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Zeolite and other heterogeneous catalysts for the transesterification reaction of dimethyl carbonate with ethanol

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Abstract

Results of screening tests are presented concerning a number of heterogeneous catalysts for the two-stage reaction of transesterification of dimethyl carbonate to diethyl carbonate. The tests were preceded by the activation of the catalysts. In the case of zeolites, dealumination led to an only slight increase in activity. For the most active catalysts kinetic parameters were determined necessary for the modelling of reactive distillation columns and process simulation. The process was analysed in which the transesterification reaction occurs in a reactive distillation column, with the best catalyst incorporated as an element of the structured packing.

Keywords: Transesterification; Screening tests; Reactive distillation; Structural packing; Dealumination

1. Introduction

A common characteristic of novel chemical processes is the emphasis on both minimum consumption of raw materials and energy as well as the reduced environmental impact. In a number of chemical reactions heterogeneous catalysts become an option of choice from both economic and environmental standpoint. Moreover, chemical syntheses tend to use biodegradable compounds of the lowest toxicity possible. Such compounds include dimethyl carbonate (DMC) [1], which can be used as a reactant in the production of esters of carbonic acid with higher alcohols via the transesterification reaction. The transesterification of dimethyl carbonate with ethanol leads to diethyl carbonate (DEC), which is a solvent and a reactant used in the manufacture of pharmaceuticals [2], fertilizers, pesticides, dyes and polymers [3].

In general, transesterification reactions can be catalysed by both acids and bases, in either homo- or heterogeneous systems; they can also occur under neutral conditions [4–7]. Heterogeneous catalysts employed in transesterification reactions include:

- zeolites, whose properties (and, therefore, catalytic activity) can be modified to some degree during or after the synthesis [5];
- ion-exchange resins [8];
- hydrotalcites [9–11];
- metal oxides, e.g. MgO, ZnO, La_2O_3, CeO_2 [6], SnO_2/SiO_2 [12];
- modified K_2CO_3 [13].

The aim of the present study was to carry out screening tests for a number of heterogeneous catalysts for the reaction of the transesterification of DMC with ethanol to DEC. The tests should form the basis for the selection of the best catalyst and for the determination of a kinetic equation necessary for both the modelling of reactive distillation and the process simulation. The study is a part of a wider research programme focused on the esterification reaction that could be conducted in a reactive distillation column in which the catalyst selected constitutes an important element of the structured catalytic packing MULTIPAK.

It has to be pointed out that reactive distillation is a novel integrated industrial process that couples a chemical reaction with an in situ separation via distillation. Reactive distillation combined with heterogeneous catalysis constitutes a process termed catalytic rectification. Such integration has a number of

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advantages that include increased conversion and selectivity and lower capital and operating costs compared with conventional processes [14].

The transesterification of DMC with ethanol to DEC is a two-stage process:

$$\underset{\text{DMC}}{C_3H_6O_3} + \underset{\text{EtOH}}{C_2H_6O} \rightleftarrows \underset{\text{EMC}}{C_4H_8O_3} + \underset{\text{MeOH}}{CH_4O} \qquad (1)$$

$$\underset{\text{EMC}}{C_4H_8O_3} + \underset{\text{EtOH}}{C_2H_6O} \rightleftarrows \underset{\text{DEC}}{C_5H_{10}O_3} + \underset{\text{MeOH}}{CH_4O} \qquad (2)$$

The system consists of two parallel reactions with respect to EtOH, and two consecutive reactions with respect to ethyl methyl carbonate (EMC). In the above system, the catalysts studied (especially ion-exchange resins) can lead to additional side reactions, namely catalytic dehydration of ethanol and methanol [15]. These reactions were not, however, taken into account.

