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**OXIDATION OF CUMENE BY MOLECULAR OXYGEN  
ON HETEROGENIZED COBALT CATALYSTS**

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In the oxidation of cumene to cumene hydroperoxide by molecular oxygen in the liquid phase, the cobalt(II) catalysts heterogenized on organic cation exchangers are active only if acid functional groups of the exchanger which bind cobalt ions show medium or weak acidity. The catalysts based on strongly acidic ion exchangers are inactive and, contrary to the above catalysts, they catalyze decomposition of the cumene hydroperoxide present in the reaction mixture to phenol and acetone.

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Cobalt–acetate complexes, known as homogeneous catalysts for oxidations by molecular oxygen, were heterogenized on strongly acidic ion exchangers<sup>1</sup>. The presence of cobalt–acetate complexes on the surface of these ion exchangers was verified spectrophotometrically<sup>2</sup> and by mass balance of the acetic acid in the system during catalyst preparation<sup>3</sup>. However, in the oxidation of 2-propanol and toluene it was found that the heterogenized catalysts do not activate molecular oxygen<sup>4</sup> and catalyze only the decomposition of peroxides, although homogeneous cobalt–acetate complexes exhibit high catalytic activity in both reactions. Quantum chemical calculations showed that the cobalt complexes bonded ionically to sulphonic acid groups of the polymer require much greater energy to chemisorb molecular oxygen than soluble cobalt complexes<sup>5</sup>. This fact is most likely the reason of the inactivity of the cobalt complexes heterogenized on strongly acidic ion exchangers.

The catalytic activity of cobalt(II) ions bonded to polymers containing medium acidic phosphoric acid groups in the oxidation of cumene by molecular oxygen has been observed by Berentsvaig and coworkers<sup>6</sup>. We have therefore decided to investigate whether heterogenization of cobalt(II) ions on styrene–divinylbenzene and other polymers containing medium or weakly acidic functional groups affords active catalysts. In our laboratory there were available differently cross-linked polymers possessing functional groups containing phosphorus of different valency and a series of polymers containing carboxylic acid groups that differed in their type and structure. The model reaction chosen was the oxidation of cumene by molecular oxygen. The reaction was carried out in the liquid phase in the absence of solvents.

## EXPERIMENTAL

### Compounds Used

Cumene, chemical purity grade (Fluka), contained 2.8 per cent of cumene hydroperoxide (determined by iodometric titration). The portion of the above sample was twice rectified, yielding the product (b.p. 152°C) which did not contain cumene hydroperoxide (as checked by iodometry and by gas chromatography). Acetone, analytically pure (Lachema), was used without further purification.

### Catalysts

Several types of organic ion exchangers differing in acidic functional groups and in the type of macromolecular skeleton have been used to synthesize the catalysts. The composition of the catalysts and their properties are presented in Table I. The catalysts were converted into  $H^+$  form with the use of 7% hydrochloric acid and then they were washed with distilled water until the eluate did not contain chloride ions. Cobalt(II) ions were introduced on the polymers by slow elution of the exchangers with 10% aqueous cobalt(II) acetate solution, using a glass column. The molar amount of the cobalt(II) salt used was five times the exchange capacity of the ion exchanger. The excess salt was removed from the ion exchanger by washing with distilled water. The ion exchanger with the exchanged cobalt was dried in a vacuum oven at 80–100°C for 6 h. The dried ion exchangers were stored in a desiccator. The catalysts are further designated by the symbol (Co) placed behind the designation of the ion exchanger. The Co content is given in Table I.

### Apparatus and Procedure

The apparatus consisted of a tubular glass reactor (its volume was 6 ml) which was equipped with two outlets. The central outlet was used to connect the inlet of oxygen and to introduce vibration for stirring with an electric vibrator. The side outlet was provided with a metallic stopper having the hole of 2 mm diameter. The stopper was provided with a resin insert for charging liquids and withdrawing samples for analysis. It was used also for deaeration of the reactor during filling the reactor with oxygen. The reactor was heated in a temperature — controlled bath and the pressure in the reactor was controlled by a manometer.

The reactor was charged with 0.1 g of the catalyst, the oxygen inlet was connected to the reactor and fastened with a shackle. Then, 3 ml of cumene were introduced by the side neck. The reactor was sealed, placed into the bath and heated to 80°C for 10 min. Then, the apparatus was purged several times with oxygen and pressurized by oxygen to 0.6 MPa. The reaction was started by switching on the vibrator. In the course of the reaction, 50  $\mu$ l samples were withdrawn and analyzed by liquid chromatography.

### Analytical Methods

Liquid chromatographic analyses were made with the use of a chromatograph equipped with 0.25 m column filled with Separon C 18 (10  $\mu$ m particle size) and a differential UV analyzer with the constant wavelength 254 nm. The mobile phase was a methanol–water mixture (4 : 1). The chromatograph was charged with 15  $\mu$ l of the reaction mixture diluted with methanol to 1 : 20.

