ORIGINAL ARTICLE

Preparation of nanostructured KOH/activated coal catalyst for vinylation of morpholine

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ABSTRACT

In this paper catalytic vinylation of morpholine with the acetylene at atmospheric pressure with formation of N-vinylmorpholine has been investigated. The influence of nature of catalysts and solvents on vinylation of morpholine in homogeneous conditions is studied. DMSO is chosen as optimal solvent and the effect of temperature influence and amount of catalyst for the vinylation process are investigated. Role of high-basic system KOH/DMSO and its nucleophilic interaction with acetylene has been shown and kinetics of morpholine vinylation is investigated. Heterogeneous catalytic vinylation of morpholine with acetylene in presence of catalysts KOH/AC-L and nanostructural KOH/activated coal has been investigated. Nanostructured KOH/activated coal catalyst proves more effective in the formation of N-vinylmorpholine.

Keywords: Nanostructured catalyst; Activated coal; Acetylene; Morpholine, vinylation; N-vinylmorpholine

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INTRODUCTION

Interest in the development of catalytically active porous materials with uniform dimension of pores, which allow diffusing specially difficulty molecules of reagents in their inner ranges, has increased lately [1,2]. Problem of sol-gel synthesis of nanostructural polymer template inorganic materials is connected with regulation of composition of reacting components and conditions of process promoting to formation of structure with given characteristics, such as functional properties, porosity, specific surface, mechanical and thermal stability [3,4].

At present interest to mediums with super high basicity and their using in organic synthesis has increased [5,6]. Phenomenon of super-basicity is consists of totality of two or more bases where activity of anion is increased owing to transformation cation in volumetrical complex cation with delocalization charge.

Application of super-basicity mediums alkali-dipolar aprotonical solvents in chemistry of acetylene has allowed optimizing conditions to obtain some vinyl- and divinil chalcogenides, their substituted nitrogen containing derivatives, N-vinyl derivatives and so on. Insufficient investigation even such system, as alkali-dimethyl sulfoxide (DMSO) didn't allow explaining catalytical activity of alkalis and influence of different factors on vinylation reactions. Discussion of literature materials devoted to obtain and using nanostructural catalytic systems and also to synthesis, properties and using of N-vinyl-compounds has shown the aromatical and heterocyclic amines including morpholine are insufficiently investigated. Preparation of N-vinyl compounds on the base of morpholine by using heterogeneous nanostructural systems are actual problem of modern organic chemistry.

In this work, nanostructured KOH/activated coal catalyst is prepared using ultrasonic dispersion process. The mechanisms, kinetics and regularities of the preparation of N-vinyl compounds with the presence of this catalyst are investigated.

EXPERIMENTAL PART

Preparation of heterogeneous catalysts

Vinylation of morpholine is carried out using activated coal catalyst impregnated with KOH. This catalyst is prepared by the following method: 21.43 g KOH is added to 50 ml of water to get 30% solution. In glass tube with 50 g of activated coal (type AC-L, Angren) is added solution of KOH prepared in advance and the mixture slowly heated at constant mixing. Obtained catalyst is dried within 3 h at 1500°C to avoid from impurities. Dimethylsulfoxide (DMSO) and dimethylformamaide (DMFA) are used as a solvent without any purification.

Method of obtain of nanostructural systems

Method is consisted of 6 glasses are taken and prepared samples at different ratios of initial components and they are precipitated. After 10, 20, 30, 40 and 60 min the liquid is poured out and the fractions of catalyst suspensions are investigated under optical microscope to determine the dimensions of particles. The obtained samples are dried at desired temperature and the yield of each fraction is determined. According to the results, density of distribution is calculated as ratio content of each fraction to difference internal limited dimensions:

$$P=m/(a2-a1)$$

Where m-mass of fraction, g; a2-dimension of large particles, m; a1-dimension of small particles, μm.

