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Gas-Phase Vinylation of *N*-Methylacetamide

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Abstract—Catalysts for selective gas-phase vinylation of *N*-methylacetamide with acetylene were studied. These catalysts were obtained by applying to wide-pore silica gel of the CdO–K_2O–ZnO system or applying to commercial Al_2O_3 of the CdO–K_2O and CdO–K_2O–ZnO systems.

N-methyl-*N*-vinylacetamide, a perspective monomer for preparing such a highly basic polymer as polyvinylamine, as well as other polymers and copolymers, is still hardly available because of the lack of economical methods of its synthesis. Known methods of direct liquid-phase vinylation of amides with acetylene in the presence of their potassium derivatives or cadmium acetate [1, 2] proved ineffective with the simplest amides, such as *N*-methylacetamide (**I**).

Gas-phase vinylation with acetylene suggests its thermal or catalytic activation. Pyrolysis of acetylene commences at temperatures above 500°C and is effectively catalyzed by such metals as V, W, Ni, Zr, Nb, and Ta. At 580–680°C, acetylene converts primarily into benzene and toluene [3]. Aromatic hydrocarbons formed by pyrolysis of acetylene are precursors of polyaromatic polymers, pyrolized coke, or soot [4–12]. These processes should be taken into account in conducting thermal and heterogeneous catalytic reactions of acetylene with various reagents.

Gas-phase vinylation of acetamides have scarcely been documented. The patent [13] describes the heterogeneous catalytic gas-phase vinylation with acetylene of 2-pyrrolidone, 2-piperidone, and amide **I**. The catalysts used were potassium (sodium, lithium) aluminates, stannates, zincates, vanadates, titanates, beryllates, bismuthates, and lanthanates, as well as mixtures of metal oxides, applied to charcoal. The reactions were performed at 290–360°C in a flow system.

The easiest vinylated are 2-pyrrolidone and 2-piperidone. On the best catalysts, such as $KAlO_2$, K_2AlO_3, K_4ZrO_4, K_2ZnO_2, and K_2O–CdO on charcoal, their conversions at 290–310°C attain 30–40%, and the selectivity of the reactions is very high (the yields of *N*-vinyl derivatives per consumed amide are 90–95%). Amide **I** is less effectively vinylated under these conditions: At 350–360°C (catalyst K_4ZrO_4–S), the conversion is 6%, and the yields of *N*-methyl-*N*-vinylacetamide (**II**) are 6% per taken and 40–50% per consumed amide.

The direct synthesis of *N*-vinylphthalimide via gas-phase reaction of acetylene with phthalimide proved to be the most effectively catalyzed by zinc and cadmium oxides applied to charcoal separately or together [14]. On the best catalyst at 270–280°C, the yield of *N*-vinylphthalimide was 83% (the conversion of phthalimide was not given).

The aim of the present work was searching for more active catalysts for gas-phase vinylation of amide **I** with acetylene. To this end, we checked combinations of potassium, zinc, and cadmium oxides, as well as cesium fluoride and lanthanum triflate on various supports.

Thermally, amide **I** does not react with acetylene up to 500°C (acetylene begins to convert into aromatic hydrocarbons after 300°C).

For gas-phase vinylation of amide **I** we developed several types of catalysts on the basis of available supports: silica gel, γ- and β-aluminas, as well as natural and synthetic zeolites. First we ranked the supports by moisture capacity. This value allows estimation of the amount of catalyst solution fully absorbed by the support. The moisture capacities (Table 1) are directly related to the porosity of the supports: the higher the moisture capacity, the larger the pore size. Some supports with low moisture capacities were not used.

The conditions and results of the reactions of amide **I** with acetylene are listed in Table 2 (horizontal reactor) and Table 3 (vertical reactor).

As seen from Tables 2 and 3, the catalyst 11.2% CdO + 2.8% ZnO on an AB-17 ferrosilicate support catalyzes vinylation of amide **I** with acetylene at 300–400°C. As the amount of the catalyst is increased from 3 to 10 g, the conversion of amide **I** at 300°C increases from 0.7 to 4%, and the yield of vinylation product **II** increases from 0.3 to 3.2% at a selectivity of 96% [Table 2, run nos. 1 (1), 1 (2), 1 (3), 1 (4), 2 (1), 2 (2), 2 (3), and 3]. The conversion is increased if a 9-fold molar excess of acetylene is used. Above 400°C, acetylene strongly pyrolyzes and cokes the catalyst. The AB-17 support is intrinsically inactive in this reaction at 300°C.

