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Complete oxidation of benzene on Cu–Cr and Co–Cr oxide catalysts

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Abstract

Supported mixture metal oxide systems, Cu–Cr and Co–Cr on γ-Al_2O_3 and γ-$Al_2O_3 + SiO_2$ were prepared and studied. They exhibited catalytic activity in the complete oxidation of benzene.

Keywords: Benzene oxidation; Cu–Cr catalysts; Co–Cr catalysts

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1. Introduction

Complete oxidation of hydrocarbons or of different waste gases containing hydrocarbons on platinic catalysts is a well developed procedure [1–3]. However, for evident reasons searching for conventional efficient oxide catalysts is at present the scope of many investigations.

The aim of the present paper is to check the catalytic activity and stability of a set of mixed oxides on supports prepared, starting with complexes of Cu–Cr and Co–Cr with tartaric acid.

The idea behind this preparation was to improve the dispersion of the oxide clusters on the supports and to eventually obtain egg-shell type catalysts.

From this point of view γ-Al_2O_3 is a very good support however, adding 20% of SiO_2, improved considerably the mechanical strength of the grains.

2. Experimental

2.1. Samples preparation

The precursors complexes were obtained by precipitation at pH 7 a mixture of Cu–Cr and Co–Cr nitrates in aqueous solution mixed with tartaric acid, in a solution of ethanol and ammonium hydroxide 10% in the ratio 1:1. After precipitation, the resulted compound was dried in vacuum at 90°C. They were subsequently submitted to chemical analysis, IR spectrometry, magnetic measurements and thermal analysis [5]. All the obtained results gave the following formula for the precursor:

$$[\mathrm{CrMe_4Ta_6}] \cdot \mathrm{H_2O} \quad \mathrm{Me = Cu, Co}$$

In order to prepare the supported catalysts two procedures have been used:

- The first one consists of the binding of the precursor on the support by successive impregnation of the solution of tartaric acid and of the nitrate mixtures.

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- The second consists in the synthesis of the precursor, its solubilisation and deposition on the support by impregnation.

Two types of supports were used for impregnation, Al_2O_3 tablets ($\phi = 6$ mm) and a mixture of $Al_2O_3 + SiO_2$ grains ($\phi = 3$–5 mm). The symbols of the prepared catalysts are presented in Table 1. The metallic content of the samples is 8.5%–10%.

The supported catalysts prepared by the two above mentioned procedures, have been dried for 12 h at 90°C and calcined at 700°C for 6 h.

Table 1
The symbols of the investigated catalysts

Type catalyst	Support	First procedure	Second procedure
Cu–Cr	γ-Al_2O_3	C_1	C_5
Cu–Cr	γ-$Al_2O_3 + SiO_2$	C_2	C_6
Co–Cr	γ-Al_2O_3	C_3	C_7
Co–Cr	γ-$Al_2O_3 + SiO_2$	C_4	C_8

The surface area of the catalysts are presented in Table 2.

All the samples prepared by the first proce-

Table 2
The surface areea of the catalysts

Sample	Surface area (m^2/g)							
	C_1	C_2	C_3	C_4	C_5	C_6	C_7	C_8
Uncalcined catalysts	160	124	143	116	122	123	136	100
Calcined catalysts	167	155	175	120	152	143	140	112
Supports	γ-Al_2O_3 161	γ-Al_2O_4 + 20% SiO_2 153						

