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Increase in Thermo-Stability of Chromia-Alumina Catalysts Used in Dehydrogenation of Paraffines by Means SHF Radiation

Oleg Khasanovich Karimov, Rustem Rifovich Daminev and Liliya Zainullovna Kasyanova

Branch of the Ufa State Petroleum Technological University in Sterlitamak,
Sterlitamak, Bashkortostan, Russian Federation

Abstract: The article investigates influence of microwave radiation thermo-stability of chromia-alumina catalysts used in the processes of de-hydrating of lowest paraffines. It was discovered that use of SHF radiation for manufacturing catalysts allows to increase thermo-stability. Increase in thermo-stability of catalysts is achieved through stabilization of active centers while drying catalysts in microwave field. Thermo-stability of catalysts correlates with temperature and duration of calcination. It was discovered that with increased temperature and duration of calcination the catalysts produced in microwave field demonstrates higher stability of active centers.

Key words: Microwaves · Chromia-alumina catalysts · Thermo-stability

INTRODUCTION

Chromia-alumina catalysts are well-spread in national industry; they are used in the processes of production of isobutylene and isoprene by methods of two-stage dehydration of isobutene and isopentane correspondingly. The dehydrogenation of hydrocarbons to monomer is a highly endothermic reaction [1]. Thermodynamics of dehydrogenation of paraffines (high temperatures up to 600 degrees °C [2, 3]) requires from chromia-alumina catalysts to posess some special characteristics, one of which is thermo-stability.

Thermo-stability of catalysts means resistance to the influence of high temperatures without changes in structure, activity and selectivity of catalysts [4]. Traditionally, in order to increase thermo-stability the catalysts are treated at preliminary stage at temperatures up to 800 °C. If the temperature of calcination is low (T<400 C), chrome-containing composites on the surface of the supporter (supporting medium) are crystals CrO3 and with higher temperatures - mainly α-Cr_2O - the source of low-active Cr^{3+} In accordance with [5] optimal temperature for activation of catalysts is 700-800 °C applied for 4 hours. But taking into consideration local over-calcination in the body of aluminium oxide supporter under SHF field [6] we can suggest that the temperature of thermo-activation of catalyst produced with the use of electro-magnetic radiation can be reduced. In previous work, [7] we found that use of SHF radiation in production of chromia-alumina catalyst allows to produce more effective catalysts.

This work is devoted to investigation of stability of chromia-alumina catalysts used for dehydrogenation of paraffines (produced by traditional dipping method and by method of SHF-field) depending on temperature and duration of thermo-treating.

MATERIALS AND METHODS

Complete cycle of production of catalysts intended for dehydrating of lowest paraffines by dipping method includes the following stages: preparation of dipping solution; dipping of aluminia supporter, drying of catalyst, activization of catalysts.

The catalyst samples were produced in the following way. In order to achieve concentration of Cr_2O_3=13.0% mass and K_2O=2.0% mass in the catalysts dipping solution H_2CrO_4+KOH was used. Catalyst supporter MITALOX-TA-240 was used. Salt solution was applied for 30 minutes after which the catalysts was stirred during 1.5 hour. Drying of catalysts precursors was done by 2 methods: 1) traditional - in sand bath for 2 hours by

Corresponding Author: Karimov, Branch of the Ufa State Petroleum Technological University in Sterlitamak, Pr. Oktyabrya, 2, Sterlitamak, 453118, Bashkortostan, Russian Federation.

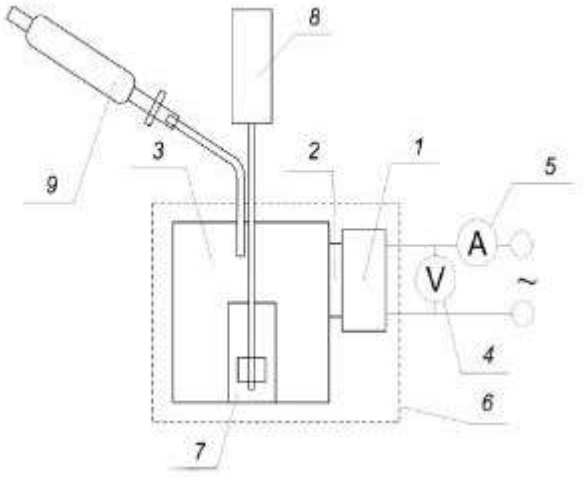

Fig. 1: Scheme of the SHF setup:
1 – generator (magnetron), 2 – waveguide, 3 – resonator chamber, 4 – voltmeter, 5 – amperometer, 6 – setup case, 7 – catalyst sample, 8 – stirrer, 9 –impregnation solution.