TABLE I  
Properties of ion exchangers used

Design. of ion exchanger	Polymer skeleton <sup>a</sup>	Functional groups	Cross- linking <sup>b</sup> , %	Specific surface m <sup>2</sup> /g	Titration exchange capacity mequiv, H <sup>+</sup> /g	Content of Co(II) ions mmol Co <sup>2+</sup> /g
GM-926	GLC-M	COOH, OH <sup>c</sup>	40	55.4	2.27	0.81
GM-968	GLC-M	COOH, OH <sup>d</sup>	40	32.6	2.50	0.74
GM-979	E-M	COOH	—	20.2	6.27	1.42
MSP-15	S-DVB	P(OH) <sub>2</sub>	15	47.0	4.74	1.94
MSP-25	S-DVB	P(OH) <sub>2</sub>	25	71.0	4.00	1.83
MSP-60	S-DVB	P(OH) <sub>2</sub>	60	311.0	2.25	0.87
MSP-15	S-DVB	PO(OH) <sub>2</sub>	15	7.0	4.2 <sup>e</sup>	1.91
MSP-25	S-DVB	PO(OH) <sub>2</sub>	25	24.0	3.9 <sup>e</sup>	1.82
MSP-60	S-DVB	PO(OH) <sub>2</sub>	60	183.0	1.8 <sup>e</sup>	0.79
MS-15	S-DVB	SO <sub>3</sub> H	15	35.0	4.37	2.10
Lewatit						
CNP 80	A-DVB	COOH	—	0.2	4.5	1.62

<sup>a</sup> GLC—M glycidylmethacrylate, E—M ethylenedimethacrylate, S—DVB styrene-divinylbenzene, A—DVB acrylate-divinylbenzene; <sup>b</sup> per-centual content of cross-linking agent; <sup>c</sup> the excess of OH groups with respect to COOH groups; <sup>d</sup> the OH content was max. half of the COOH content; <sup>e</sup> titrated to the first dissociation step.

## RESULTS AND DISCUSSION

The oxidation of cumene by molecular oxygen in the absence of catalysts proceeds autocatalytically. However, the freshly distilled cumene not containing cumene hydroperoxide (CHP) does not yield the reaction product even after 4 h-reaction. The cumene containing 2.8 per cent of CHP affords 4.3 per cent of CHP after 3 h-reaction. The rate of the autocatalytic reaction is thus slow and depends on the content of CHP in the starting cumene. In the presence of ion exchanger catalysts saturated with cobalt, the freshly distilled cumene does not undergo oxidation even after several hours. This shows that the heterogenized cobalt catalysts do not affect the initiation stage of the chain oxidation reaction. Therefore, the cumene containing 2.8 per cent of CHP has been used in further experiments.

The catalytic effect of different ion exchanger catalysts with cobalt bonded ionically on the oxidation of the cumene containing 2.8 per cent of CHP by molecular oxygen at 80°C and 0.6 MPa oxygen pressure is shown in Fig. 1. The reaction product was CHP accompanied by a small amount of 1-phenyl-1-methylethanol (up to 1 per cent). This amount changed only slightly with reaction conditions. Therefore, the formation of 1-phenyl-1-methylethanol was disregarded in interpreting the results. It becomes evident that the autocatalytic reaction is accelerated by the catalysts which have cobalt bonded to medium or weakly acidic functional groups, while the catalyst MS-15(Co) containing strongly acidic sulphonic acid groups decomposes – even

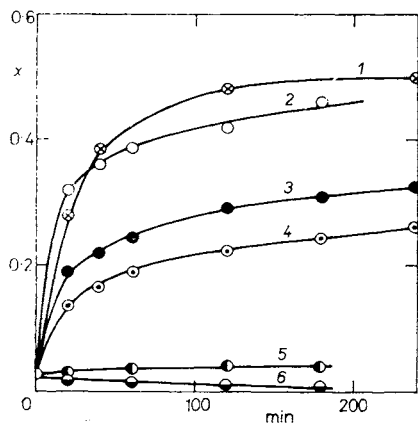


FIG. 1

Kinetic curves of the oxidation of cumene ( $x$  denotes conversion to CHP) by oxygen on different heterogenized cobalt catalysts. 1 Homogeneous catalyst  $[\text{Co}(\text{HOAc})_4]^{2+}$ , 2 GM-926d(Co), 3 MSP-25(Co), 4 MSPO-25(Co), 5 without catalyst, 6 MS-15(Co)

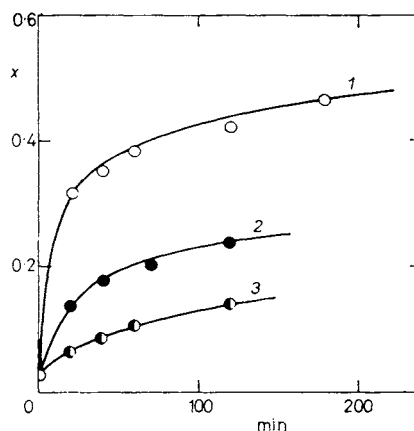


FIG. 2

Kinetic curves of the oxidation of cumene on cobalt-carboxylate ion exchangers. 1 GM-926(Co), 2 GM-968(Co), 3 GM-979(Co)

in the presence of oxygen in the reaction medium — only CHP in the cumene, but does not catalyze its formation by oxidation. The catalyst Lewatit CNP80(Co) containing weakly acidic functional groups is inactive. This can be explained by negligible specific surface of the gel ion exchanger used. Since these catalysts do not swell in the reaction medium, only very small number of active centres is thus available for the catalytic reaction.