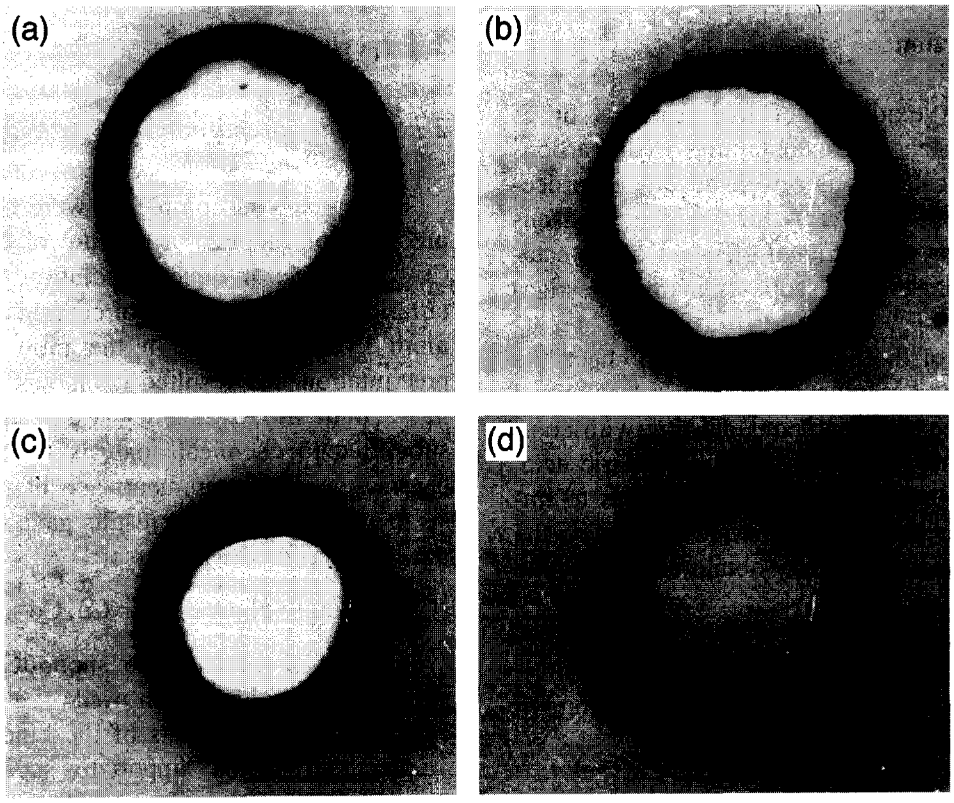


Fig. 1. Egg-shell type impregnation profile for the catalysts prepared by the first procedure: (a) Cu–Cr/γ-Al_2O_3; (b) Co–Cr/γ-Al_2O_3; (c) Cu–Cr/γ-$Al_2O_3 + SiO_2$; (d) Co–Cr/γ-$Al_2O_3 + SiO_2$.

