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INVESTIGATION OF CATALYTICAL REACTION OF ACETYLENE WITH MORPHOLINE

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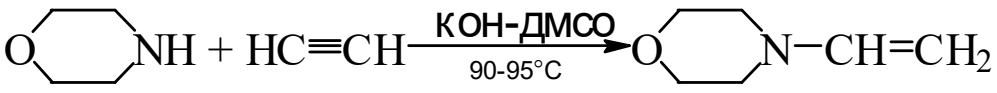
Abstract:Method of N-vinylmorpholine synthesis by vinylation of morpholine was elaborated in homogeneous and heterogeneous conditions and also in the presence of nanostructural catalysts on the base of activated coal and potassium hydroxide.
Key words: Morpholin, heterogeneous catalyse, nanostructural catalysers, vinylation, kinetics of this process, energy of activation.
Аннотация:Разработан метод синтеза N-винилморфолина винилированием морфолина в гомогенных и гетерогенных условиях, а также в присутствии наноструктурных катализаторов на основе активированного угля и гидроксида калия.
Ключевые слова:Морфолин, гетерогенный катализ, наноструктурный катализ, винилирование, кинетика процесса, энергия активации.

In last years a great progress has been achieved in obtain and investigation of properties of modified nanostructural heterogeneous catalysts for vinylation of organical compounds having in their composition an active atoms of hydrogen[1].

It is known that vinyl compounds are used in different braches of industry and agriculture and ther are synthesized by different methods, among which by importance and actuality is vinylation of corresponding organical compounds by action on them by acetylene [2-4].

From above-mentioned reaction of vinylation of morpholine in the presence of KOH with using super base systems such as KOH-DMSO and KOH-DMF (DMSO-dimethylsulfoxide; DMF-dimethylformamide) has been investigated and it was determined that reaction is carried out according to following scheme:



At this influence of solvent nature on carring out of this reaction was investigated. Experimental results have shown that in absence of dipolar aprotonical solvents vinylmorpholine also has been obtained but in small quantities (before 2,0 %). In solution of DMF at 70 °C and duration 4 h. aproduct was obtained with yield 8-10 %. At substitution of DMF and DMSO the yield of forming N-vinylmorpholine has increased in high degree (at the same conditions as at using DMF the maximal yield of product was equaled22 %). In all cases yield of N-vinylmorpholine has been increased with increasing of reaction duration (1-4 h.).

Influence of quantity of catalyst on vinylation was investigated by chanding it's quantity in reaction system from 10 to 20 % from mass of morpholine in the presence of solvent - DMSO. Obtained results have shown that quantity of catalyst has influenced on the yield of

forming N-vinylmorpholine with increasing of it's contant in interval 10-15 % yield of product also was increased. The following increasing of catalyst quantity negatively influenced on formation of N-vinylmorpholine what canbe explained by following fact – at content of KOH in system more 15 % quantity of oligomers or polymers has increasing of resinous compounds during reaction of vinylation. Correspondenly it is possible to conclude, that optimal contance of catalyst (KOH) for vinylation of morpholine by acetylene is 15 mass.%.

Also it was investigated influence of nature of using catalysts hydroxides LiOH, NaOH and KOH (in solid state) on the vinylation of morpholine. It was determined that in all cases N-vinylmorpholine was formed but KOH was the most active catalyst – in it's presence yield of N-vinylmorpholine was equaled 23,0% (in the presence of LiOH or NaOH yield of product was equaled 16,6 and 19,4% correspondenly).

Kinetics of vinylation of morpholine with acetylene at atmospheric presence in the presence of system KOH-DMSO and different temperatures and durations of reaction carring out has been investigated. On the base of obtained kinetical data the graph in coordinates lgW-1/T has been constructed (figure 1) and also value of the activation energy (E) of vinylation of morpholine has been calculated which was equaled 55,6 kDj/mole.

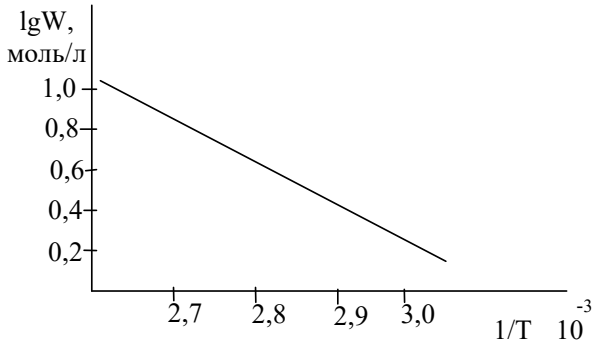


Fig. 1. Dependence of lgW from 1/T for reaction of morpholine vinylation.

Also heterogeneous – catalytical vinylation of morpholine in running reactor in the presence of heterogeneous catalyst (KOH) beared on granulated activated coal (30% from mass of bearer) has been carried out. It was determined that in these conditions also N-vinylmorpholine was formed.

For optimization of conditions of morpholine vinylation influence of temperature on it's carring out in heterogeneous system that is on yield of the forming at this N-vinylmorpholine has been investigated. Obtained results are presented in table 1.