The reaction mixture contains five components that form three azeotropic mixtures: MeOH–DMC, EtOH–EMC and EtOH–DMC. The separation of azeotropic systems is a serious challenge that requires the use of a series of extractive distillation columns, with a concomitant expenditure of energy and reactants. Catalytic distillation makes it possible to avoid this step due to the occurrence of chemical reactions and, consequently, leads to considerable savings.

2. Experimental

2.1. Experimental set-up and procedure

The experiments were done in a thermostatted glass tank reactor equipped with a stirrer, a temperature probe, a tube for sample withdrawal and a condenser cooled with water supplied from a thermostat at 278 K. The experiments were conducted over the temperature range 313–348 K, at a catalyst concentration of 60 g/dm^3. A single experimental point took from 350 to 4500 min, depending on the conversion obtained. Weighed amounts of reactants (100 g DMC and 100 g EtOH) were introduced into the reactor and heated to the desired temperature. Next a given amount of catalyst (13.5 g) was added; this moment was regarded as the beginning of the reaction. At certain intervals samples of the reacting mixture were collected and analysed by gas chromatography. The catalyst activity was assessed based on the amount of diethyl carbonate formed, selectivity towards DEC and the conversion of DMC. These quantities were compared for the subsequent series of experiments after some 1600 min from the start of the reaction.

2.2. Catalysts tested

The following catalysts were tested:

1. commercial zeolites: Zeocat PB (beta), with a molar ratio SiO_2/Al_2O_3 of 20 (Zeochem); Zeocat FM-8 (mordenite), $SiO_2/Al_2O_3 = 12$ (Zeochem); Zeolyst USY, $SiO_2/Al_2O_3 = 5.2$ (Zeolyst International); Zeolyst H-Beta, $SiO_2/Al_2O_3 = 150$ (Zeolyst International)
2. ion-exchange resins:
   - strongly acidic of the gel type: Lewatit K1221 (Bayer), Purofine PFC-100H (Purolite), Dowex Marathon C (Dow Chemical), Dowex Marathon MR-3 (Dow Chemical), Amberlyst 119 Wet (Rohm and Haas), Lewatit K1131 (Bayer), Lewatit K 1461 (Bayer), Amberlyst 35 Dry (Rohm and Haas) – matrix – styrene-divinylbenzene, with sulfonic acid as a functional group
   - superacidic: Nafion SAC-13 (Engelhard)—a copolymer of tetrafluoroethylene and perfluoro-3,6-dioxa-4-methyl-7-octenesulfonyl fluoride, converted to the proton H^+ form
   - weakly acidic, macroporous: Dowex MAC-3 (Dow Chemical) – matrix – polyacrylic with carboxylic acid as a functional group
   - basic: Amberlyst A26 OH (Rohm and Haas)—amine divinylbenzene/styrene copolymer with OH^- ion form
3. hydrotalcites: Pural MG 70 (Sasol), EMX (HSA)696 (Süd-Chemie), Pural MG 30 (Sasol), Syntal HSAC 701 (Süd-Chemie)
4. modified K_2CO_3
5. ZrO_2.

2.3. Catalyst treatment

Prior to the tests the catalysts underwent activation.

Zeolites were activated by one of the three methods:

- Method I: calcination at 773 K for 4 h.
- Method II (dealumination [16]): calcination at 823 K for 5 h, then triple ion exchange with a 0.1 M solution of NH_4NO_3, washing with distillated water, calcination at 823 K for 5 h, treating with a 1 M solution of oxalic acid, washing with distilled water and again, calcination at 823 K for 5 h.
- Method III: treating with a 1 M solution of HNO_3 at 318 K for 18 h, then calcination at 773 K for 4 h.

Ion-exchange resins were prepared by washing with distilled water, washing with a 3.02 M solution of HCl, again washing with distilled water, drying at 323 K for 18 h, washing with ethanol and drying at 323 K.

Hydrotalcites were activated by calcination at 723 K for 8 h and rehydration in air at a room temperature.