The catalysts on the basis of a TsVM–Ti(IV)O_2 (20%) commercial synthetic zeolite with applied CdO (10%), ZnO (10%), or their mixture [CdO (11.2%) and ZnO (2.8%)] proved inactive in the reaction studied at 300°C (Table 2, run no. 4 and Table 4, run nos. 7 and 8). The catalysts 11.2% CdO + 2.8% ZnO on a natural zeolite (clinoptilolite), as well as TsVM-Al_2O_3(10%) and TsVM-Al_2O_3 (35%) zeolites, proved almost inactive. In this case, the conversion of compound **I** is no higher than 2.4% at 300–350°C [Table 2, run no. 5 and Table 3, run nos. 6 (1) and 6 (2)].

The support γ-Al_2O_3 (OPP-2) was found to be more perspective. An active catalyst is formed by applying 10% of CdO to this support. The conversion of amide **I** on it at 300°C is 4%, and the yield of vinylation product **II**, 3.2% (selectivity 91%). The conversion of substrate **I** on the catalyst prepared by applying 10% of ZnO to this support is 1.6%, the yield of product **II** is 1.8%, and the selectivity is 92%. Better results were obtained with the catalyst prepared by applying to this support a mixture of CdO and ZnO in a 4 : 1 weight ratio (11.2 and 2.8%, respectively). The conversion of amide **I** is 5.3%, and the yield of vinyl derivative **II** is 4.8% at a selectivity of 91% (Table 3, run nos. 9–11). These results (in terms of the yield of compound **II**) are close to those in the patent [13] but obtained at a lower temperature (300°C).

Silica gel-1 with a high moisture capacity (113%) proved a prospective support. With On the catalyst obtained by applying 10% of CdO to this support, the conversion of amide **I** at 300°C is 6.2%, and the yield of target product **II** is 5.5% at a selectivity of 91% (Table 3, run no. 12). The catalyst 10% ZnO + silica gel-1 proved too active. With this catalyst, an exothermic effect is observed already at 260°C. Therewith, substrate **I** decomposes completely (Table 3, run no. 13). Thermal polymerization of acetylene and catalyst coking also enhance. The most active catalyst was prepared by applying a mixture of CdO and ZnO (4 : 1) to silica gel-1. It begins to work already at 250°C. At this temperature, the conversion of amide **I** is 5.4%, and the yield of vinyl derivative is **II** is 3.8%, and the selectivity is 87%. At 300°C, the conversion of substrate **I** increases to 13.7%, and the yield of vinyl derivative **II** attains 7.4%. However, the selectivity of the process decreases (53%). Apparently, product **II** decomposes under the action of zinc oxide. These results surpass patent data, and they were further improved by varying the ratio of cadmium and zinc oxides and introducing into the catalytic system potassium oxide or other active components.

Table 1. Catalysts of vinylation of amide **I**[a]

Support	Moisture capacity, %	Applied catalytic systems		
		CdO, 10%	ZnO, 10%	CdO–ZnO, 11.2 : 2.8%
AB-17 ferrosilicate	60	–	–	+
Clinoptilolite (natural zeolite)	14.0	+	+	+
TsVM–Ti(IV)O_2(20%) synthetic zeolite	27.4	+	+	+
TsVM–synthetic zeolite Al_2O_3(10%)	45	+	+	+
Zeolite 65% TsVM–35% Al_2O_3	52	–	–	+
Zeolite Na, K-erionite	48	–	–	–
OPP-2 support (Al_2O_3)	72	+	+	+
Silicagel-1, fine[b]	113	+	+	+
Silica gel-2, coarse	37.5	+	+	–
Zeolite β-Al_2O_3 (50%)	48	–	–	–
Granulated syntetic zeolite, NaX	49	–	–	–

[a] Sign "+" denotes supports used for preparing catalysts. [b] With addition of $(CF_3SO_3)_3La$ (1%) and CsF (10%).

