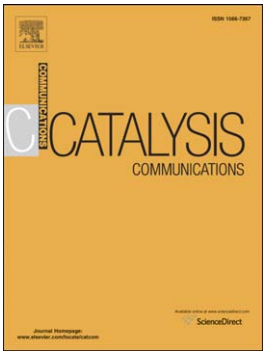

Vinylation of phenol by acetaldehyde: ¡!–[INS][a]–¿A¡!–[/INS]–¿ new reaction for the synthesis of *o*-vinylphenol

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Vinylation of phenol by acetaldehyde: a new reaction for the synthesis of o-vinylphenol

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Abstract

A new catalytic reaction for the single-step synthesis of o-vinylphenol from phenol and acetaldehyde in the gas phase is investigated in this work. A search for an efficient catalyst was made. The best results were obtained with a modified Cr_2O_3 catalyst supported on γ-Al_2O_3. The effect of content of Cr_2O_3 and potassium as a modifying additive was studied. It was shown that the catalyst containing 13% Cr_2O_3 and 1% K makes it possible to obtain o-vinylphenol with a selectivity of 100% referred to phenol and up to 87% referred to acetaldehyde. The influence of reaction conditions on the activity, selectivity and stability of catalyst operation was elucidated.

Keywords: Vinylphenol; Phenol; Acetaldehyde; Monomer.

1. Introduction

Incorporation of the vinyl CH_2=CH− group into the molecule of a substance allows obtaining monomers for polymerization reactions and building blocks for fine chemistry. Long-term studies have been performed to find the vinylation methods that are most topical for aromatic compounds. Well arranged and efficient processes have been devised for the synthesis of the simplest substances of this type, for example, styrene [1]. Methods for obtaining more complicated compounds with heteroatoms are under development [2–5].

Of particular interest are vinylphenols (VPh)[1] – the substances whose molecules include two functional groups bound to the aromatic ring: hydroxyl and vinyl ones. Depending on relative positions of these groups, three isomers of vinylphenol can exist: para-, meta- and ortho-.

[1] Abbreviations: VPh – vinylphenol; p-VPh – p-vinylphenol; o-VPh – o-vinylphenol; m-VPh – m-vinylphenol; AA – acetaldehyde.

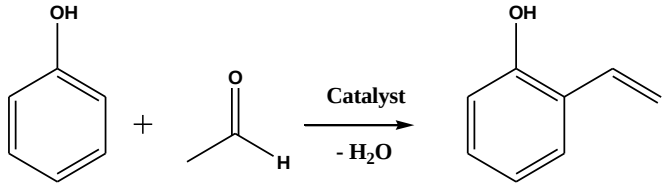
Such a bifunctional structure determines wide possibilities in the application of these compounds.

Vinylphenols are used as precursors in the production of medicinal substances and materials for cosmetic and food industries. Polymers based on vinylphenols – polyvinylphenols – are employed to obtain photosensitive materials, in the production of liquid crystals, antibacterial polymers, etc. [6].

The available methods used for the synthesis of vinylphenols are quite complicated. Only the synthesis of p-vinylphenol (p-VPh) is implemented on industrial scale. One of the early methods of p-VPh production is based on decomposition of Bisphenol-E (1,1-bis(4-hydroxyphenyl)ethane). This method gives a complex mixture of products with a significant degree of resinification; the recovery of the target p-VPh from this mixture is quite difficult [7]. Another method is based on electrophilic acylation of phenol followed by the reduction of ketone to alcohol and dehydration of the latter. Although this is a complex multi-step process, the indicated method has been implemented by Maruzen Petrochemicals Co. [6,8].