The modification of *potassium carbonate* consisted in covering the pellets of K_2CO_3 with polyethylene glycol [17]. Polyethylene glycol was dissolved in methanol (5, 10 or 15 wt.% relative to K_2CO_3), a weighed amount of the carbonate was added, the solvent was evaporated and the solid phase was dried at 403 K for 3 h.

ZrO_2 was calcined at 823 K for 7 h.

3. Results and discussion

The activity tests reveal that the zeolites, irrespective of the activation method employed, do not show sufficient catalytic activity towards diethyl carbonate (Table 1). The fact that the calcination of the zeolites does not influence their activity is most probably due to the steric effect. The pores of Zeocat PB

Table 1
Conversion of DMC and yields of EMC and DEC for heterogeneous catalysts after about 1600 min from the start of the reaction at 348 K

Catalyst	Method	Conversion of DMC (%)	Yield of EMC (%)	Yield of DEC (%)
Zeolyst USY	I	17	1	0
	II	19	14	0
	III	0	0	0
Zeocat PB	I	16	14	0
	II	18	17	0
	III	0	0	0
Zeocat FM-8	I	0	0	0
Zeolyst H-Beta	I	0	0	0
Lewatit K1221	For ion-exchange resins	54	53	12
Purofine PFC-100H	For ion-exchange resins	23	18	0
Dowex Marathon C	For ion-exchange resins	37	29	4
Dowex Marathon MR-3	For ion-exchange resins	10	5	0
Amberlyst 119 Wet	For ion-exchange resins	31	29	8
Lewatit K 1131	For ion-exchange resins	47	27	3
Lewatit K 1461	For ion-exchange resins	72	44	11
Nafion SAC-13	For ion-exchange resins	61	52	10
Dowex MAC-3	For ion-exchange resins	0	0	0
Amberlyst A26OH	For ion-exchange resins	64	40	4
Pural MG70	For hydrotalcites	25	21	0
EMX	For hydrotalcites	16	9	0
Syntal HSAC701	For hydrotalcites	21	7	0
Pural MG70 (Sasol)	For hydrotalcites	16	10	0
K_2CO_3	For potassium carbonate	76	51	26
ZrO_2	For ZrO_2	21	4	0

of dimensions 6.4 × 7.6 and 5.5 × 5.5 Å and these of Zeocat FM-8 (6.5 × 7.0 and 2.6 × 5.7 Å) are too narrow to allow the free passage of DMC, EMC and DEC. The modification of Zeocat PB via dealumination leading to the removal of some aluminium from the crystal lattice and the formation of secondary mesopores slightly increased the activity of this catalyst towards DEC. Desirable product appeared in the reacting mixture long after the beginning of the reaction (2809 min), with a molar fraction of 0.003676 for the experiments conducted at 348 K. The products of the first reaction step (EMC and MeOH) appeared within 73 min; this is about 6 times faster compared to experiments with calcinated zeolites. REM photographs of Zeocat PB taken both before and after the dealumination reveal certain structural changes (Fig. 1). Following the modification, the surface of the zeolite seems to be larger and more porous. Thus, more active sites become available for the reactants, and the mesopores formed facilitate the diffusion of the reacting species.

Of the ion-exchange resins tested, Lewatit K1221 and Nafion SAC-13 showed the highest activity. In the case of Lewatit K1221, in experiments performed at 348 K the conversion of DMC reached 55% (after 1600 min), while the selectivity towards DEC was about 22% (Fig. 2). Also, the experiments were done to test the utility of Lewatit K1221 for repeated use. It has been demonstrated that the regeneration carried out in exactly the same way as the initial activation almost completely restores the catalytic activity. The conversion of DMC remains practically unaltered, while the selectivity is only marginally lower than that for the fresh catalyst. Subsequent regenerations produced virtually the same result. The activity of Lewatit K1221 is probably due to swelling behavior associated with a low degree of crosslinking.