The acid strength of functional groups of organic ion exchangers was determined by Jeřábek<sup>7</sup> who used both titration and sorption methods. The author found that apparent  $pK$ 's values of the exchangers are close to those reported for analogous acids:  $-\text{SO}_3\text{H}$  1.9;  $-\text{PO}(\text{OH})_2$  2.9;  $-\text{P}(\text{OH})_2$  3.9. Based on tabulated data for organic carboxylic acids,  $pK$  4.9 can be taken for  $-\text{COOH}$  functional groups. It is seen that the oxidation catalytic activity of investigated cobalt catalysts increases with decreasing acid strength of the functional groups of ion exchanger catalysts to which cobalt atom is attached. At the same time, the catalyst containing carboxylic acid groups shows the activity which is comparable to that of the homogeneous analogue, the cobalt-acetate complex, *i.e.* the medium with the acid strength of the carboxylic acid.

On comparing the catalytic effect of individual ion exchanger catalysts, one should take into account that they differ from each other in some parameters (degree of cross-linking, specific surface, exchange capacity, *etc.*) which affect also their activity. Based on our experience, these changes as such cannot cause such differences in the activity which were observed by us for the catalysts under study.

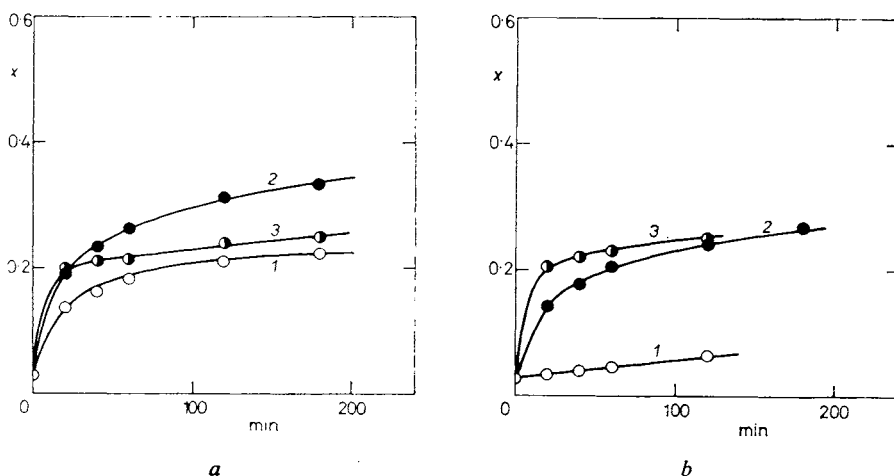


FIG. 3

Kinetic curves of the oxidation of cumene on phosphorus (a) and phosphoric (b) ion exchangers. 1— $\text{P}(\text{OH})_2$  on 15% S—DVB, 2— $\text{P}(\text{OH})_2$  on 25% S—DVB, 3— $\text{P}(\text{OH})_2$  on 60% S—DVB

In Fig. 2 are shown kinetic curves of the oxidation of cumene catalyzed by the catalysts with cobalt bonded to carboxylic acid groups. The ion exchangers were not prepared from the same starting copolymer, and in order to achieve the required properties, different procedures were used in their synthesis. Hence, the interpretation of the results can be influenced by differences in the structure of these polymer gels. Despite of this fact, the kinetic curves allow to conclude that the oxidation activity of these catalysts decreases with decreasing content of hydroxyl groups. This indicates that the presence of hydroxyls affects favourably the catalytic oxidation reaction.

Kinetic curves of the oxidation of cumene on the catalysts containing phosphorous and phosphoric acid groups are shown in Fig. 3. It is seen that the dependence of the catalytic activity on cross-linking of the ion exchanger is similar to that observed by us earlier for other ion-exchanger catalyzed reactions<sup>8-10</sup>. From comparison of both parts of Fig. 3 it becomes evident that the less acidic ion exchangers containing  $-\text{P}(\text{OH})_2$  groups are more active.

The above results show that heterogenized cobalt catalysts based on organic ion exchangers are efficient in the oxidation of cumene to cumene hydroperoxide by molecular oxygen only if cobalt(II) ions are bonded to medium acidic ( $-\text{PO}(\text{OH})_2$ ) or weakly acidic ( $-\text{P}(\text{OH})_2$  and  $-\text{COOH}$ ) groups. In the case of the ion exchangers containing carboxylic acid groups, their catalytic activity is affected favourably by the presence of hydroxyl groups on the macromolecular skeleton. The catalysts with cobalt(II) ion bonded to the strongly acidic sulphonic acid groups do not catalyze this reaction. On the contrary, because of their acidity, the catalysts decompose CHP to phenol and acetone. As in the oxidation of cumene the reaction mixture is not acidic, leaching of cobalt(II) ions to the liquid phase does not take place even with the catalysts containing weakly acidic groups.

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