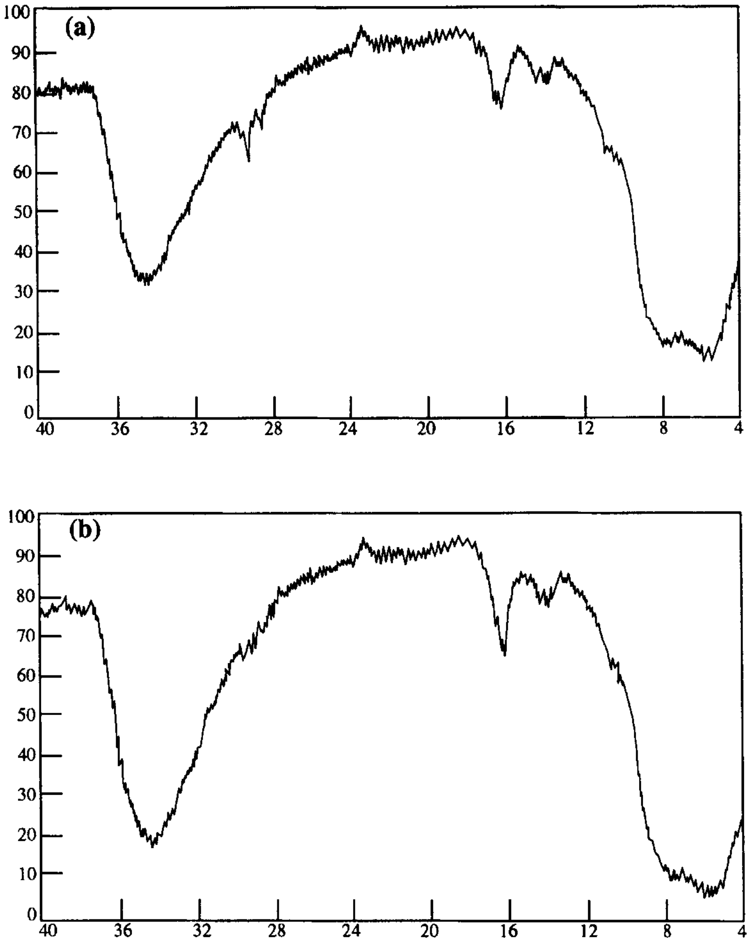


Fig. 2. The IR spectra of the supports: (a) γ-Al_2O_3; (b) γ-Al_2O_3 + SiO_2.

Table 3
The characteristics of the IR spectra

Sample	$\nu_{(OH)}$ *R*–OH *R*–COOH	$\nu_{(OH)}$ H_2O	ν_{unsymm} (C–O) *R*–COOH	ν_{symm} (C–O) *R*–COOH	$\delta_{(OH)}$ $\nu_{(C-O)}$	$\gamma_{(OH)}$ $\nu_{(C-C)}$ $\delta_{(OH)}$ *R*–OH *R*–COOH $\nu_{(CH3)}$	$\nu_{(Me-O)}$ $\nu_{unsymm\,(Me-O)}$ $\nu_{symm\,(Me-O)}$
Cu–Cr–Ta (unsupported complex)	3475	2940	1628	1375	1120	700	590
	3100	2850			1062	680	460
Cu–Cr–Ta/γ-Al_2O_3	3460	2960	1620	375	1088	840	610
	3200	2850			1040	710	480
Cu–Cr–Ta/γ-Al_2O_3 + SiO_2	3480	–	1640	375	1075	810	630
	3340	–	1620		1045	720	510
Co–Cr–Ta (unsupported complex)	3400	2880	1610	1375	1130	840	680
	3100	2860	1580		1062	780	480
Co–Cr–Ta/γ-Al_2O_3	3500	–	1630	1375	1080	830	640
	3300	–	1600		1040	700	510
Co–Cr–Ta/γ-Al_2O_3 + SiO_2	3460	2920	1640	1375	1070	800	670
	3240	2840	1600		1020	720	510

dure gave egg-shell type catalysts (thickness 0.7–1 mm) after calcination (see Fig. 1).

2.2. Chemical and physical properties

IR and electronic spectra as well as magnetic measurements have indicated that both COO^- and partially HO^- are coordinated at metallic ions in the precursors.

An IR investigation was carried out on all the samples in the spectral range 4000–400 cm^{-1} (Fig. 2, Fig. 3, Figs. 4 and 5). The main characteristic IR absorption bands are presented in Table 3.

A large and intensive absorption band at 3400–3000 cm^{-1} is typical for stretching vibrations of associated HO^- groups (ν_{OH}) and could be found in all the samples.

The bands at 1620–1580 cm^{-1} as well as the sharp band at 1375 cm^{-1} are usually attributed to asymmetric stretching vibration and symmetric vibration of the C–O bonds in carboxylic ion, respectively. These are also common to all samples and could be assigned to tartaric acid salts (Cu–Cr and Co–Cr).

Sharp and weak bands are found in the region 590–420 cm^{-1} which are attributed to Me–O bonds. These are sometimes screened by intensive absorption bands of the supports.