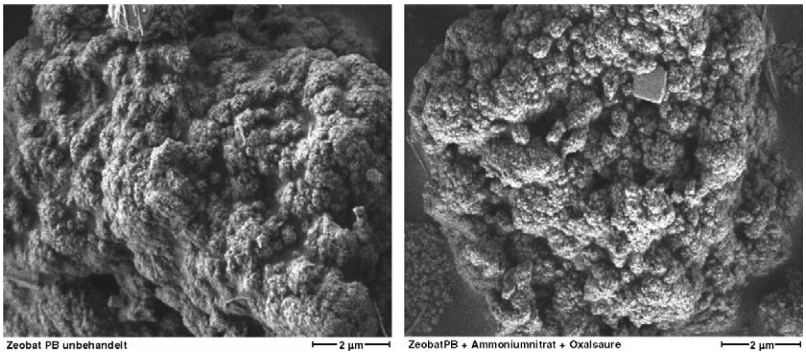

Fig. 1. REM image of Zeocat PB before dealumination (left) and after dealumination (right).

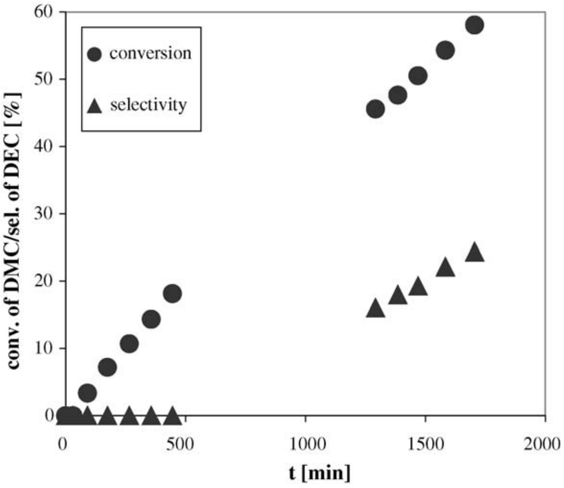

Fig. 2. Conversion of DMC and selectivity of DEC vs. time for Lewatit K1221. $T = 348$ K, catalyst concentration = 60 g/dm^3, weight ratio DMC to EtOH = 1:1.

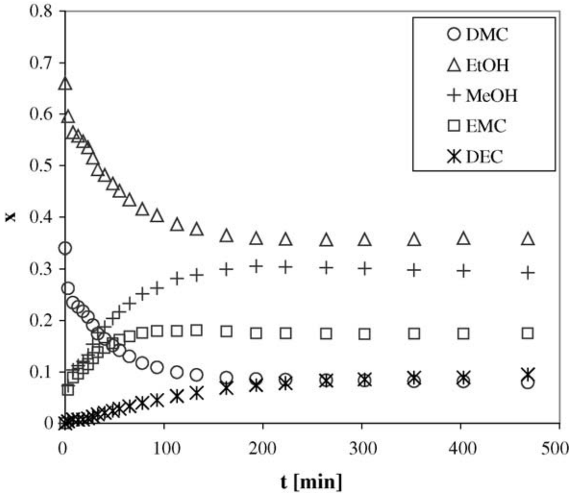

Fig. 3. Mole fractions for the coated K_2CO_3 (5 wt.% of PEG). $T = 348$ K, catalyst concentration = 60 g/dm^3, weight ratio DMC to EtOH = 1:1.

With a low amount of divinylbenzene in the resin matrix the swelling increases, thus improving the diffusion of the reactants and the reaction rate. Nafion SAC-13, which consists of 13 wt.% of perfluorinated ion-exchange polymer supported on a porous silica matrix formed into cylinders 1 mm in diameter and 4.5 mm long, had activity comparable with that of Lewatit K1221. Nafion is effective probably due to the electron-withdrawing forces of the neighboring—$CF_2CF_2SO_3H$ groups that cause the superacidity of the sulfonic group. In catalytic experiments Nafion was used as purchased. It has, however, to be pointed out that, according to some reports [18], there is a risk of Nafion being washed off the silica support. This has to be taken into account in the context of using this catalyst in the reaction zone of a reactive distillation column.

