reaction was investigated by determining the remaining acetone concentration.

The oxyalkylation reactions were investigated using a manometric installation [3], enabling to determine the ethylene oxide concentration in the liquid phase by measuring its partial pressure in the gas phase. For all reactions it was initially determined, that the rate of reaction does not depend on the stirrer speed, which says that the reactions are not diffusion-limited.

After execution of experiments the reaction products were analysed by gas chromatography using on internal standard.

The reaction of ethylene oxide with alcohols can proceed in the presence of acidic as well as of basic catalysis; the main distinction is in the quantitative distribution of reaction products. In the presence of base catalysts the reaction rate grows with increase in molecular weight of product, and the molecular mass distribution of products becomes broad. Oxyethylation reactions with homogeneous base catalysts have been well investigated, researches of heterogeneous base catalysts on the other hand started with our works [3–5].

The kinetic experiments of aldol condensation of acetone were conducted in a glass reactor equipped with stirring device and water bath for heating. The catalyst and acetone were loaded in the reactor, and after execution of the reaction the quantity of acetone and the conversion were determined. From literature it is known, that in the given conditions the main product of reaction is diacetone alcohol. Besides we observed dehydration.

The layered hydroxides of Mg-Al, Zn-Cr, as well as the products of their thermal processing at temperatures up to 600 ^{o}C were investigated as catalysts.

Determination of basic properties of layered double hydroxides was carried out using procedures reported previously [6]. About 0,1 g of catalyst was put in a closed measuring flask filled with nitrogen gas. A benzene and the corresponding indicator were added at once. The indicator adsorption rate on the surface of catalyst depends on the basicity of catalysts. Carrying out the titration with indicators of different pKa we obtained the strength distribution of basic sites of the catalysts (Mg-Al: pK_a=7,2–0,92; pK_a=9,3–0,30; pK_a=12,2–0,01 mmol/g; Zn-Cr: pK_a =7,2–0,72; pK_a=9,3–0,27; pK_a =12,2–0,05 mmol/g).

RESULTS AND DISCUSSION

The basic properties of the hydroxides are listed in Table 1.

Table 1

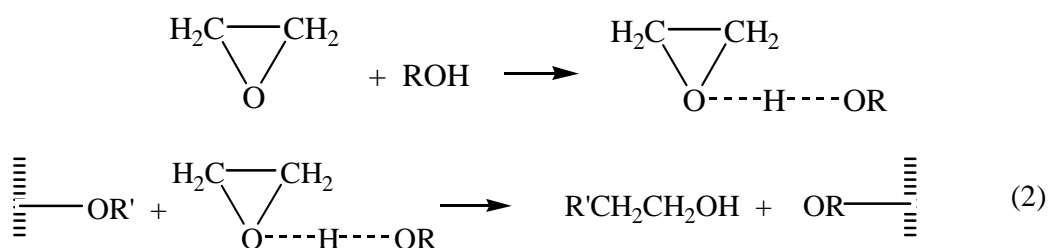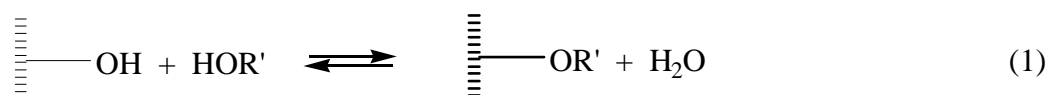**The concentration of Bronsted basic sites (12,2 < H_0< 17,2)**

T, ^{0}C	100	200	300	400	500	600
Mg_2–Al	0,95	0,55	0,31	0,08	0,04	–
Zn_2–Cr	0,75	0,45	0,30	0,13	0,03	-
Mg_2–Al	-	0,15	0,19	0,17	0,17	0,10
Zn_2–Cr	-	0,01	0,14	0,22	0,20	0,12