Ultrasonic treatment of the obtained samples

To decrease of dimensions of activated coal particles before fractionation samples are undergone to ultrasonic treatment using dispergator USDN-1T. Each fraction of activated coal samples has been treated by ultrasonic in regime 0.6 A, 38 kG during 3 min with interval 30 sec in ice cooled water.

Microscopical investigations of the obtained samples

Microscopical investigations are carried out using optical microscope MBI-6 in passing and polyarizated light. Samples are heated within 603 K and the changes during their thermal treatment process are fixed. Electron-microscopical (EM) investigations are investigated in REM-200 in scanning regime after coating with silver in vacuum post VUP-4K.

Centrifugation is carried out within 2500-3000 speed during 3-5 min and particles with diameter 3-7 μm are remained in centrifuge. Suspensions of samples with particles diameter 3-5 μm are undergone ultrasonic treatment. Precipitation of large particles is undergone to

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sedimentational fractionation. Obtained samples with nanosized particles are used as catalyst for morpholine vinylation in vertical reactor of continuous action.

Thin layer chromatography (TLC) of the reaction products is carried out on «Silufol-UV-25» plates with following systems (in volume ratios):

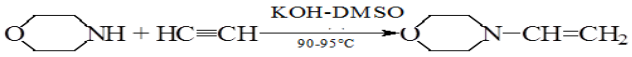
1. Benzene: ether-methanol–10:5:2 (System 1).
2. Benzene: ether-ethanol–10:6:2 (System 2).

In all cases the chromatograms are displayed using crystalline iodine camera.

RESULTS AND DISCUSSION

Vinylation of morpholine in homogeneous conditions

Reaction of morpholine vinylation in super-basic systems such as KOH-DMSO and KOH-DMFA is carried out in accordance with the following scheme:



The influence of the solvent nature on vinylation process is carried out (Figure 1).

The obtained results show that vinylmorpholine are formed with low yield (about 2%) without using any solvents. In the presence of DMFA reaction product with yield 8% to 10% is obtained with duration of reaction 4 h and temperature 700°C. When DMSO is used as a solvent, the yield of product is increased to 22%. In all cases yield of obtained product is increased with increasing of reaction time until 4 h, but there is no practically change in case of absence of solvent.

In order to investigate the effect of catalyst amount on vinylation process, this reaction is carried out in the presence of different concentrations of KOH (10% to 20% from initial morpholine) in the presence of DMSO. The obtained results are shown in Figure 2.

The obtained results show that amount of catalyst have influence on yield of synthesized N-vinylmorpholine and the yield of reaction product is also increased by increasing its amount to 10% to 15%. However with increasing of its quantity has negatively influenced on the formation of N-vinylmorpholine that is caused by increasing of quantity of forming oligomers and polymer and correspondenlyte formation of resinous compounds in vinylation reaction. Thus the optimal quantity of catalyst (KOH) for morpholine ninylation equals 15%.

Also, in this work the influence of the catalyst nature on vinylation process is also investigated. Hydroxides such as LiOH, NaOH and KOH are used as catalysts in the form of powder (Table 1).

Obtained results have indicated that from used catalysts KOH is very active and correspondently optimal–by its presence yield of N-vinylmorpholine reaches to 23%.

Kinetics of morpholine vinylation by acetylene at atmospheric pressure in presence of KOH-DMSO system is investigated. Obtained results are presented in Table 2.

On the base of obtained data graph of dependence of lg Won 1/T is constructed (Figure 3); on its base the energy of activation (Ea=55.6 kJ/mole) of morpholine vinylation has been calculated.

