An assessment of the industrial behavior of Cu - Cr/γ-alumina catalysts for combustion of exhaust gases

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Introduction

As it is known [1, 2], the catalytic oxidation of methanol on iron-molybdenum catalysts is accompanied by formation of toxic products, mainly CO and dimethyl ether. The high concentration of these compounds in the outlet gases requires the use of an additional reactor for their complete oxidation. This work studies the effect of preparation conditions and the industrial application on the active component composition and on the activity behavior of the γ–alumina supported Cu-Cr oxide catalysts by means of both laboratory and industrial scale experiments.

Materials and Methods

Commercial pure and modified γ-Al_2O_3 with particle size of 4,8 mm and total pore volume of 0.5 sm^3/g was used as a carrier in both laboratory and industrial experiments. The catalysts were prepared by impregnation of the support with an aqueous solution of copper nitrate and chromium nitrate or CrO_3 under different conditions [3]. X-Ray, XPS and SEM – EDS analysis were performed on the catalysts' balk and surface composition. The distribution of the active component on the entire carrier surface was found to be uniform. Two types of equipment for activity measurement were used - (i) flow-line equipment with isothermal reactor, allowing precise control on the methanol oxidation and amount of by-products and (ii) flow-line equipment with an adiabatic reactor for additional deep oxidation of the by-products. The reactant and product gases were analyzed for methanol, DME, CO and CO_2 by means of on-line gas chromatographs. Formaldehyde was analyzed separately.

Results and Discussion

Laboratory experiments

The effect of preparation conditions on the chemical composition, activity and selectivity of the γ–alumina supported CuO/Cr_2O_3 catalysts toward deep oxidation of CO, DME, formaldehyde and methanol oxidation was investigated. Chemical composition strongly influences catalytic properties, this influence being quite variable with regards to the different processes. Notwithstanding the low concentration of methanol and formaldehyde, their measurable oxidation begins at temperatures, significantly inferior than 180° C and reaches 100 % at about 190°C for all catalysts investigated. Considerably different is the activity of the catalysts with respect to the CO and DME. Their oxidation increases rapidly with increasing chromium content in the active component. On the basis of X-ray and XPS analysis it can be concluded that the active component of the mixed Cu-Cr/ γ–alumina catalysts consists of at least four compounds – CuO, Cr_2O_3, $Cu_2Cr_2O_4$ and $CuCr_2O_4$. CO oxidation. SEM –EDS analysis of the active component spaces (Fig. 1) revealed domination of $Cu_2Cr_2O_4$ particles.

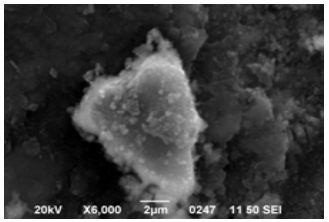

Figure 1. SEM image and energy dispersive X-ray microanalysis of "fresh" Cu - Cr/γ-alumina catalyst**.**

Element	Weight %	Atomic %
Cr	45.8	50.8
Cu	54.2	49.2

Industrial experiment

A six months' industrial experiment was carried out to verify the results from the laboratory experiments. The industrial installation monitored consists of an adiabatic reactor with 600 kg catalyst and possibilities to maintain the space velocity in the range of 5000 to 15000 h^{-1} and inlet gas' temperature of 180 – 240°C. Inlet concentration of the exhaust gases was as follows: CO – 1.2 to1.5 %, DME – 0.3 to 0.4 %, CH_3OH – 0.1 % and CH_2O – 0.1 to 0.2 %. Outlet gas composition was in the range of the ecological norms – CO < 100 ppm, DME < 100 ppm, CH_3OH < 100 ppm and CH_2O < 20 ppm. SEM –EDS analysis (Fig. 2) showed significant change in the catalyst composition. Iron and molybdenum, obviously coming from the oxide catalyst in the main reactor for methanol oxidation, appear on the active component surface. This results in the aggregation of the Cu-Cr spaces. Possibilities for catalyst regeneration by temperature treatment are discussed.

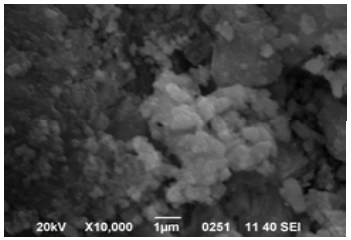

Figure 2. SEM image and energy dispersive X-ray microanalysis of "spent" Cu - Cr/γ-alumina catalyst**.**

Element	Weight %	Atomic %
Al	38.8	31.3
Cr	1.4	0.6
Cu	10.2	3.5
Fe	0.39	0.15
Mo	2.05	0.46

Conclusions

The CuO – Cr_2O_3/γ–alumina supported catalysts have enhanced activity toward CO, DME, formaldehyde and methanol oxidation and these catalysts are suitable for industrial application. The main reason for catalyst deactivation seems to be the location of iron and molybdenum, coming from the main reactor, on the active component surface.

References

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2. Tatibouët J. M. *Appl. Cat. A: General*, 148, 213 (1997).
3. Ivanov K., BG patent No 60779 B_1 (1993).

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