Finally, we think that there are credible argu-

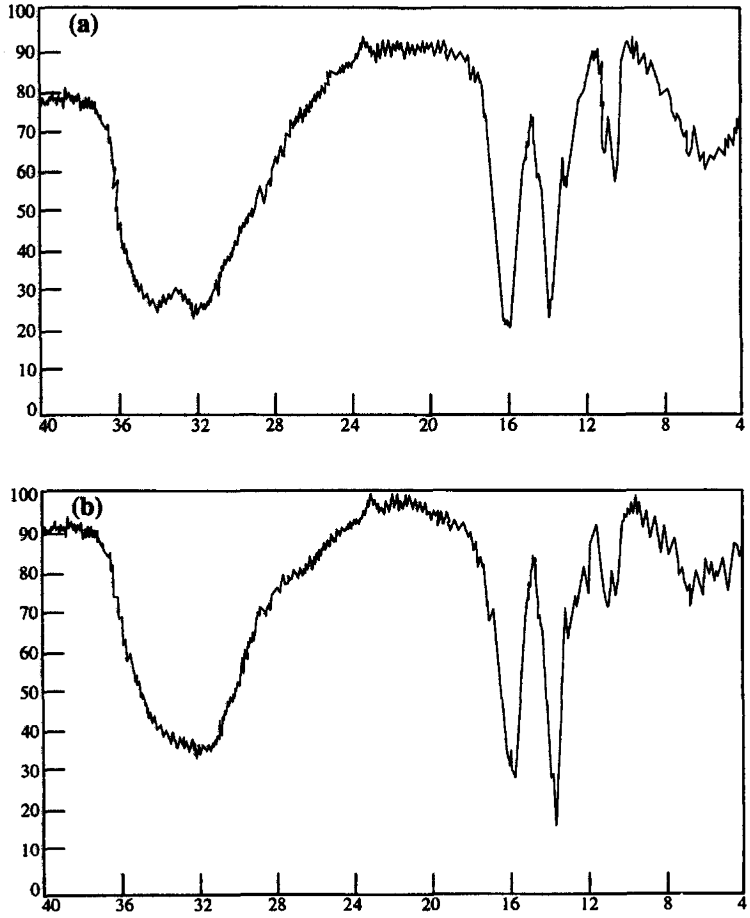


Fig. 3. The IR spectra of the unsupported precursor complexes: (a) Cu–Cr–Ta; (b) Co–Cr–Ta.

ments for both COO^- and partially HO^- coordination even on alumina and alumosilica.

Also, the UV–vis. reflection spectra indicated the octahedral coordination of the tartaric acid to both metallic ions [5,6]. The 410 nm band of the $CrCo_4Ta_6 \cdot 5H_2O$ complex was ascribed to the transition: ^4A 2g → ^4T 1g(F) within an octahedral configuration of the Cr^{III} (d^3) ion. The 535 nm peak can be explained by the superposition of the bands corresponding to the: ^4A 2g → ^4T 2g (P) of Cr^{III} (d^3) in an octahedral configuration and: ^4T 1g → ^rT 1g (P) (ν_3) of Cr^{II} (d^7) in an octahedral configuration (high spin) transitions, respectively.

For the $CrCu_4Ta_6 \cdot 5H_2O$ complex, in addition to the 420 nm band, ascribed to the ^4A 2g → ^4T 1g (F) transition of the Cr^{III} (d^3) in octahedral configuration a 590 nm peak is evidenced, characteristic to an octahedral configuration of the Cu^{II} (d^9) ion [5,6].

The transformations of the complexes into oxides were checked by TGA analysis. Although the mass loss process stops at 550°C for all samples, the tested catalyst were calcined at 700°C, in order to stabilize the oxide phase.

XRD spectra of the calcined samples revealed CuO, $CuCr_2O_4$ and $Cu_2Cr_2O_4$ on the copper–chromium supported catalysts and solid solutions of Co_3O_4 with $CoCr_2O_4$ on the cobalt–chromium supported catalysts.