Of the hydrotalcites tested Syntal HSAC 701 proved to be the most active. The products of the first reaction (EMC and methanol), carried out at 348 K, appeared almost immediately after the catalyst was introduced into the system. After 467 min the conversion of dimethyl carbonate was about 74%, and the selectivity to diethyl carbonate reached 30%. Unfortunately, the reproducibility of the results for this catalyst was poor at 348 K; moreover, Syntal did not show any activity towards DEC at lower temperatures.

The most active catalyst for the reaction studied was modified potassium carbonate. Diethyl carbonate appeared immediately upon adding the catalyst, and the reaction attained equilibrium after some 480 min (Fig. 3). The maximum conversion of DMC was 75% and the selectivity towards DEC was 31%. The high activity of the carbonate is probably due to the formation of the PEG–K^+ complex which increases the basic strength of the salt [1,17]. An increase in the amount of glycol with respect to K_2CO_3 during the modification did not enhance the activity. However, the resistance of the carbonate pellets to attrition was improved.The catalytic activity of zirconia was found to be low.

For the most active catalysts, i.e. modified K_2CO_3, Lewatit K1221 and Nafion SAC-13 (Fig. 4) kinetic parameters were determined based on the Arrhenius equation. These parameters are shown in Table 2 and in Figs. 5 and 6. The order and the rate constants for the two reactions were estimated by introducing the experimental data into kinetic equations of different orders. Equations which led to the least scatter of the rate constants were selected as representative of the "true" kinetics of the process. Since these equations are found to correspond to the stoichiometric equations, the two reactions can be regarded as elementary [19]

$$r_1 = k_1\left(x_{\mathrm{DMC}}x_{\mathrm{EtOH}} - \frac{x_{\mathrm{EMC}}x_{\mathrm{MeOH}}}{K_1}\right) \quad (3)$$

$$r_2 = k_2\left(x_{\mathrm{EMC}}x_{\mathrm{EtOH}} - \frac{x_{\mathrm{DEC}}x_{\mathrm{MeOH}}}{K_2}\right) \quad (4)$$

where r denotes reaction rate, k is the reaction rate constant, K the reaction equilibrium constant, 1 and 2 the first and second reaction, respectively, and x is the molar fraction of the species. Concentration equilibrium constants were determined. For instance, at 323 K the equilibrium constant for the first reaction

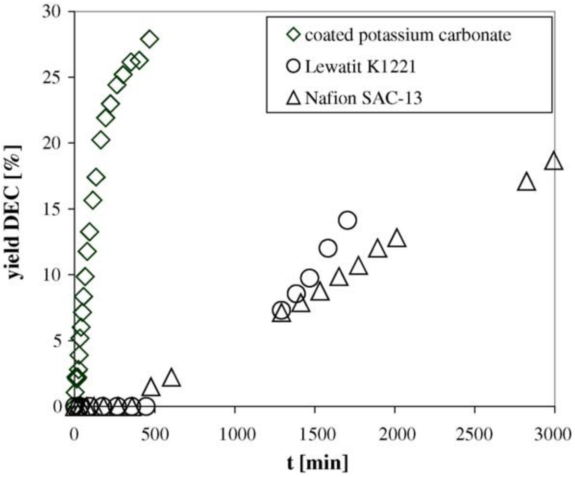

Fig. 4. Comparison of the performance of the best catalysts. $T = 348$ K, catalyst concentration = 60 g/dm^3, weight ratio DMC to EtOH = 1:1.