Morpholine vinylation in heterogeneous conditions

Heterogeneous vinylation of morpholine in presence of catalyst KOH impregnated on granulated activated coal in quantity 30%

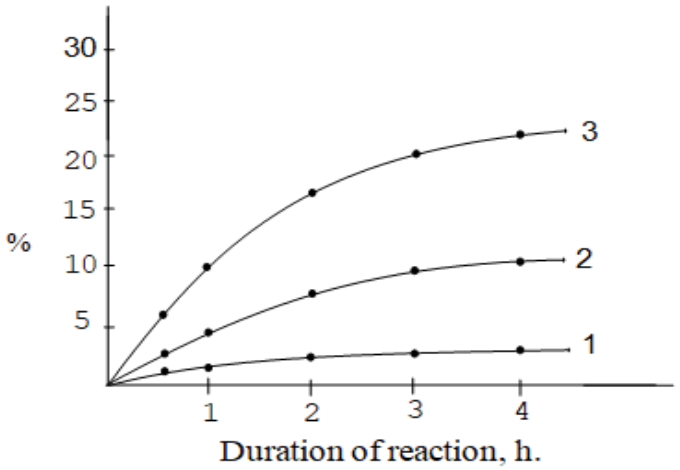


Figure 1: Kinetic curves of morpholine vinylation in presence of different solvents (quantity of KOH-15%; temperature 700°C): 1-without solvent; 2-DMFA; 3-DMSO.

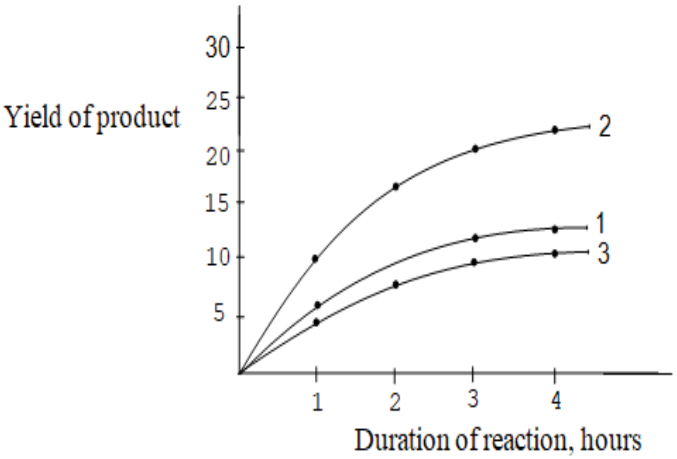


Figure 2: Influence of catalyst amount (mass %) on vinylation of morpholine (temperature – 70°C to750°C): 1-10; 2-15; 3-20.

Table 1: Effect of catalysts nature on N-vinylmorpholine yield (amount of catalyst is 15% from morpholine mass, temperature-900□).

Catalyst	Yield of N-vinylmorpholine (%)
LiOH	16,6
NaOH	19,4
KOH	23,0

from mass of support in following reactor has been investigated. It is determined that in these conditions also N-vinylmorpholine is obtained. Mechanism of vinylation is following in morpholine between hydrogen atom at nitrogen and oxygen atom of KOH interaction has carried out with formation of hydrogen bond. And changing of potassium ions with hydrogen ions has carried out with establishment of equilibrium at dissociation. Then nucleophilic addition morpholine ion to acetylene with formation of carbanion has carried out. Forming carbanion has reacted with morpholine molecule with formation of N-vinylmorpholine and its ion which has continued vinylation process.

In order to optimization of conditions of morpholine vinylation the influence of temperature has been investigated. As known its influence play key factor of product yield of vinylation in heterogeneous conditions. The obtained results are presented in Table 3. The results showed that with increasing temperature in the range 100°C to 255°C, the yield of N-vinylmorpholine is also increased from 10.0% to 31.7% correspondingly. Further increasing of temperature caused to sharp decreasing of vinylation product due to side processes (Table 3).

Table 2: Kinetic data vinylation of morpholine with acetylene at atmospheric pressure.