Absolutely inactive in the reaction at 300°C proved lanthanum triflate (1%) or cesium fluoride (10%) on silica gel-1 (Table 2, run nos. 17 and 18). Cesium fluoride even inhibited acetylene pyrolysis: The catalyst underwent no coking in the course of the reaction, and one may probably make use of this property in designing more stable catalytic systems.

Table 2. Vinylation of amide **I** with acetylene (horizontal reactor, rate of amide **I** 1 ml/h)

Run no.	Catalyst; weight, g	T, °C	Amide **I**, g (mmol)	Amide **I**:C_2H_2[a]	C_2H_2 time, l/h	Contact time, s	Reaction time, s	Condensate weight, g	Conversion of amide **I**, %	Yield of compound **II**,[b] %
1 (1)	AB-17+CdO(11.2%)+ ZnO(2.8%); 3	300	0.25 (3.5)	1 : 6	1.8	11	1000	0.31	0.0	0.0
1 (2)	AB-17+CdO(11.2%)+ ZnO(2.8%); 3	350	0.15 (2.1)	1 : 6	1.8	10.5	600	0.25	1.2	0.9 (93.9)
1 (3)	AB-17+CdO(11.2%)+ ZnO(2.8%); 3	400	0.5 (6.8)	1 : 6	1.8	10	2000	0.5	2.4	1.8 (94.1)
1 (4)	AB-17+CdO(11.2%)+ ZnO(2.8%); 3	400	0.23 (3.1)	1 : 10	3.0	6	900	0.23	0.7	0.3 (96.8)
2 (1)	AB-17+CdO(11.2%)+ ZnO(2.8%); 6	300	0.25 (3.4)	1 : 2	0.6	24	900	0.25	1.6	0.9 (95.1)
2 (2)	AB-17+CdO(11.2%)+ ZnO(2.8%); 6	300	0.27 (3.6)	1 : 6	1.8	10	1000	0.27	2.6	1.8 (91.4)
2 (3)	AB-17+CdO(11.2%)+ ZnO(2.8%); 6	300	0.20 (2.7)	1 : 9	2.8	7	700	0.20	3.5	3.0 (90.0)
3	AB-17+CdO(11.2%)+ ZnO(2.8%); 10	300	0.29 (4.0)	1 : 9	2.8	5	1100	0.37	3.8	3.2 (96.0)
4	TsVM-Ti(IV)O_2 (20%)+ CdO(11.2%)+ ZnO(2.8%); 6	300	0.65 (8.9)	1 : 8	2.4	8	2300	0.64	0.0	0.0
5	Clinoptilolite- CdO(11.2%)+ ZnO(2.8%); 6	300	0.57 (7.8)	1 : 10	3.0	7	2000	0.48	0.5	0.21

[a] Molar ratio. [b] Per taken and reacted (in parentheses) amide **I**.

Table 3. Vinylation of amide **I** with acetylene [vertical reactor, rate of amide **I** 1 l/h, amide **I** : C_2H_2 molar ratio 1 : 6; C_2H_2 rate 1.8 l/h, contact time 7 s]

Run no.	Catalyst; weight, g	T, °C	Amide **I**, g (mmol)	Reaction time, s	Weight of condesate, g	Conversion of amide **I**, %	Yield of compound **II**,[a] %
6 (1)	TsVM-Al_2O_3(10%)+CdO(11.2%)+ ZnO(2.8%); 6	300	0.5 (6.8)	1800	0.5	0.6	0.4
6 (2)	TsVM-Al_2O_3(10%)+CdO(11.2%)+ ZnO(2.8%); 6	350	0.5 (6.8)	1800	0.57	0.3	0.2
7	TsVM-Ti(IV)O_2 (20%)+ CdO(10%); 6	300	2.2 (30.1)	9200	2.02	0.0	0.0
8	TsVM-Ti(IV)O_2 (20%)+ ZnO(10%); 6	300	2.0 (27.4)	8200	1.9	0.0	0.0
9	Al_2O_3 (OPP-2)+CdO (11.2%)+ ZnO(2.8%); 8.8	300	1.9 (26)	680	1.92	5.3	4.8 (91.1)
10	Al_2O_3 (OPP-2)+ZnO(10%); 8.65	300	1.9 (25)	6700	1.76	1.6	1.8 (92.2)
11	Al_2O_3 (OPP-2)+CdO (10%); 8.3	300	1.8 (23.9)	6300	1.79	4.0	3.2 (91.0)
12	Silica gel-1+CdO (10%); 6.5	300	1.8 (24.5)	6400	1.87	6.2	5.5 (90.6)
13	Silica gel-1+ZnO (10%); 7.4	260[b]	0.5 (6.8)	1800	0.47	100	0.0

Table 3. (Contd.)