Only the preparative methods are available for the production of other vinylphenol isomers – o-VPh and m-VPh; this strongly limits the application of such substances. It seems that the first method of o-vinylphenol synthesis was decarboxylation of 2-hydroxycinnamic acid [9]. Later, the reaction of phenol with ethylene oxide catalyzed by sulfuric acid [10] was proposed as a method of o-vinylphenol synthesis. However, all attempts to reproduce results of this work have failed [11–13]. A method of direct vinylation of phenol and its derivatives using acetylene was also proposed. The reaction is performed in the liquid phase in organic solvents (acetonitrile, chlorobenzene) in the presence of $SnCl_4$ and Bu_3N [6,14]. The reaction proceeds with a yield up to 80%, probably referred to phenol. However, the use of explosive acetylene and the necessity to run the reaction in the liquid phase may limit the application of this method.

In this work, we explored the reaction of catalytic gas-phase condensation of phenol with acetaldehyde (AA) that was recently discovered by our research team. The main product of this transformation is o-VPh (equation 1).



(1)

2. Experimental

γ-Al_2O_3 (Sasol Germany GmbH) was used as a support for the catalysts. The catalysts were prepared by incipient wetness impregnation of the support with aqueous solutions of

appropriate salts or acids. Details of catalyst preparation and characterization (including chemical composition, textural characteristics and XRD data) are summarized in Supporting Information.

The catalytic experiments were carried out in a flow setup with on-line chromatographic analysis of the gas phase. Gas lines of the setup were mounted in an oven heated to 200°C. A preliminarily weighed 0.5 cm^3 catalyst sample was placed in a tubular quartz reactor. The initial reaction mixture contained 2 mol.% AA and 8 mol.% phenol. The total flow rate of the reaction mixture through the reactor was 30 cm^3/min. For more details about catalysts pretreatment, products identification, and calculation of reaction parameters, see Supporting Information.

3. Results and Discussion

3.1. Preliminary experiments

Table 1 lists data of preliminary experiments on the reaction of phenol with acetaldehyde. In run 1, a mixture containing 2% AA and 8% phenol was fed to the 2%Pt/A_2O_3 catalyst. A consumption of AA and phenol was observed; their conversions were not higher than 10 and 0.9%, respectively. o-VPh was detected in the reaction products, the selectivity for o-VPh was 34%. Other products of the reaction were represented by crotonal and a considerable amount of other substances with a low concentration. According to the NMR and GC-MS data (see Supporting Information), o-VPh is a single product of phenol conversion, while the other products are formed due to side transformations of AA.

We suggested that o-VPh was formed due to a reaction between AA and phenol. To verify this assumption, the following experiments were carried out. The initial mixture containing 2% AA in helium and not containing phenol was fed to the same 2%Pt/A_2O_3 catalyst. As seen from Table 1, run 2, in this case the conversion of AA increased to 86%. A complex mixture of products was formed. We did not made its detailed analysis; it should be noted only that the mixture contained a significant amount of crotonal. In the next experiment (Table 1, run 3), the initial mixture containing 8% phenol in helium and no AA was fed to the catalyst. One can see that in this case the reaction did not proceed (neither the conversion of phenol, nor the formation of any products were observed). These results indicate that o-VPh formation is a result of the reaction between AA and phenol.

In order to elucidate whether the formation of o-VPh can occur in the gas phase without catalyst, an appropriate experiment was performed. As seen from Table 1, run 4, in the absence of catalyst neither the conversion of AA or phenol nor the formation of products take place.

In run 5 (Table 1), the catalyst was represented by pristine Al_2O_3. It is seen that in this case o-VPh is not formed, only a weak conversion of AA into by-products (essentially crotonal) is observed. Hence, the deposition of active component is necessary to obtain o-VPh.

3.2. Effect of the nature of the catalyst active component

We screened a series of catalysts represented by metals and metal oxides supported on Al_2O_3. To compare the catalysts, a similar amount of the deposited component was used, 2 wt.%.

Since the first catalyst used in our work contained Pt, we primarily tested other noble metals: Pd and Ru (see Table 2, runs 2 and 3). These samples did not show good results. On the 2% Pd/Al_2O_3 sample, both the conversion of AA and the selectivity for o-VPh were not high (taking into account that selectivity for o-VPh referred to phenol was close to 100%, hereinafter selectivity for o-VPh will imply the selectivity referred to AA). On 2% Ru/Al_2O_3, the AA conversion reached 34% at a selectivity for o-VPh of 19%.

