

COMPLETE OXIDATION OF METHYL-ETHYL KETONE AND TOLUENE OVER SUPPORTED COPPER-CHROMIUM AND COBALT-CHROMIUM OXIDE CATALYSTS

I. Spasova¹, G. Ivanov¹, V. Georgescu², D. Mehandjiev¹

¹ Institute of General and Inorganic Chemistry,
Bulgarian Academy of Sciences,
Acad G. Bonchev Str., bl.11, 1113, Sofia, Bulgaria
E-mail: ispasova@igic.bas.bg

² Institute of Physical Chemistry, Romanian Academy,
Spl. Independentei 202, Bucharest, Romania

Received 11 January 2006

Accepted 08 February 2006

ABSTRACT

Alumina and alumina-silica supported copper-chromium and cobalt chromium oxides were investigated as catalysts for complete oxidation of methyl-ethyl-ketone and toluene. It was found the spinel phases formed to play a decisive role in the catalytic process. The nature of the support does not affect substantially on the activity of the samples.

Keywords: complete oxidation, supported catalysts, environmental protection.

INTRODUCTION

The purification of harmful organic substances from waste gases is important task in respect to environmental protection [1]. The main problem of this to synthesize catalysts, active even at low temperatures and low concentrations of the harmful component.

Irrespective to the large number of publications on this topic the investigations continue in respect to optimization of the processes of complete oxidation of harmful organic substances. In some papers was found [2-5] that alumina supported copper-chromium and cobalt-chromium oxides are efficient towards the complete oxidation of carbon monoxide and benzene.

It was of interest to determine the activity of the prepared catalysts towards harmful organic compounds. The aim of the present study is to investigate the catalytic activity in complete oxidation of methyl-ethyl-ketone and toluene by molecular oxygen.

EXPERIMENTAL

Metal oxide copper-chromium and cobalt-chromium systems supported on two supports (γ -Al₂O₃ and γ -Al₂O₃+20 % SiO₂) were prepared as described in [3].

According to the method the precursor was deposited on the support by successive impregnation of the latter with tartaric acid solution and mixed solutions of the corresponding metal nitrates. The supported precursors were dried in vacuum at 90°C for 24 h and then calcined at 650°C for 12 h.

The samples denoted as **C1**- CuCr/ γ -Al₂O₃, **C2**- CoCr/ γ -Al₂O₃, **C3**- CuCr/ γ -Al₂O₃+20 % SiO₂ and **C4**- CoCr/ γ -Al₂O₃+20 % SiO₂ were prepared.

The metal content in the samples was determined by chemical analysis. The specific surface areas of the samples investigated were measured by the BET method.

The catalytic activity of the samples was measured with respect to the complete oxidation of methyl-

ethyl-ketone and toluene with oxygen. The experiments were carried out in a flow reactor, with a catalyst volume of 0.6 cm³ (0.4-0.5 g), a space velocity of 50 000 h⁻¹, and concentrations of hydrocarbons of 0.035 vol. % in oxygen.

The inlet and outlet gas mixtures were analyzed by a gas-chromatograph CHROM-4 with a FID detector. The CO₂ content was determined by an infrared analyzer Infracal 2106.

TPR measurements were carried out with a thermal conductivity cell [6] by determination of the hydrogen consumption from a flowing gas mixture, containing 10 % hydrogen in argon. The gas flow rate was 6 cm³ · s⁻¹. The heating was linear with 10 K · min⁻¹ rate.

RESULTS AND DISCUSSION

Table 1 presents the data for the metal content and the specific surface area of the investigated samples.

The total concentration of the metals in the samples follows the ratio between mass. % Cu/Co and the chromium as nearly 4:1. The specific surface area of the supported samples remains relatively high- the metal oxide phases do not stop the pores of the two kinds of the support. The presence of silica in the support of the samples **C3** and **C4** does not change the specific surface area of the samples substantially.

XRD spectra of the calcined samples revealed that CuO, CuCr₂O₄ and Cu₂Cr₂O₄ are present on the copper-chromium supported catalysts while solid solutions of Co₃O₄ with CoCr₂O₄ on cobalt-chromium catalysts.