Run no.	Catalyst; weight, g	*T*, °C	Amide **I**, g (mmol)	Reaction time, s	Weight of condesate, g	Conversion of amide **I**, %	Yield of compound **II**,[a] %
14	TsVM-Al_2O_3 (35%)+CdO (11.2%)+ ZnO (2.8%); 9.42	300	1.3 (17.0)	4500	1.26	2.4	1.2 (94.2)
15	Silica gel-1+CdO (11.2%)+ ZnO(2.8%); 7.1	300	1.16 (16.0)	4200	1.36	13.7	7.4 (53.4)
16	Silica gel-1+CdO (11.2%)+ ZnO(2.8%); 7.4	250–260	1.3 (18.0)	4700	1.29	5.4	3.8 (87.5)
17	Silica gel-1+$(CF_3SO_3)_3La$; 5.6	300	1.4 (18.0)	4900	1.31	0.0	0.0
18	Silica gel-1+CsF (10%);5.9	300	1.2 (16.0)	4200	1.29	0.0	0.0

[a] Per taken and reacted (in parentheses) amide **I**. [b] At this temperature, exothermic effect and complete decomposition of amide **I** are observed.

Table 4. Moisture capacities of catalytic systems[a]

Support	Moisture capacity, %	Applied components, %			
		K_2O, 10	CdO–K_2O, 10-5	CdO–K_2O, 15-10	CdO–K_2O–CsF, 10-5-1
Silica gel-1	113	+	+	+	+
OPP-3 (Al_2O_3)	94	–	+	+	–
A-64 (Al_2O_3)	82	+	+	+	+
Charcoal	173	–	+	–	–

[a] Sign "+" denotes supports used for preparing catalysts.

Table 5. Vinylation of amide **I** with acetylene [vertical reactor, support silica gel-1, amide **I** rate 1 ml/h, C_2H_2 rate 1.8 l/h, **I** :C_2H_2 molar ratio amide 1 : 6, 300°C]

Run no.	Catalyst (% of applied components); weight, g	Amide **I**, g (mmol)	Contact time, s	Reaction time, s	Weight of condencate, g	Conversion of amide **I**, %	Yield of compound **II**,[a] %
19[b]	CdO+K_2O (10–5); 7.0	1.3 (18)	7	4600	1.30	14.1	11.2 (96.2)
20[b,c]	CdO+K_2O (10–5); 6.7	1.3 (18)	7	4800	1.35	5.5	3.3 (91.0)
21[b]	CdO+ZnO (12.5–1.5); 7.2	1.5 (21)	7	5600	1.60	15.0	5.2 (63.3)
22[b,d]	CdO+ZnO (12.5–1.5); 7.1	0.9 (12)	7	3200	0.90	2.2	1.3 (88.9)
23[b]	K_2O (10); 7.1	1.4 (19)	7	5200	1.50	0	0 (0)
24[e]	CdO+K_2O (10–5); 10.4	1.2 (16)	9	4400	1.30	17.5	13.6 (78.6)
25[e]	CdO+K_2O+CsF (10–5–1); 10.1	1.5 (21)	9	5300	1.57	16.8	12.8 (73.8)
26[e,f]	CdO–K_2O (10–5); 10.3	1.4 (19)	9	5100	1.50	13.8	10.0 (83.6)
27[e,f]	CdO+K_2O–CsF (10–5–1); 10.1	1.3 (18)	9	4800	1.40	18.7	11.1 (67.5)
28[e]	CdO+K_2O (15–10); 10.3	1.1 (15)	9	4100	1.20	19.3	9.0 (47.7)
29[e]	CdO+K_2O+ZnO (10–5–1); 10.3	1.6 (22)	9	5700	1.70	18.0	16.0 (90.0)

[a] Per taken and reacted (in parentheses) amide **I**. [b] Reactor with an internal diameter of 12 mm and a reaction zone length of 120 mm. [c] The support was impregnated with KOH. [d] Reaction temperature 250°C. [e] Reactor with an internal diameter of 15 mm and a reaction zone length of 150 mm. [f] The support was impregnated with aqueous solutions of reagent mixtures.