The screening was continued with a series of metal oxides (V, Mn, Co, Ni, Cr) supported on A_2O_3. The results are listed in Table 2, runs 4-8. It is seen that o-VPh forms on all the catalysts; however, the catalysts have radically different activity and selectivity. Samples $2\%V_2O_5/Al_2O_3$ and 2% NiO/Al_2O_3 showed a moderate activity toward AA, but their selectivity for o-VPh was very low. On the other hand, 2% MnO/Al_2O_3 and 2% CoO/Al_2O_3 were characterized by a low activity, but selectivity for o-VPh on these samples was close to 50%.

Of particular interest are the results observed for the 2% Cr_2O_3/Al_2O_3 sample. At the AA conversion near 20% the selectivity for o-VPh exceeded 60%. This made the chromium catalyst most promising for a further investigation.

3.3.Optimization of chromium catalysts

Table 3 lists the results of experiments with the modified chromium catalysts.

The effect of chromium oxide content, which was varied from 2 to 17 wt.%, on the reaction performance was studied. The results are listed in Table 3 (runs 1-5) and on Fig. 1a. One can see that an increase in the chromium oxide content strongly enhanced the activity of the sample. Thus, the conversion of AA increased from 21 to 49%. Therewith, a change in the chromium oxide content from 13 to 17% increased the AA conversion only from 47 to 49%. The selectivity for o-VPh also depended on the chromium oxide content. A change in the Cr_2O_3 content from 2 to 13% exerted virtually no effect on the selectivity, which remained at a level of ~60%. Meanwhile, a further increase in the chromium oxide content produced a considerable drop in selectivity, to 52%. Thus, for this catalyst the optimal content of chromium oxide was

13 wt.%. Selectivity for crotonal somewhat decreased with increasing the amount of chromium oxide.

Quite a low (ca. 60%) selectivity of the reaction on chromium catalysts is caused by side reactions of AA on the catalyst surface. This may be related to some acidity of the catalyst surface. We tried to improve the selectivity by modifying the catalyst via the deposition of potassium. The 13% Cr_2O_3/Al_2O_3 sample was chosen for the study. Results of these experiments are presented in Table 3 (runs 6-8) and on Fig. 1b. It is seen that modification of the sample substantially suppressed its activity (AA conversion decreased from 47% on non-modified sample to 7.0% on the sample containing 1.5% K). Selectivity for o-VPh increased upon addition of potassium and reached 83% at a K content of 1.0%. A further increase in the amount of the modifier somewhat decreased the selectivity. Thus, the optimal content of potassium was 1.0%.

3.4. Effect of temperature

The effect of temperature on the reaction of AA with phenol was studied on the 13%Cr_2O_3, 1%K/Al_2O_3 sample in the temperature region from 300 to 400°C with a step of 25°C. The results are presented in Table 4. One can see that raising the temperature strongly increased the conversion of AA (from 14 to 41%) with a moderate decrease in the selectivity for o-VPh from 87 to 81%. The main by-product was crotonal. Selectivity for this product slightly changed in the course of reaction; hence, selectivity for o-VPh decreased due to formation of other by-products. Data of Table 4 allow calculating the apparent activation energy of the reaction, which was equal to 16.3 kcal/mol. For more details see Supporting Information.

3.5. A study of catalyst stability

Taking into account high reactivity of both the reactants (AA) and products (o-VPh) as well as their ability to polymerization and catalyst coking, it seemed interesting to estimate their operational stability. Fig. 2 displays results of the experiment on stability of the 13%Cr_2O_3, 1%K/Al_2O_3 catalyst. The reaction was conducted for 5 hours. In the first two hours, the catalyst activity decreased (AA conversion dropped from 32 to 14%) and then remained virtually constant. Selectivity for o-VPh showed a slight decrease in the experiment, from 84 to 78%.

It should be noted that high activity upon deactivation of the catalyst can be ensured by raising the temperature, because on this catalyst the selectivity decreases slightly with temperature elevation.