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As the alcohol oxyethylation can proceed in the presence of basic as well as acidic catalysts, it is necessary to deactivate the acid sites. The quantity of acid active sites could be determined by the reduction of activity of catalysts after the addition of alkali. The increase in rate of reaction after the addition of more than superstoichiometric quantities of poison shows their total elimination [6]. If the layered double hydroxide had Bronsted base sites in the hydroxide form then anion exchange (1) was observed initially.
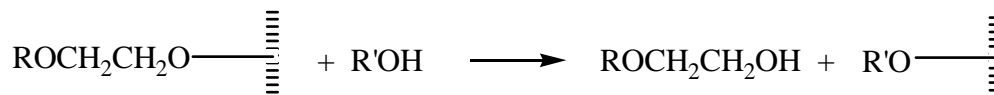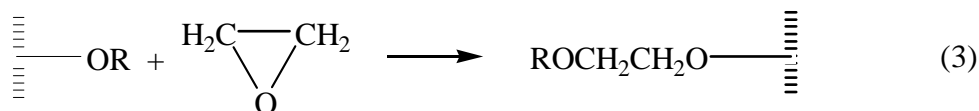
The initial dependence of the oxyethylation reaction rate on the initial ethylene oxide concentration was directly proportional in all cases thus the concentration order in ethylene oxide was equal to 1 in all cases. The dependence of the reaction rate on the current ethylene oxide concentration, especially for high molecular weight alcohols was initially not directly proportional, that is, the temporary order in ethylene oxide was more than 1. There was an increase of the rate constant and the reaction rate was determined by a differential method initially [7].

To explain this fact we assume that the internal space of clays increases by penetration of organic molecules (bulky hydrocarbon radicals), which is indirectly confirmed by the increase of efficiency of layered double hydroxide clays in oxyethylation reactions after a heat treatment in the reactant alcohol. (However, these deviations from first order are insignificant and in oxyethylation process in surplus of alcohol during 1–2 hours may be neglected). The increase of reaction rate with increasing reaction time depends on two processes – the purely catalytic reaction and the process of thickening of hydroxide layers. With increase of temperature larger deviation from first order should not be expected, as these processes have different temperature sensitivity – the enthalpy of clay reconstruction is about $_\Delta H = 2$ kcal/mol and the activation energy of the oxyethylation reaction is about 20 kcal/mol.
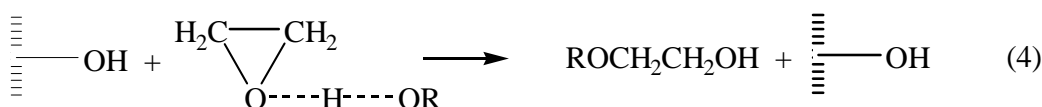
One-parametrical kinetic experiments have shown that the reactions are first concentration order in the layered double hydroxide clay and the two reactants. The following mechanism is assumed:

$$ \text{---OH} + \text{HOR'} \rightleftharpoons \text{---OR'} + H_2O \qquad (1) $$

$$ \underset{O}{H_2C\text{---}CH_2} + ROH \longrightarrow \underset{O\text{----}H\text{----}OR}{H_2C\text{---}CH_2} $$

$$ \text{---OR'} + \underset{O\text{----}H\text{----}OR}{H_2C\text{---}CH_2} \longrightarrow R'CH_2CH_2OH + OR\text{---} \qquad (2) $$

The interaction of the alcohol reactant with ethylene oxide proceeds through a threemolecular transition state. In the first stage the ethylene oxide ring is activated by formation of hydrogen bonding. The activated C---O bond is opened by nucleofilic attack of the surface alkoxide OR'. Similarly a two-step mechanism can be envisaged:

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$$\text{—OR} + \underset{\displaystyle O}{H_2C\!\!-\!\!CH_2} \longrightarrow ROCH_2CH_2O\text{—} \qquad (3)$$

$$ROCH_2CH_2O\text{—} + R'OH \longrightarrow ROCH_2CH_2OH + R'O\text{—}$$

Equilibrium (1) is defined by the concentration of the alcohol and its acidity. As all alcohols, except methanol, are less acidic than water, reaction according to equation (4) can occur:

$$\text{—OH} + \underset{\displaystyle O\text{----}H\text{----}OR}{H_2C\!\!-\!\!CH_2} \longrightarrow ROCH_2CH_2OH + \text{—OH} \qquad (4)$$

From experiments at various temperatures it was established, that the reaction proceeds in the kinetic area and the activation parameters of reaction (Table 2) were determined.