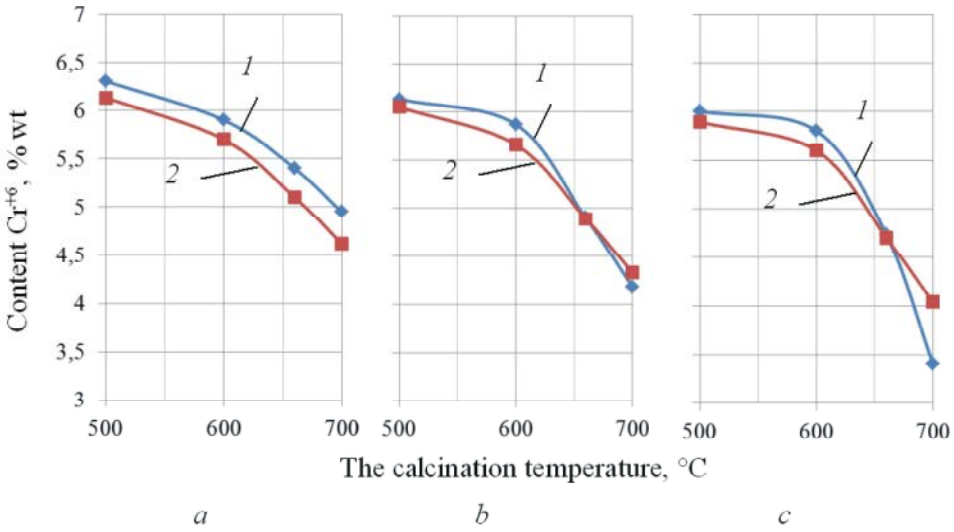

Fig. 2: Dependency of stability of catalysts on the calcination temperature
(1 - traditional catalyst, 2 - dried in SHF field)
a - 4 hours; b - 5 hours; c - 6 hours.

temperature of 120 °C (then such catalyst samples will be called by us traditional catalysts); in SHF unit with power of 900 W for 3 minutes (this followed by drying in SHF-field). The SHF-unit is shown in Figure 1. Thermo-activation of catalysts was carried out at different temperatures and durations in muffle oven with regulated calcination.

Active component content in produced catalysts was identified with the use of chrome extraction method (IV) in acid medium of iodine from solution of potassium iodine.

Thermo-stability of catalysts was also checked by use of express-method by means of calcination at temperature of 800 °C for 4 hours.

Main Part: Stability of catalysts depending on temperature and time of thermo-treating is shown in Figures 2 and 3. You can see that high-valent chrome content is reduced with increase in temperature and duration of calcination. This is determined by restoring of Cr^{6+} to Cr^{3+} and reduction of specific surface because of transformation of

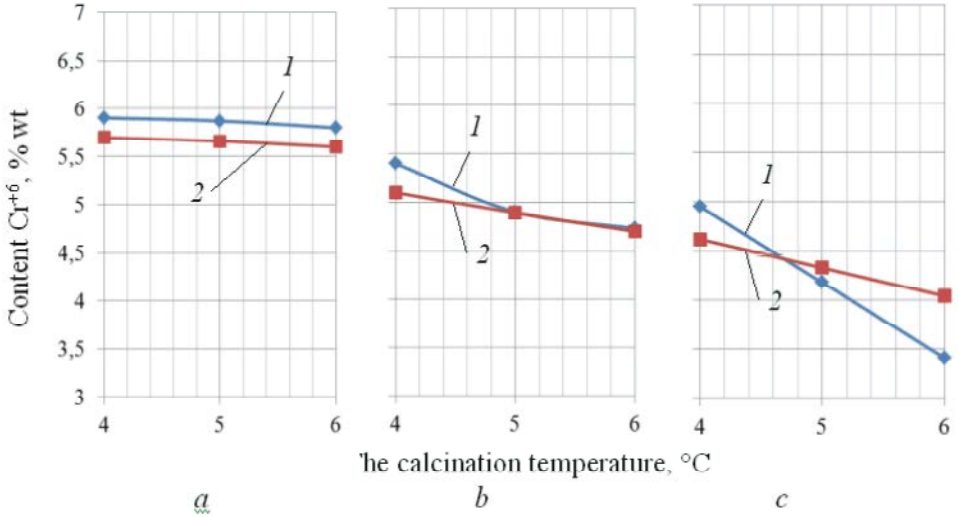

Fig. 3: Dependency of catalysts stability on duration of calcination
(1 - traditional catalyst, 2 - dried in SHF field)
a - 600 °C; b - 660 °C; c - 700 °C.

Table 1: Results of express-method to identify catalysts stability

	Content C_r^{6+}, % mass.		
Catalyst sample	Original	After calcination800 °C 4 hours.	Losses of C_r^{6+} after calcination, %
Traditional	5.38	3.41	36.62
Dried in SHF field	4.70	3.51	25.32

micro-pores into meso-pores with increase in temperature [8, 9]. This leads to blockage of a part of active chrome between particles of aluminum oxide which makes them inaccessible for further reaction.

In the interval of temperature 500-600 C content of Cr^{6+} decreases abruptly because of reactions of restoring of Cr(IV) to Cr(III). Here in traditional catalyst residual contents of six-valent chrome at these temperatures is a little higher than in catalyst produced by drying in SHF-field. The greatest difference of contents of high-valency chrome is observed when the time of calcination is the least - 4 hours. But with increase of time and temperature of activation traditional catalyst starts to loose active chrome abruptly.

At temperature 660 °C and the time of calcination for 5 hours both catalysts has practically the same content of active chrome. With further increase of temperature up to 700 C dried in SHF-field catalyst starts to reveal more stable characteristics.

The results of express-method also proves what was said above (Table 1).

CONCLUSION

Loss of chrome in traditional catalyst with increase in duration and temperature of calcination depend on reduction of specific surface of catalysts because of transformation of micro-pores into meso-pores with increase of calcination temperature [10]. As a result a part of active chrome get between the particles of aluminum oxide which makes them inaccessible for further reactions.

As we see from results of express-method of identification of catalysts stability, dried in SHF-field chromia-alumina catalyst is for 11% more stable than catalysts produced by traditional technology.

Inference: Thus, use of micro-wave radiation at the stage of drying of catalyst allows to increase thermo-stability of catalyst. Increase in stability of catalyst dried in SHF-field at high temperatures and prolonged calcination is possibly determined by stabilization of parameters of pore-structure of the catalyst's supporter under influence of SHF-radiation

and partial stabilization of active centers even at the stage of catalyst's drying. The result of it is that with further thermo-treating catalyst has a better stability.

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