Conclusion

In this work, the single-step gas-phase synthesis of o-VPh from phenol and acetaldehyde has been discovered and studied for the first time. A wide-scope screening of the catalysts supported on γ-Al_2O_3, including noble metals and metal oxides, was performed. The best results were observed for the chromium oxide catalyst modified with potassium, which made it possible to obtain o-VPh with a selectivity up to 100% for phenol and up to 87% for acetaldehyde. However, it cannot be ruled out that optimization of the catalyst and reaction conditions could give even more interesting practical results. In addition, crotonal, which is the main by-product of the reaction, is also a valuable compound and can readily be recovered from the reaction mixture.

It should be noted that the development of a simple and efficient method for the synthesis of o-VPh could significantly reduce the cost of this substance and open new ways of its application both in polymerization reactions and as an intermediate in the fine chemistry reactions.

The nature of catalyst active sites and mechanism of the reaction are not discussed in this work but could be found in further more detailed studies using a set of physicochemical methods and quantum-chemical calculations.

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We thank A. S. Noskov for useful discussion, M. V. Shashkov for GC-MS analysis, and T. Yu. Kardash for XRD analysis. This work was supported by RAS and FASO (Project No. V.44.2.3).

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Figures

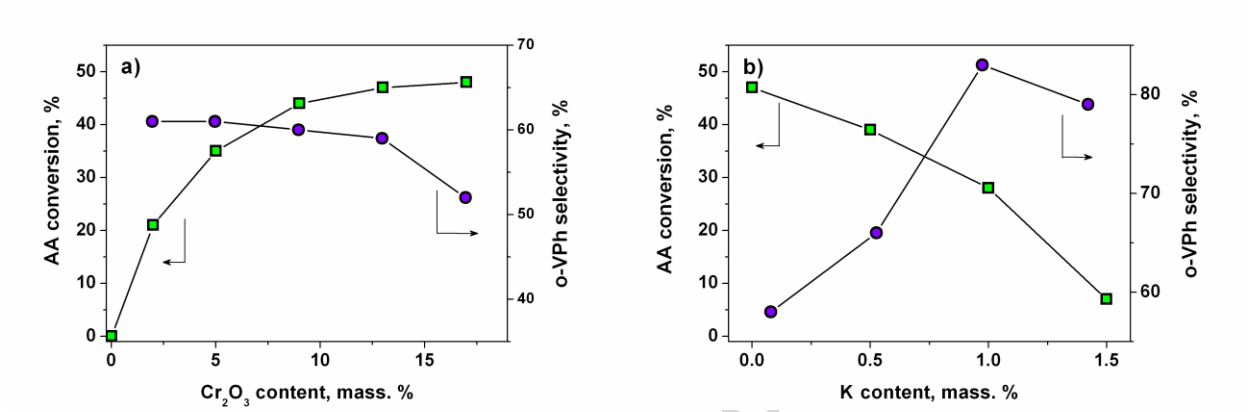


Fig. 1. The dependence of activity and selectivity of catalyst vs

a) the Cr_2O_3 content

b) the K content

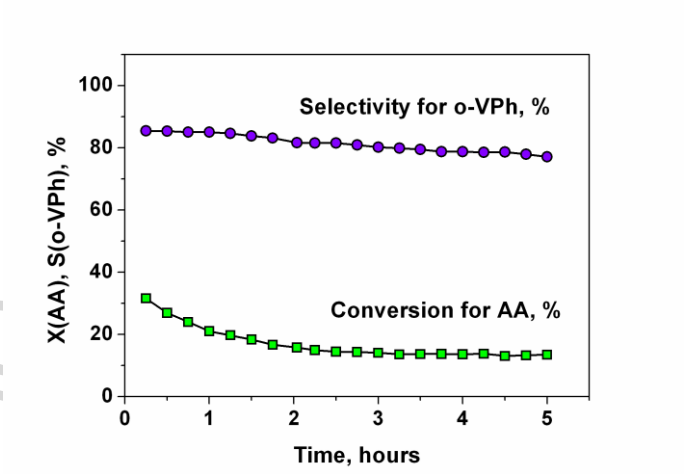


Fig. 2. The time dependence of o-VPh formation parameters at 375°C on the 13%Cr_2O_3, 1%K/Al_2O_3 sample.