Fig. 1 and Fig. 2 show the results from the catalytic experiments. All samples manifest higher activity towards the complete oxidation of methyl-ethyl ketone (MEK) than

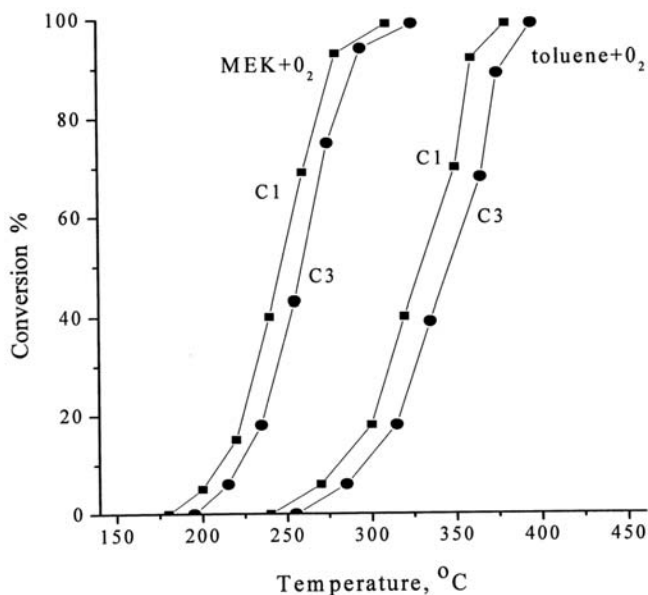


Fig. 1. Dependence of the conversion degree of alumina- supported samples towards MEK and toluene on the temperature.

those of toluene. All samples are active up to 300°C for the oxidation of MEK and up to 400°C for toluene.

The presence of higher oxygen content does not affect the efficiency. The copper-containing catalysts are slightly more active than the cobalt-chromium supported catalysts and the catalysts supported on a pure γ -Al₂O₃ are more active than those supported on a mixed γ -Al₂O₃+20 % SiO₂ support.

Table 2 shows the data concerning the “light off” temperatures of the investigated samples in both processes. The difference between the activity of the copper and cobalt containing samples is 10°C.

Substantial differences show the catalysts towards the two reactions- complete oxidation of methyl-ethyl

Table 1. Characteristics of investigated samples.

Sample	Metal content, mass. %			S, m ² g ⁻¹	Phase composition
	Copper	Cobalt	Chromium		
C1 -CuCr/ γ -Al ₂ O ₃	7.4	-	1.8	167	CuO, CuCr ₂ O ₄ , Cu ₂ Cr ₂ O ₄
C2 -CoCr/ γ -Al ₂ O ₃	-	7.2	2.1	175	Co ₃ O ₄ , CoCr ₂ O ₄
C3 -CuCr/ γ -Al ₂ O ₃ +20% SiO ₂	7.3	-	1.9	155	CuO, CuCr ₂ O ₄ , Cu ₂ Cr ₂ O ₄
C4 -CoCr/ γ -Al ₂ O ₃ +20% SiO ₂	-	7.2	2.0	140	Co ₃ O ₄ , CoCr ₂ O ₄

Table 2. "Light off" temperatures of the investigated samples in both reactions.

Sample	methyl-ethyl ketone	toluene
C1 -CuCr/ γ -Al ₂ O ₃	244	323
C2 -CoCr/ γ -Al ₂ O ₃ +20% SiO ₂	246	325
C3 -CuCr/ γ -Al ₂ O ₃	255	342
C4 -CoCr/ γ -Al ₂ O ₃ +20% SiO ₂	256	344

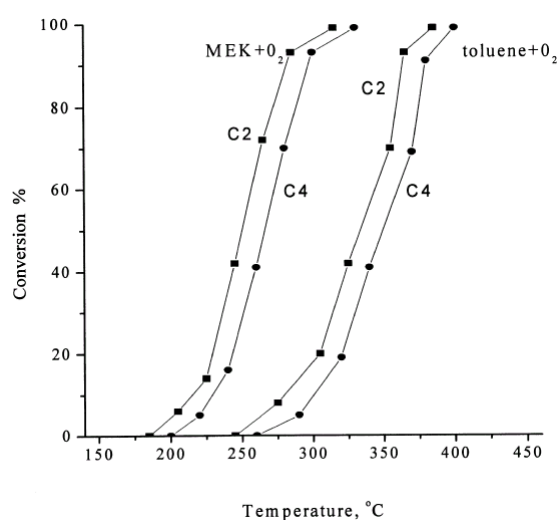


Fig. 2. Dependence of the conversion degree of alumina-silica supported samples towards MEK and toluene on the temperature.