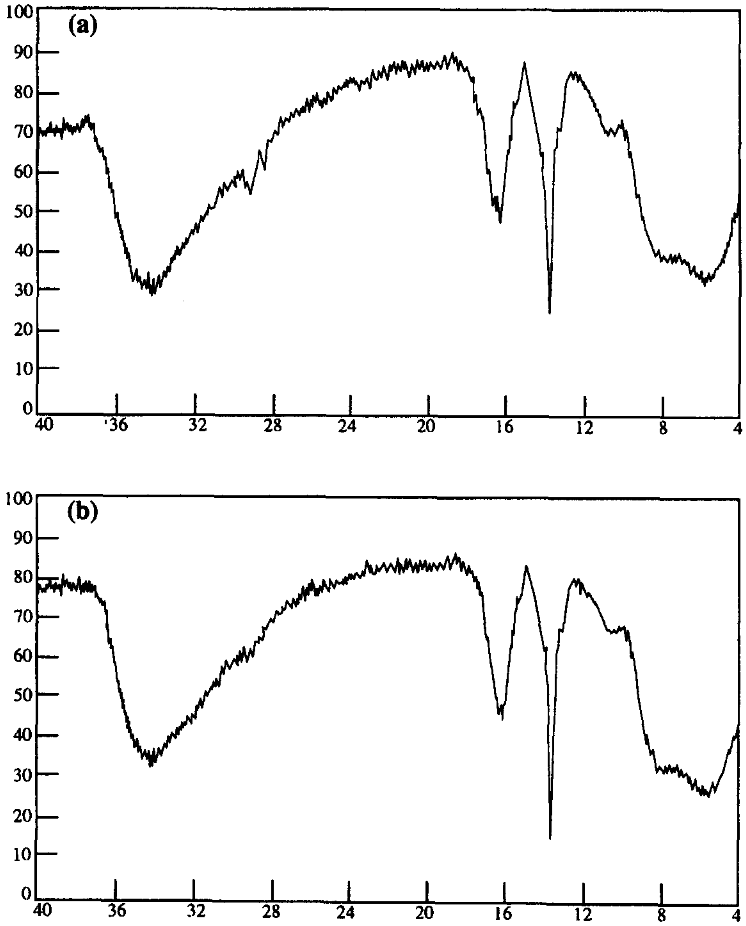


Fig. 4. The IR spectra of the Cu–Cr–Ta precursor on the support: (a) Cu–Cr–Ta/γ-Al_2O_3; (b) Cu–Cr–Ta/γ-Al_2 O_3 + SiO_2.