Table 1

Влияние температуры на винилирование морфолина

№	Temperature, ^{0}C	Yield of N-vinylmorpholine, %	№	Temperature, ^{0}C	Yield of N-vinylmorpholine, %
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

Obtained results have shown that with increasing of temperature in interval 100-255^{0}C yield of forming N-vinylmorpholine was increased from 10,0 to 31,7% correspondenly. Than increasing temperature above 225 ^{o}C has carried out to shar decreasing of yield of synthesised

compound and for example at temperatures 280-285^{0}C and 290-300^{0}C it was equaled 19 and 12% correspondenly.

Structure of synthesised N-vinylmorpholine was prowed by method of IR-spectroskopy.

In IR-spectrum of N-vinylmorpholine there ar following bands: 1520-1610 sm^{-1} –valent vibrations C=C bond of vinyl group; 1050-1250 sm^{-1}valent vibrations C-O-C fragment of morpholine molecule; 2950-2960 sm^{-1}simmetrical and unsimmetrical vibrations of methylenic group (-CH_2-).

Determined experimental data have shown that catalyst KOH/activate coal has an enough activity at synthesis of N-vinylmorpholine by heterogeneous-catalytical vinylation of morpholine by acetylene.

Dor development of catalytical systems for reaction of acetylene with morpholine some nanostructural matrixes of activated coal were obtained which were used as bearer of catalysts. It was determined influence of initial dimensions of obtained activated coal on carring out synthesis of N-vinylmorpholine. The optimal dimensions of using of activated coal were equaled 1-3m.

Dispersion analysis was carried out by method of microscopy. With in of decreasing of dimensions of particles of activated coal sample be for fractionation were undergone to ultrasonic treatment, for which water suspension of activated coal has been prepared (150 ml H_2O:5g of activated coal) and than it was undergone to ultrasonic treatment in regime 0,6 A; 38 kGc during 60 min. Through every 3 min the treatment was stoped and glass with mixture was cooled in during 30 sec. in water. Through 10, 20, 30 and 60 min. probes were separated and dimensions of particles of activated coal were determined by method of microscopy.

Analysis of obtained results has shown that dimensions of dispergated particles of activated coal were equaled 700-900 nm.

Sedimension fractionation of particles of activated coal during 20, 30, 40 and 60 min. has shown that in investigated intervals of time their distribution by dimension has changed markedly.

Dimensions of particles of obtained fraction after 20 min. dispergation were equaled 500-750 nm, and after intervals 30, 40 and 60 min. of dispergation they were equaled 300-350; 200-320 and 200-250 nm correspondenly. Obtained results are presented in table 2.

Table 2
Influence of dispergation time on dimensions of particles
of activated coal

Time of dispergation, min.	Dimensions of particles of activated coal, nm
-	1-3 мкм
10	700-900
20	500-750
30	300-550
40	200-320
60	100-250

Such the results of dispersion analysis by method of microscopy have shown that in installation of ultrasonic dispergater UZDH2T by dispergation of suspension of activated carbon by water it is possible to active of dimensions of particles of activated coal to 200-250 nm durining 60 minutes. Increasing of dispergation time didu't influenced on dimensions of obtained particles.

Heterogeneous – catalytical reaction of acetylene with morpholine in the presence of catalyst on the base of nanostructural activated coal with dimensions of particles 200-250 nm has been investigated. Conditions of carring reaction were the same as in the presence of catalyst activated coal/KOH. Quantity of KOH in the presence of catalyst was equaled 30 mass.%. Influence of temperature on reaction of acetylene with morpholine in heterogeneous conditions in the presence of catalyst on the base of activated coal winy dimension of particles 200-250 nm has been determined.

It was determined that in this case also N-vinylmorpholine was synthesised. Obtained results are presented in table 3.

Table 3
Influence of temperature on yield of N-vinylmorpholine in the presence of catalyst activated coal /KOH with particles dimensions of activated coal 200-250 nm

№	Temperature of reaction, °C	Yield of N-vinylmorpholine, %
1	160	24,3
2	180	27,0
3	200	29,5
4	220	34,4
5	240	38,2
6	260	25,6
7	280	20,4

Obtained results have shown that in this case temperature in interval 160-180^{0}C in gratedegree has influenced on the yield of forming N-vinylmorpholine. In investigated interval of temperatures yield of N-vinylmorpholine was carried out through maximum (38,2%) observed at 240^{0}C. With increasing of temperature in interval 160-240^{0}C yield of product has increased from 24,3 to 38,2%. The following increasing of temperature has negative influence of yield of N-vinylmorpholine for example it's yield at 260 and 280^{0}C was equaled 25,6 and 20,4% correspondenly.

Analysis of obtained data has shown that for reaction of acetylene N-vinylmorpholine in the presence of catalyst an the base of nanostructural activated coal with dimensions of particles 20-250 nm the optimal temperature was 240^{0}C and at this yield of N-vinylmorpholine was equaled 38,2%.

Such heterogeneous – catalytical reaction of acetylene with morpholine in the presence of catalysts: activated coal AV-L/KOH and nanostructural activated coal/KOH has been investigated. It was shown that in both cases N-vinylmorpholine was obtained. Activity of catalyst on the base of nanostructural activated coal was higher in comparasion with catalyst on the base activated coal AV-L.

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