Table 6. Vinylation of amide **I** with acetylene (vertical reactor)

Run no.	Catalyst (% of applied components); weight, g	Amide **I**, g (mmol)[a]	Reaction time, s	Weight of condensate, g	Conversion of amide **I**, %	Yiels of compound **II**,[b] %
30[c]	K_2O (10); 8.3	1.55 (0.20)	5600	1.06	0	0.0
31[d]	$CdO+K_2O$ (10–5); 11.7	1.28 (18)	4600	1.29	2.7	2.0 (92.3)
32[d]	$CdO+K_2O$ (15–10); 13.0	1.15 (16)	4100	1.21	77.8	24.1 (31.0)
33[d]	$CdO+K_2O$ (15–5); 13.0	1.29 (18)[e]	4600	1.29	1.6	1.0 (93.2)
34[f]	$CdO+K_2O$ (10–5); 11.93	1.06 (14.4)	3800	1.1	12.3	9.0 (80.9)
35[f]	$CdO+K_2O$ (15–10); 14.05	1.47 (20)	5300	1.5	4.1	3.5 (84.9)
36[f]	$CdO+K_2O+CsF$ (10–5–1); 13.93	0.95 (13)	3400	1.0	13.2	7.7 (76.3)
37[f]	$CdO–K_2O$ (15–5); 14.4	1.1 (15)	3975	1.2	15.5	13.2 (91.0)
38[f]	$CdO–K_2O–ZnO$ (15–5–1); 14.4	1.57 (21)	5662	1.65	16.0	13.8 (90.0)

[a] Amide **I** rate 1 ml/h, C_2H_2 rate 1.8 l/h, amide **I**$:C_2H_2$ molar ratio 1:6, contact time 11 s, reaction temperature 300°C. [b] Per taken and reacted (in parentheses) amide **I**. [c] Support OPP-2 alumina. [d] Support OPP-3 alumina. [e] Reaction temperature 250°C. [f] Support commercial A-64 alumina.

As seen from Tables 2 and 3, the activity of the catalyst correlates with the moisture capacity of the support, i.e. with its pore size. Supports with a high moisture capacity are wide-pore. The catalyst is the more active the larger is the pore size of the support. Moreover, the activity of the catalyst coorelates wuth the nature of the support whose surface forms chemical bonds with applied components. Thus, Zinc oxide on alumina is more active than cadmium oxide on the same support. At the same time, the opposite situation occurs with cadmium and zinc oxides on silica gel-1 (run nos. 10–13). Mixed catalysts ($CdO:ZnO = 4:1$) applied to alumina and silica gel-1, too, differ in activity (run nos. 9 and 14). It is these supports which we consider perspective for development of catalysts for gas-phase vinylation of amides.

The dependence of the reaction result of the catalyst pore size suggests that the vinylation of amides is diffusion-controlled. Therefore, the pore size of narrow-pore supports is expedient to increase, for example, by treatment with water vapor or by crushing. It is expedient to use wide-pore supports and to enlarge the area of contact of reagents with catalyst active centers. To this end, more active components may be applied and increase their amounts, thus increasing the length and width of the reaction zone.

Table 4 lists the characteristics of the catalytic system developed with account for the revealed regularities.

Tables 5 and 6 present the results of vinylation of amide **I** with acetylene on improved catalysts on the basis of potassium oxide.

Potassium oxide was formed on the surfaces of two wide-pore supports (silica gel and alumina) by impregnating with aqueous potassium nitrate followed by heat treatment. Pure potassium oxide is catalyticallly inactive (run no. 23).

The catalytic system 10% CdO + 5% K_2O was formed on the wide-pore silica gel-1 surface by applying, successively or simultaneously, aqueous solutions of cadmium acetate and potassium nitrate with subsequent heat treatment. The catalyst obtained by applying first cadmium oxide and then potassium oxide exhibited enhanced activity. At 300°C, the conversion of amide **I** attains 14.1%, and the yield of compound **II** is 11.2% at a selectivity of 96.2% (reactor 12 × 120 mm). With increased catalyst volume (reactor 15 × 150 mm), the reagent contact time increases from 7 to 9 s, which intensifies the reaction: At 300°C, the conversion of amide **I** is 17.5%, and the yield of vinyl derivative **II** is 13.6% at a selectivity of 78.6% (run nos. 19 and 24, respectively).