Table 2

Kinetics of alcohol oxyethylation reaction in the presence of Zn-Cr-hydroxide clay as the catalyst at 100 ^{0}C

Alcohol	$k \cdot 10^4$ m^6/mol$^2 \cdot$s	ln A	E, kJ/mol
1-Heptanol	1,71	25,0	96
1-Dodekanol	2,14	16,3	77,3
n-C$_{17-20}$OH	1,06		
i-C$_{17-20}$OH	1,29		

Deceleration of the oxyethylation reaction, connected with deactivation or blocking of sites, was not found, showing about high efficiency of catalysts.

An interesting observation was made when using the calcined products of Zn-Cr-hydroxide clay as catalysts. Depending on the heat treatment all calcined samples has different colouring (red-green-yellow-brown). They all display catalytic activity in oxyethylation reactions, though with increase in calcination temperature the activity decreases. During the process there is change of catalysts colour (the colour changes from colour of catalyst, treated at high temperature, to colour of catalyst with low temperature of activation) and some increase of activity in the course of the reaction takes place. Obviously restoration of hydrotalcite-like structure occurs. Similar observations were made upon addition of stoichiometric amounts of water to the reaction mixture. When calcined at 500 ^{0}C Mg-Al-hydroxide clay catalyst showed good activity in reactions of polymerising 2–10 moles of ethylene oxide onto C$_4$–C$_{18}$ alcohols [8]. Upon increasing calcining time of the catalyst more reaction time was required to achieve the appropriate conversion.

Table 3 lists the value of rate constants, obtained on the basis of the initial concentration of reactants and clays [8].

Table 3

The effective rate constants of oxyethylation of different alcohols at 180^0 C (Mg-Al-hydroxide clay)

A L C O H O L S	Calc. time, h	k 10^4, m^6/mol^2 min
1-Dodecanol + 6 EO	8	1,64
1-Dodecanol + 6 EO	4	1,74
1-Dodecanol + EO	4	2,15
1-Dodecanol and 1-tetradecanol mixture + 2 EO	8	1,95
1-Dodecanol and 1-tetradecanol mixture + 2 EO	4	2,96
1-Octanol + 4 EO	8	0,55
1-Octadecanol + 4,6 EO	8	2,35
Secondary octadecanol + 2 EO	4	14,3
Cyclohexanol + 4 EO	4	3,6
1- Butanol + 10 EO + 10 PO	4	12,2

Clays were calcined at 500 ^{0}C. EO - ethylene oxide, PO - propylene oxide.

When increasing the treatment temperature of Mg-Al-hydroxide clay catalyst the effective rate constant of oxyethylation of 1-heptanol decreases (Table 4).

Table 4

The effect of the calcination temperature of Mg-Al-hydroxide in the oxyethylation of 1-heptanol at 100 ^{0}C

Calcination temperature, ^{0}C	110	250	400	600
k 10^4 s, $m^6/kmol^2$	1,5	0,8	0,3	–

The given course of change of the reaction rate can be explained by the change of Bronsted and Lewis active sites upon thermal processing of clay. A comparison of effective rate constant permits to discuss participation of Lewis, as well as Bronsted sites. For all investigated base hydroxide clays the alcohol oxyethylation reaction is described by the kinetic equation:

$$R = - dC_{eo}/dt = k \cdot C_{eo} \cdot C_{alc} \cdot C_{clay} \qquad (I)$$

Table 5 shows the rate constants of the third order of oxyethylation reactions catalysed by two base hydroxide clays.