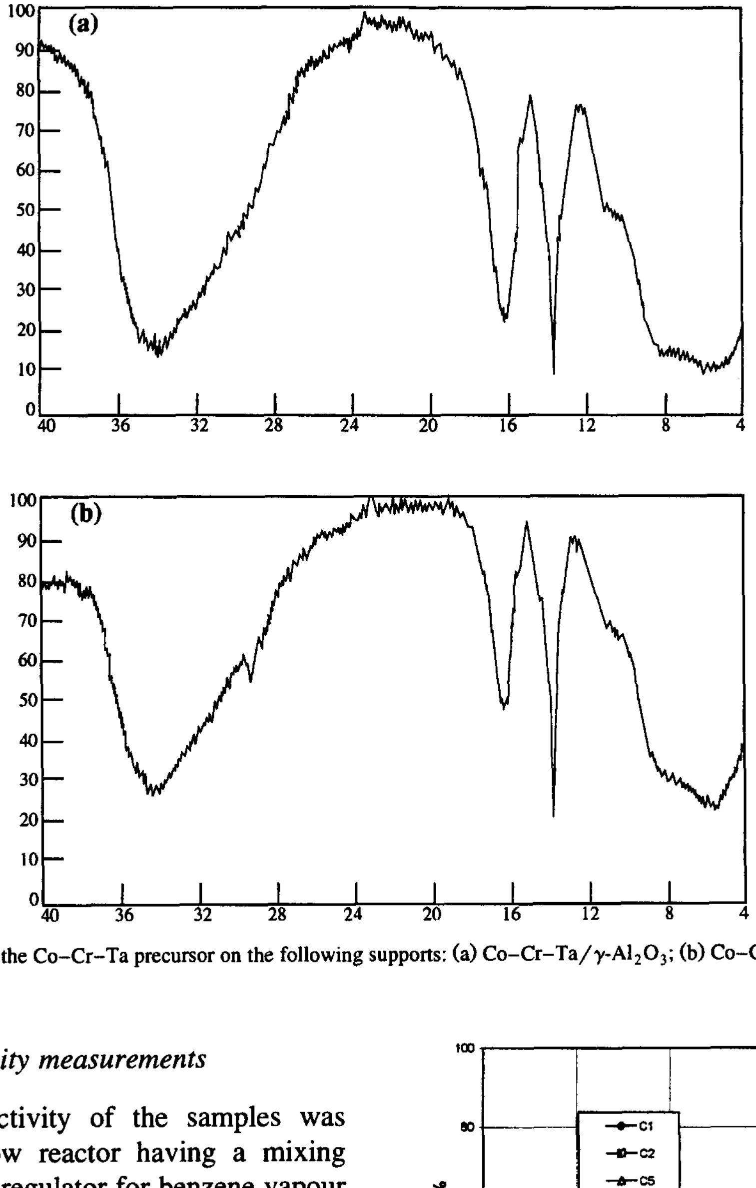


Fig. 5. The IR spectra of the Co–Cr–Ta precursor on the following supports: (a) Co–Cr–Ta/γ-Al_2O_3; (b) Co–Cr–Ta/γ-Al_2O_3 + SiO_2.

2.3. *Catalytic activity measurements*

The catalytic activity of the samples was measured in a flow reactor having a mixing system, thermostat regulator for benzene vapour control and flow controls for air. The analysis was carried out with an in line Hewlett Packard Gas Chromatograph model 5840A and using a Chromosorb 102 and Porapak Q packed column.

3. Results and discussion

Two sets of tests were effectuated:

- First, at 5% concentration of benzene in air and 4000 h^{-1} space velocity.

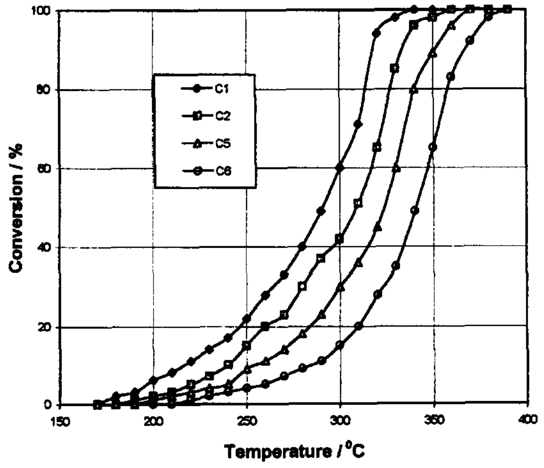


Fig. 6. Variation of conversion with temperature at 5% concentration of benzene in air and 4000 h^{-1} space velocity on Cu–Cr catalysts.

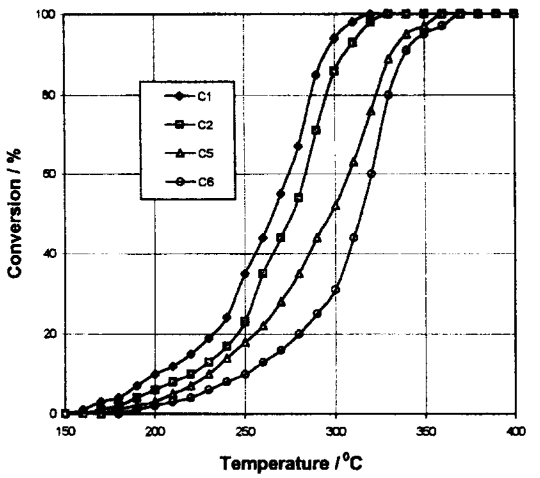


Fig. 7. Variation of conversion with temperature at 1% concentration of benzene in air and 10000 h^{-1} space velocity on Cu–Cr catalysts.