The catalytic system 10% CdO + 5% K_2O + 1% CsF on silica gel-1 is slightly less active. At 300°C, the conversion of amide **I** is 16.8%, and the yield of product **II** is 12.8% at a selectivity of 73.8% (run no. 25). The catalysts obtained by simultaneously impregnating supports with active components, too, proved active in the reaction studied (run no. 27). With increased amounts of active components on silica gel-1, a less selective catalyst was obtained. At a high conversion of amide **I** (19.3%), the yield of its vinylation product **II** and the reaction selectivity are low (9.0 and 47.7%, respectively) (run no. 28). The most effective and selective catalyst was obtained by applying to silica gel-1 a ternary catalytic system (10% CdO + 5% K_2O + 1% ZnO). In this case, the convesion of amide **I** is 18.0%, and the yield of vinyl derivative **II** attains 16.0% at a selectivity of 90% (run no. 29).

The catalytic system 12.5% CdO + 1.5% ZnO on silica gel-1 is much less active. At 300°C, the conversion of amide **I** is 15.0%, the yield of vinyl derivative **II** is 5.2%, but the selectivity is low (63%) (run no. 21, reactor 12×120 mm). As the reaction temperature is decreased to 250°C, the conversion of amide **I** and the yield of its vinylation product **II** fall.

The catalytic systems formed by successively applying aqueous solutions of cadmium acetate and potassium acetate to an OPP-3 wide-pore alumina and an A-64 commercial alumina. The resulting data privedeny are listed in Table 6. The catalyst on the basis of potassium oxide and OPP-3 is inactive (run no. 30). The catalyst 10% CdO + 5% K_2O on OPP-3 exhibits a low activity (run no. 31). The conversion of amide **I** is 2.7%, and the yield of vinyl derivative **II** is 2.0% (at a high selectivity of 92.3%). As the amount of the catalytic system 15% CdO + 10% K_2O on the OPP-3 support is increased, the reaction is sharply intensified. The conversion of amide **I** attains 77.8%, and the yield of vinyl derivative **II** is 24%. However, the selectivity of the reaction falls, probably, on account of thermolysis of substrate **I**. At 250°C, the conversion of amide **I** and the yield of its vinylation product fall (to 1.6 and 1.0%, respectively), whereas the reaction selectivity is high (93.2%) (run nos. 32 and 33). By applying CdO + K_2O = 15–10% to charcoal we failed to obtain an active catalyst for vinylation of amide **I**.

The catalyst 10% CdO + 5% K_2O on A-64 alumina proved active (Table 6). The conversion of amide and the yield of vinyl derivative **II** at 300°C are 12.3 and 9.0%, respectively (selectivity 80.9%). With increased amounts of active components (15% CdO + 10% K_2O), the effectiveness of the vinylation reaction decreases. The conversion of amide **I** and the yield of vinyl derivative **II** fall to 4.1 and 3.5%, respectively, at a selectivity of 84.9%. The catalytic system 10% CdO + 5% K_2O + 1% CsF on the same support is of moderate activity (Table 6). The most active catalysts were obtained by applying to A-64 the catalytic systems 15% CdO + 5% K_2O and 15% CdO + 5% K_2O + 1% ZnO. In the first case, the conversion of amide **I** and the yield of vinyl derivative **II** at 300°C are 15.5 and 13.2%, respectively (selectivity 91.0%). In the second case, the results are slightly better, 16.0 and 13.8%, respectively (selectivity 90.0%).

Thus, we developed more effective catalysts for gas-phase vinylation of amide **I** than those described in the patent [13]. The wide-pore silica gel-1 and A-64 commercial alumina are the best supports. The ternary system 10% CdO + 5% K_2O + 1% ZnO is best applied to silica gel-1. The A-64 alumina support is best suited for catalytic systems with increased contents of cadmium oxide. The results reported in the patent [13] were overridden in run nos. 15 (Table 3), 19, 24–27, and 29 (Table 5), and 32, 34, and 36 (Table 6).