Duration of reaction, hours	Yield of N-vinylmorpholine, (mol/l)	Middle rate of reaction, w	
		%/hour	mol/l♦h
	Temperature-60		
2	0,2	1,0	0,10
4	0,8	2,0	0,20
6	1,0	1,7	0,17
8	1,4	1,75	0,18
	Temperature-700		
2	0,5	2,5	0,25
4	1,3	3,2	0,33
6	1,5	2,5	0,25
8	1,6	2,0	0,20
	Temperature-800		
2	1,0	5,0	0,50
4	2,2	5,5	0,55
6	2,5	4,2	0,42
8	2,5	3,1	0,31
	Temperature-900		
2	1,2	6,0	0,60
4	2,5	6,2	0,62
6	2,6	4,3	0,43
8	2,4	3,0	0,30

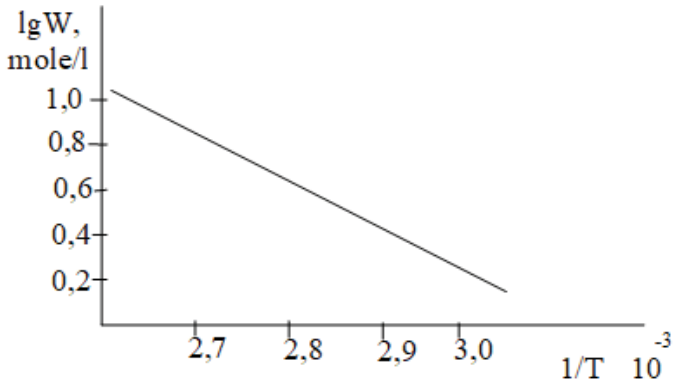


Figure 3: Dependence of lgW on 1/T of vinylation reaction of morpholine.

Table 3: Temperature effect on vinylation of morpholine with acetylene at atmospheric pressure.

No	Temperature ( )	Yield of N-vinylmorpholine, mass (%)	No p/p	Temperature ℃	Yield of N-vinylmorpholine, mass (%)
1	65–70	-	6	210–215	23,2
2	100 –105	10,6	7	225–230	25,0
3	120–125	18,4	8	250–255	31,7
4	140–160	19,8	9	280–285	19,0
5	180–190	21,5	10	290–300	12,0

Obtain of nanostructural matrixes of activated coal

In order to develop of catalytic systems for reaction of morpholine with acetylene some nanostructural matrixes of activated coal are obtained. Initial dimensions of particles of activated coal using as supports of catalyst for synthesis of N-vinylmorpholine by the reaction of morpholine with acetylene have been determined. Initial demensions of activated coal are in range 1-3 μm (Figure 4).

In this study, dispersion analysis is carried out by microscopic method. To decrease of dimension of activated coal particles before fractionation samples of coal are undergone to ultrasonic treatment. For this water suspension of activated coal (150 ml of water 5 g of activated coal) is obtained which is undergone to ultrasonic treatment in regime 0.6 A, 38 kg in during 60 min. Through every 3 min process is stopped and glass with suspension is cooled during 30 sec by ice water. Probes are selected through 10, 20, 30, 40 and 60 min and dimensions of particles by method microscopy have been determined.

Figure 5 shows microscopic photo of samples of activated coal treated in ultrasonic dispergator with 1 μm scale are presented. Analysis of obtained data has shown that dimensions of dispergated particles of activated coal equal 700 nm to 900 nm. Sedimentation fractionation processing of activated coal particles during 20, 30, 40 and 60 min has shown that their dimensions have significantly changed. The results are given in Table 4.

Thus, the results of dispersion analysis using microscopy method have shown that dispergation of suspension of activated coal in water by Ultrasonical dispergator USDN2T, it is possible to achieve dimensions of activated coal particles to 100 nm to 150 nm during 60 min. Further increasing of dispergation time would not influence on their particle sizes.