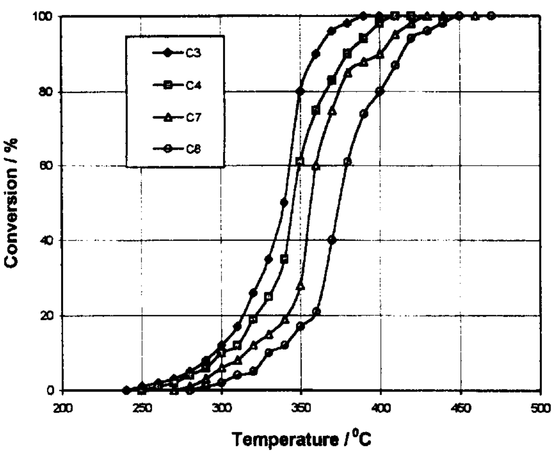


Fig. 9. Variation of conversion with temperature at 1% concentration of benzene in air and 10000 h^{-1} space velocity on Co–Cr catalysts.

- Second, at 1% concentration of benzene in air and 1000 h^{-1} space velocity.

Fig. 6, Fig. 7, Figs. 8 and 9 show the variation of conversion of benzene with temperature obtained with copper–chromium and cobalt–chromium catalysts, respectively. It can be seen that the copper–chromium catalysts even at temperatures below 300°C have a higher activity as compared to cobalt–chromium samples.

Also, the catalysts supported on γ-Al_2O_3 are more active than the catalysts supported on γ-Al_2O_3 + SiO_2. If the method of preparation is concerned, the catalysts obtained by precursor complex formation directly on the support are more active.

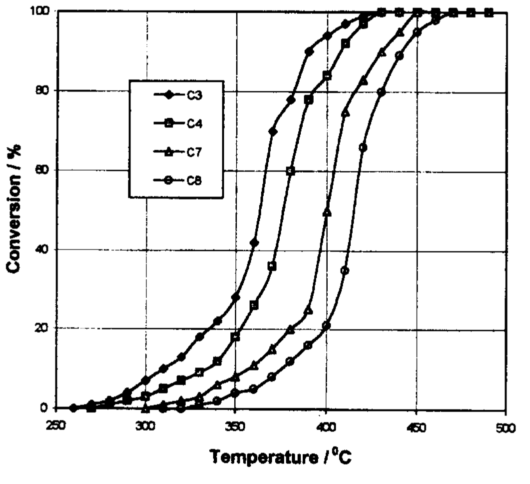
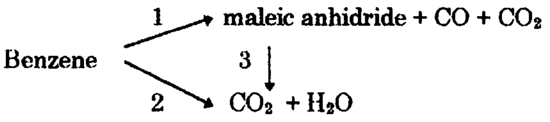


Fig. 8. Variation of conversion with temperature at 5% concentration of benzene in air and 4000 h^{-1} space velocity on Co–Cr catalysts.

At temperatures where conversion was 70%–80%, traces of maleic anhydride were detected in the conversion products.

This suggest that the reaction could take place according to the following scheme [4]:



4. Conclusions

Egg-shell type catalysts were obtained by impregnating the supports with precursor complexes. Poor activity for all Co–Cr samples is somewhat surprising. Better activity and stability of the Cu–Cr catalysts as compared to some older results obtained by simple impregnation of γ-Al_2O_3 with corresponding nitrates was evidenced.

References

[1] J.A. Barnard and D.S. Mitchell, J. Catal., 12 (1968) 386.

[2] A. Schwartz, L. Holbrook and H. Wise, J. Catal., 21 (1971) 199.

[3] C.I. Cullis and B.M. Willott, J. Catal., 86 (1984) 187.

[4] A. Inglot, React. Catal. Lett., 2 (1989) 241.

[5] V. Pocol, L. Patron and P. Spacu, Rev. Roumaine de Chim, 39 (1994) 1113.

[6] L. Patron, V. Pocol, N. Stanica and D. Crisan, Rev. Roumaine de Chim., in press.