Table 1. Preliminary experiments, 375°C, contact time 1 s, reaction time 30 min

No.	Sample	Composition of initial mixture	X(AA), %	X(PhOH), %	S (o-VPh), %
1	2% Pt/Al_2O_3	2% AA + 8% phenol in He	10	0.9	34
2	2% Pt/Al_2O_3	2% AA in He	86	0.0	0.0
3	2% Pt/Al_2O_3	8% phenol in He	-	0.0	0.0
4	no catalyst	2% AA + 8% phenol in He	0.0	0.0	-
5	Al_2O_3	2% AA + 8% phenol in He	3.0	0.0	0.0

Table 2. Preliminary experiments, 375°C, contact time 1 s, reaction time 30 min. Composition of the initial mixture 2% AA + 8% phenol in He

No.	**Sample**	**X(AA), %**	**X(PhOH), %**	**S (o-VPh), %**
1	2% Pt/Al_2O_3	10	0.9	34
2	2% Pd/Al_2O_3	14	0.2	5.0
3	2% Ru/Al_2O_3	34	1.6	19
4	2%V_2O_5/Al_2O_3	11	0.1	5.0
5	2% MnO/Al_2O_3	7.0	0.9	54
6	2% CoO/Al_2O_3	2.0	0.3	52
7	2% NiO/Al_2O_3	20	0.2	4.0
8	2% Cr_2O_3/Al_2O_3	21	3.2	61

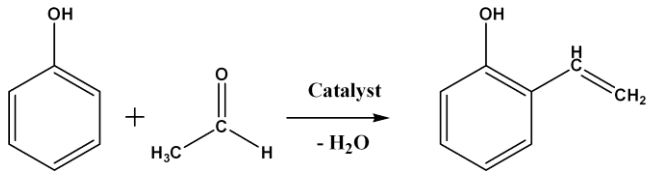
Table 3. Properties of Cr_2O_3 samples, 2% AA + 8% phenol in He, 375°C, contact time 1s, reaction time 30 min

No.	Sample	X(AA), %	X(PhOH), %	S (o-VPh), %	S (crotonal), %
1	2% Cr_2O_3/Al_2O_3	21	3.2	61	16
2	5% Cr_2O_3/Al_2O_3	35	5.3	61	18
3	9% Cr_2O_3/Al_2O_3	44	6.6	60	17
4	13% Cr_2O_3/Al_2O_3	47	6.8	58	15
5	17% Cr_2O_3/Al_2O_3	49	6.4	52	14
6	13%Cr_2O_3, 0.5%K/Al_2O_3	39	6.4	66	16
7	13%Cr_2O_3, 1%K/Al_2O_3	28	5.8	83	14
8	13%Cr_2O_3, 1.5%K/Al_2O_3	7.0	1.4	79	21

Table 4. Effect of temperature on reaction performance. Sample 13%Cr_2O_3, 1%K/Al_2O_3, 2% AA + 8% phenol in He, contact time 1s, reaction time 30 min

No.	T, °C	X(AA), %	X(PhOH), %	S (o-VPh), %	S (crotonal), %
1	300	15	3.3	87	13
2	325	16	3.4	84	14
3	350	18	3.7	83	15
4	375	28	5.8	83	14
5	400	41	8.3	81	15

Graphical abstract



Catalyst: 13% Cr_2O_3, 1% K / Al_2O_3

Highlights

1. The catalytic reaction of o-vinylphenol synthesis from phenol and acetaldehyde was discovered
2. A series of catalysts (metals and metal oxides) supported on alumina was screened
3. The chromium catalyst modified with potassium was shown to be optimal
4. Selectivity for o-VPh on the optimal catalyst was up to 87%