Reaction of acetylene with morpholine in presence of nanostructural catalyst on the base of activated coal

Heterogeneous catalytical reaction of morpholine with acetylene

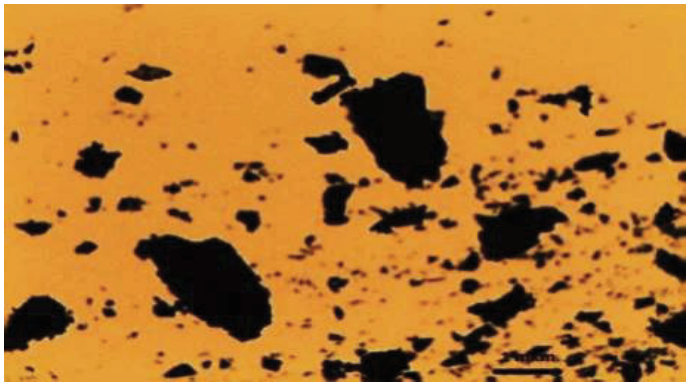


Figure 4: Microscopic photo of initial activated coal particles.

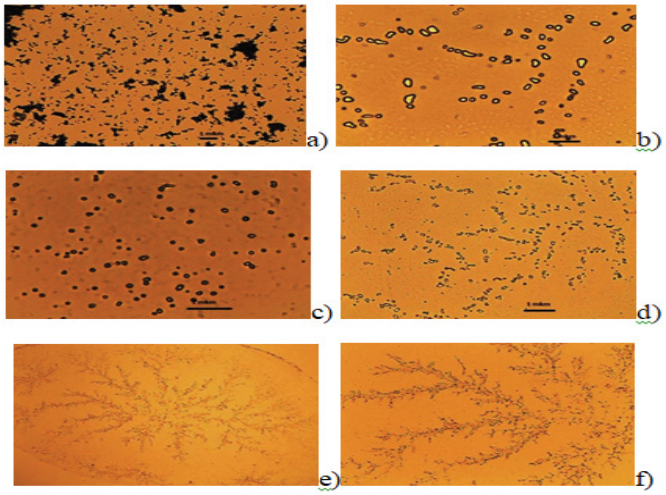


Figure 5: Microscopic photos of activated coal particles after ultrasonical dispersion during (min): a-10; b-20; c-30; d-40; e, f- 60.

Table 4: Influence of despergation time on dimensions of activated coal particles.

Time of despergation, min	Dimensions of activated coal particles, nm
-	1-3 mkm
10	700-900 nm
20	500-750 nm
30	300-550 nm
40	200-320 nm
60	100-150 nm

Table 5: Effect of temperature on N-vinylmorpholine yield using nanostructured activated coal/KOH (Dimension of particles is 100 nm to 150 nm).

Temperature of reaction ( )	Yield of N-vinylmorpholine, mass (%)
160	52,3
180	57,8
200	59,4
220	64,7
240	68,5
260	65,2
280	60,4

in presence of catalyst on the base of nanostructural activated coal with dimentions of particles 100nm to 150 nm has been investigated. Conditions of reaction process are analogical as shown above system (in the presence of catalyst activated coal and content of KOH in composition of this catalyst system is 30 mass%). The obtained results of the investigation are presented in Table 5.

Results of investigation indicated that in the case of temperature interval 160°C to 280°C, it has significant influence to the yield of N-vinylmorpholine with maximum yield (68.5%) at 240°C. Further increase of temperature (more than 240°C) negatively influenced on its yield.

Thus, heterogeneous catalytical vinylation of morpholine with acetylene in presence of catalysts on the base of activated coal AC-L/KOH and nanostructural activated coal/KOH has been investigated. The formation of N-vinylmorpholine in both cases was founded. It was observed the activity of catalyst on the base of nanostructural activated coal on vinylation process is higher than catalyst on the base of commercially activated coal, type AC-L.

CONCLUSION

It has been investigated the reaction of morpholine with acetylene in homogeneous and heterogeneous conditions. The influence of temperature and amount of catalyst for the vinylation of morpholine is determined; conditions of its vinylation are optimized; and also kinetics of this process is investigated and value of the energy of activation is determined. Facile preparation of heterogeneous nanostructural catalytic system on the base of activated coal has been elaborated and vinylation of morpholine with acetylene in heterogeneous conditions is investigated. The yield of N-vinylmorpholine using of nanostructural activated coal/KOH was achieved to 68.5%.

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CONFLICT OF INTEREST

No conflict of interest.

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