<div align="right">**Table 5**</div>

Oxyethylation of alcohols over heterogeneous base clays (100 ^{0}C)

Catalyst	*E, kJ/mol*	ln A	k, m^6/kmol$^{2 \cdot}$ s
Zn$_2$ - Cr	96	25,0	0,17$\cdot$10^{-3}
Mg$_2$- Al	95	22,0	0,15 $\cdot$10^{-3}

The aldol condensation of carbonyl compounds, acetone in particular, can serve as another model reaction when studying the base catalytic processes. Here larger molecular weight products are formed, which enables to monitor the course of reaction by the quantity of remaining reagents.

The aldol condensation of acetone was investigated using calcined layered double hydroxide clays as catalysts [10–14], i.e. Mg-Al, Cr-Zn, Ni-Al hydroxides. Before the reactions clays were subjected to heat treatment at 450 ^{0}C for 18 h. Such heat treatment results in the total dehydration of the clay and the disappearance of the hydroxide layer.

The clay basicity depends on the cation ratio in the oxide layer, and it is expected that the degree of the isomorphous replacement have a significant influence on the catalytic activity (Table 6).

<div align="right">**Table 6**</div>

The influence of the cation ratio in hydroxide clays on catalytic activity in acetone condensation

Mg(II)/Al(III)	1,33	1,39	2,24	2,27	3,04	6,27
Conversion, %	21,0	37,5	24,6	15,0	22,5	24,2

The size of the initial anion also influences the catalytic activity (Table 7). The clay catalysts exhibit a "memory" effect about their precursor.

<div align="right">**Table 7**</div>

The dependence of activity of Zn-Cr-oxide catalyst on the size of the dicarboxilate in the initial hydroxide

ANION	Conversion of acetone, %
Adipate	29,1
Decadicarboxylate	44,7
Dodecadicarboxylate	55,5

The dicarboxylates in base heterogeneous clay catalysts connect the hydroxide layers, in a perpendicular position, and increase the availability of active centres. It may be noticed that the specific surface of catalyst hardly depends on the structure of the anion. The change of the clay's specific surface, varying with the temperature of heat treatment, does not explain the changes in activity. It is assumed that the number of base sites (Bronsted and Lewis) depends on the processing temperature. The change of effective rate constant of the acetone condensation [12], in relation to the weight of the clay catalyst, is listed in table 8 [7, 17]) together with the concentration of base sites.

Table 8

The dependence of effective rate constant (k_{eff}) on loss of Zn-Cr-hydroxide clay catalyst weight (dm, %). W – reaction rate (relat. un.), C – concentration of base sites $(kmol/m^3)$

t_{calc} ^{0}C	W	dm	k_{eff}	C
250	0,70	0,12	0,79	0,14
300	0,85	0,17	0,97	0,17
400	0,90	0,25	1,20	0,21
450	0,70	0,31	1,10	0,20
600	0,56	0,43	0,93	0,12

Calcinated layered double hydroxide clays (oxide catalysts) are subject to deactivation in aldol condensation reactions. The liberated water sorbs on to the high basicity sites upon dehydration of diacetone alcohol. The kinetic equation of the acetone condensation is as follows:
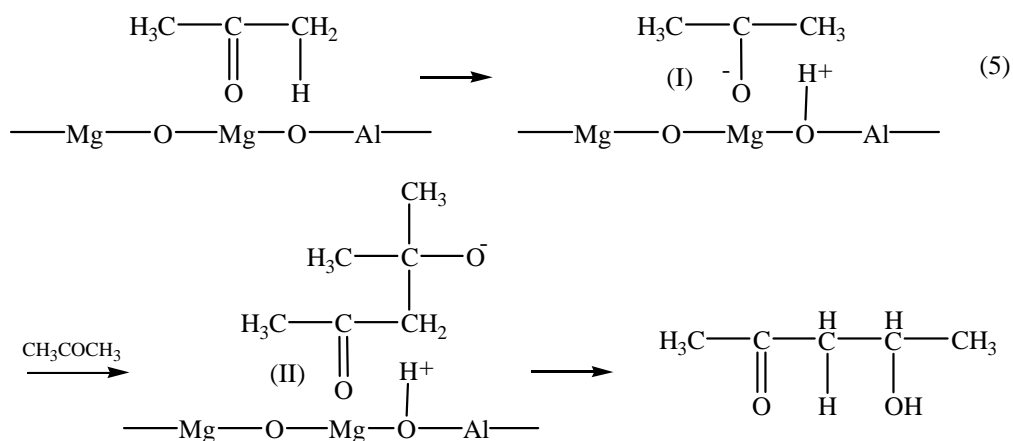
$$R = - dC_{ac}/dt = k \cdot C_{ac} \cdot C_{clay} \qquad (II)$$