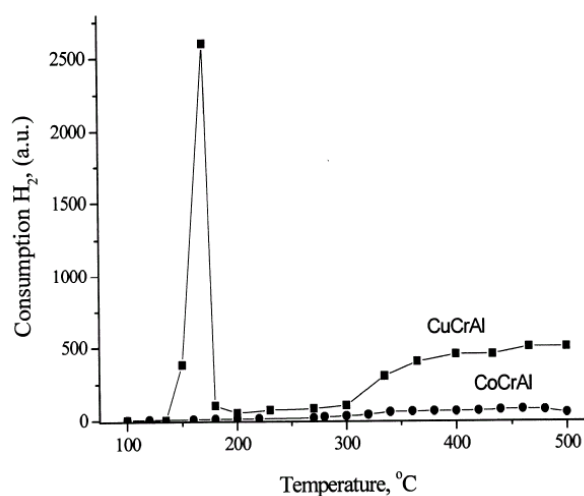


Fig. 3 TPR spectra of alumina supported Cu-Cr and Co-Cr samples.

ketone and toluene. Obviously, the presence of aromatic nucleus hinders the complete oxidation of toluene and the complete oxidation of toluene occurs at temperatures with merely hundred degrees higher. The difference between copper and cobalt containing catalysts is negligible.

It is known, that the reactions of the complete oxidation on oxide catalysts proceed through oxidation-reduction mechanism. It is important condition for this mechanism the presence of metal couples in a different oxidation state that could be oxidized or reduced so that to be realized the reaction. These metal ions in various oxidation states form catalytic active sites mentioned earlier as catalytic active complex. In this case the oxidation-reduction mechanism in the complete oxidation of organic substances is facilitated by this complex and the catalysts show high activity at low temperatures. This was proved in some reactions

with spinel catalysts as CuCo₂O₄ [7], CuMn₂O₄ [8], MnCo₂O₄ and CoMn₂O₄ [9] and spinel-like catalysts of type Cu_{1.5}Mn_{1.5}O₄ [10].

In order to elucidate the role of the reducibility of the investigated catalysts TPR experiments were made. The results for samples **C1**-CuCr/ γ -Al₂O₃ and **C2**-CoCr/ γ -Al₂O₃ are given in Fig.3. The curves for alumina-silica supported respective samples are analogous. It is evident, that up to 200°C the properties of the samples are different. For **C1**-CuCr/ γ -Al₂O₃ one peak appears with T_{max}=170°C and above 300°C monotonously increases. With the sample **C2**-CoCr/ γ -Al₂O₃ a reduction is observed only above 300°C. The consumption of hydrogen with this sample is lower. The phase analysis of the samples show the presence of the single oxide phases of CuO and Co₃O₄ on copper and cobalt supported catalysts, respectively. It is known that CuO is relatively easy reducible and

that is why we consider the low temperature peak for **C1-CuCr/ γ -Al₂O₃** in TPR spectra with $T_{\max}=170^{\circ}\text{C}$ to be connected with it. The presence of the single oxide phases does not influence substantially on the activity of the investigated samples as the difference between copper and cobalt supported catalysts have comparable activity. Thus, the activity is mainly determined by the spinel phases formed – CuCr₂O₄ and CoCr₂O₄.

CONCLUSIONS

The results reported above show that the oxide catalysts based on couples Cu-Cr and Co-Cr supported on alumina and silica-alumina have relatively high catalytic activity in reactions of complete oxidation of MEK and toluene. This activity is determined by the spinel phase formation and the presence of couples of transition metal ions in different oxidation states.

REFERENCES

1. F. Nakajima, *Catal. Today*, **10**, 1991, 1-20.
2. K. S. R. Murthy, J. Ghose, *J. Catal.*, **147**, 1994, 171-176.
3. D. Mehandjiev, I. Dimitrova, B. Dyakova, *Compt. Rend. Acad. Bulg. Sci.*, **41**, 2, 1988, 67- 69.
4. D. Mehandjiev, K. Cheshkova, A. Naydenov, V. Georgescu, *React. Kinet. Catal. Lett.* **76**, 2, 2002, 287-293.
5. M. I. Vass, V. Georgescu, *Catal. Today* **29**, 1996, 463-470.
6. M. Teodorescu, I. Sitaru, A. Banciu, E. Segal, *Thermochim. Acta*, **233**, 1994, 233-239.
7. S. Angelov, D. Mehandjiev, B. Piperov, V. Zarkov, A. Terlecki, D. Jovanovic, Z. Jovanovic, *Appl. Catal.*, **16**, 1985, 431-437.
8. D. Panayotov, *React. Kinet. Catal. Lett.*, **58**, 1, 1996, 73-78.
9. K. Cheshkova, D. Mehandjiev, *Bulg. Chem. Comm.*, **26**, 1, 1993, 115-121.
10. I. Spassova, M. Khristova, D. Panayotov, D. Mehandjiev, *J. Catal.* **185**, 1999, 43-57.