Table 2
Pre-exponential (frequency) factors and the energy of activation for reactions 1 and 2 and for the three most active catalysts

Catalyst	$k_{1,0}$ (mol/s g)	$k_{2,0}$ (mol/s g)	$E_{A,1}$ (kJ/mol)	$E_{A,2}$ (kJ/mol)
Coated K_2CO_3 (5% PEG)	9.7073×10^{-2}	2.4948×10^{-2}	17.82	16.78
Lewatit K1221	7.1358×10^{4}	4.5975×10^{5}	67.71	73.98
Nafion SAC-13	2.7659×10^{6}	2.7858×10^{10}	77.06	107.57

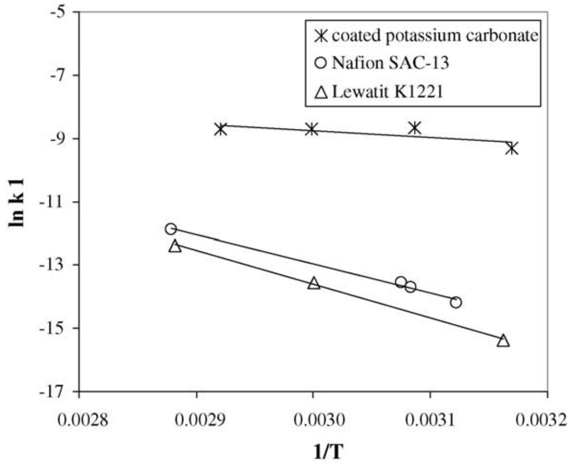

Fig. 5. Rate constants for reaction 1 vs. temperature for the three most active catalysts.

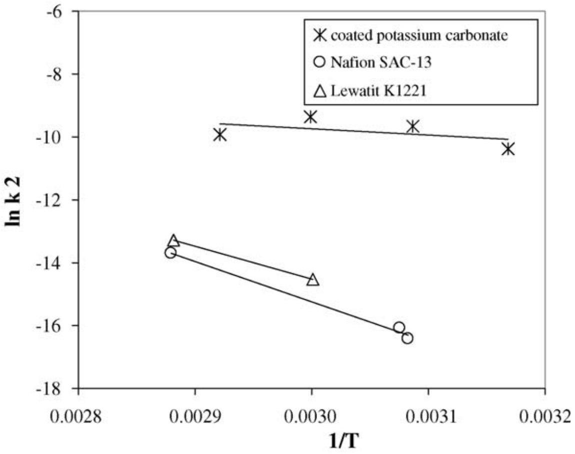

Fig. 6. Rate constants for reaction 2 vs. temperature for the three most active catalysts.

$K_1 = 1.7408$, and for the second $K_2 = 0.3981$. As can be seen, reaction 1 is much faster than reaction 2. Furthermore, the concentration of EMC, passing through a maximum, remained high in the reacting mixture. Therefore, it is reaction 2, which is a rate-limiting step for the whole transesterification process.

4. Conclusions

Modified potassium carbonate, Lewatit K1221 and Nafion SAC-13 are proved to be the most active heterogeneous catalysts for the transesterification of dimethyl carbonate with ethanol. For these catalysts kinetic equations were estimated based on the Arrhenius relation. It is found that the reactions studied are elementary and that reaction 2 is a rate-limiting step. From the standpoint of the possibility of incorporating these catalysts into the structured packing MULTIPAK in a reactive distillation column, the most promising catalyst seems to be Lewatit K1221. During the catalytic tests the reacting mixture always remained clear and the results were reproducible. It was also found that Lewatit can be easily regenerated without any adverse effect on its activity. This catalyst is relatively cheap, readily available and, according to the manufacturer's data, thermally stable up to 403 K. Ion-exchange resins of this type are widely used in structured packings of industrial columns. Compared with Lewatit K1221, Nafion SAC-13 is by far more expensive, and its industrial application always carries the risk that the catalyst will be washed off its silica support. On the other hand, the potential use of the most active catalyst—the modified potassium carbonate in the structured packing requires further studies concerning its mechanical strength and chemical resistance, as well as an efficient regeneration procedure.

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