The experiments at various temperatures afforded the activation parameters of the acetone condensation (Table 9).

Table 9

The activation parameters of aldol condensation reaction for layered double hydroxide clays (50 ^{0}C)

Catalyst	E, kJ/mol	ln A	k, $m^6/kmol^{2} \cdot s$
Zn_2 - Cr	19,2 $\pm$ 2,4	27 $\pm$ 3	0,16
Mg_2- Al	18 $\pm$ 2	25,6 $\pm$ 0,7	0,21

The role of the base sites consists in the formation of the carbanion, which subsequently attacks the carbonyl group of a second acetone molecule to form the dimeric anion (II).

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The rate constants for various clays are close and it is interesting to compare them with similar rate constants for the aldol condensation of acetone, proceeding in the presence of some other base heterogeneous catalysts (Table 10). Comparison of the results shows a greater value of the rate constants for the homogeneous process. However because the concentration of active sites in the heterogeneous process is considerably higher, the estimated reaction rate is approximately the same for both processes.

Table 10

The significance of effective rate constants of aldol condensation reaction
($m^6/kmol^2 \cdot s$, 50 ^0C)

Catalyst	T, ^0C	Reactor	k	Reference
MgO	0	Tubular	5,3	[15]
Ba(OH)$_2$	100	Mixture	1,3	[16]
MgO-Al$_2$O$_3$	300	Tubular	4,6	[9]

CONCLUSIONS

1. It has been shown the changes of the accessibility of basic sites of the catalysts due to the ion exchange process.
2. The interaction of the alcohol with ethylene oxide proceeds through a threemolecular transition state and activated C---O bond is opened by nucleofilic attack of the surface alkoxide.
3. At the aldol condensation the formation of the carbanion take place, which subsequently attacks the carbonyl group of a second acetone molecule to form the dimeric anion.
4. The correlation between the activity and selectivity of catalysts with a temperature of heat treatment has been shown. It has been found that the presence of moderate strength sites on the surface of catalyst is more important than the presence of strong Lewis sites.

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Капустина Е.В. Гидроксидные глины в качестве основных катализаторов / Е.В. Капустина, Р.А. Козловский, А.Е. Капустин // Ученые записки Таврического национального университета им. В.И. Вернадского. Серия «Биология, химия». – 2014. – Т. 27 (66), № 1. – С.283-291.

Описаны основные гетерогенные катализаторы нового типа. Изучены особенности протекания процессов органического синтеза в присутствии глинных катализаторов. Получены кинетические уравнения реакций оксиэтилирования и альдольной конденсации, обсуждены механизмы протекающих реакций.

Ключевые слова: слоистые двойные гидроксидные глины, основные катализаторы.

Капустіна О.В. Гидроксидні глини як основні каталізатори / О.В. Капустіна, Р.О. Козловський, О.Є. Капустін // Вчені записки Таврійського національного університету ім. В.І. Вернадського. Серія „Біологія, хімія". – 2014. – Т. 27 (66), № 1. – С. 283-291.

Описані основні гетерогенні каталізатори нового типу. Вивчені особливості протікання процесів органічного синтезу у присутності глинистих каталізаторів. Отримані кінетичні рівняння реакцій оксиетилювання і альдольної конденсації, обговорені механізми протікаючих реакцій.

Ключові слова: шаруваті подвійні гидроксидные глини, основні каталізатори.