EXPERIMENTAL

The IR spectra were obtained on an IF.S.25, Sample Scant : 250 instrument in thin films for liquids and in KBr pellets for solids. The NMR spectra were registered on a Bruker DPX-400 spectrometer (400 MHz) in $CDCl_3$, internal reference HMDS.

Pilot lots of specially prepared wide-pore silica gel and alumina, as well as commercial A-64 alumina and zeolites were used for preparing catalysts.

Wide-pore supports were prepared by heat treatment of normal supports under steam and air. The steam and air rates were 100 kg/h and 225 m^3/h, respectively. Steaming was began at 400–500°C. After steam heat treatment was, the oven was cooled in air.

The main stages of preparation of OPP-2 and OPP-3 wide-pore aluminas after steam heat treatment of A-64 alumina were as follows: drying at 110–120°C (4 h), heating to 700–750°C (6 h), keeping at 700–750°C (6–8 h), and cooling.

The steam heat treatment increases the pore size of the supports but decreases their specific surface area by beaking narrow pores.

Determination of moisture capacity of supports. Support (zeolite, alumina, or silica gel), 10 g, precalcined (200–250°C) in a drying oven to constant weight, was placed into a porcelain dish, poured over with water, and left to stand for 1 h. The water was then decanted, the support was dried on a filter paper, and weighed. The difference in weights between wet and dried supports was used to measure the amount of absorbed water.

Preparation of catalytic systems by applying catalysts from solution to support. A mixture of support dried to constant weight and catalyst in distilled water whose amount was estimated from moisture capacity was vigorously shaken for 30 min. The catalyst was separated and dried first in air and then in a drying oven to constant weight. The oxides CdO and K_2O were successively applied by the above procedure by impregnating supports first with aqueous cadmium acetate and then (after drying and calcination) with aqueous potassium nitrate. After drying and calcination in a drying oven, the resulting catalytic system was calcined again. The catalysts 10% CdO + 5% K_2O + 1% CsF + silica gel 1, 10% CdO + 5% K_2O + Al_2O_3, and 10% CdO + 5%K_2O + 1% CsF + Al_2O_3 were prepared in a similar way.

Gas-phase vinylation of amide I with acetylene was performed in a quartz tubular reactor 12 mm in internal diameter and 180–270 mm in reaction zone length, mounted in a horizontal electric oven. Amide **I** was fed using a syringe autosampler in acetylene. Acetylene was obtained in a Kipp apparatus, passed through a calcined calcium chloride, and fed into the reactor at a rate ensuring required reagent ratio. The temperature in the reactor was controlled using a thermocouple placed in the middle of hot zone, on the outside of the reactor in a quartz pocket. The reaction mixture was condensed into receivers and cooled traps and then analyzed by GLC [Tsvet-500 chromatograph, linear temperature programming at 12 deg/min (from 35 to 230°C), 2000 × 3-mm stainless-steel column, liquid phase XE-60, 5% on Chromaton N-AW-HMDS and DC-550, 5% on Chromaton N-AW-HMDS, carrier gas helium]. An authentic sample of compound **II** was used as reference.

The reaction of amide **I** with acetylene in the vertical mode was performed in a quartz tubular reactor 12 mm in internal diameter and 120 mm in reaction zone length (or 15 × 150 mm), mounted in a vertical electric oven. The temperature in the reactor was controlled with a thermocouple placed in a qurtz pocket solded inside the reaction tube. The reactor was filled with catalyst preliminarily activated by heating at 400°C for 4 h in argon. Then the reactor was cooled to 300°C, and amide **I** was fed into it at a rate of 1 ml/h in acetylene (1.8 l/h).

Vinyl derivative **II** was isolated by vacuum distillation of the reaction mixtures, bp 83–87°C (19 mm) and characterized by IR and ^1H NMR spectroscopy and GC–MS. IR spectrum, ν, cm^{-1}: 1623 ($CH=CH_2$), 1655 (C=O), 2964, 2993, 3020, 3080 (CH). ^1H NMR spectrum, δ, ppm: 2.2 s ($CH_3C=O$), 3.05 s (CH_3–N), 4.36, 4.45 d.d (=CH_2), 6.85 q (=CH). The mass spectrum contains a molecular ion peak at *m/z* 99.

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