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Thermal stability improvement of hopcalite catalyst

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The properties of hopcalite in alumina matrix formed by rehydration of transition aluminas have been investigated in comparison with conventional hopcalite catalyst. By using X-ray diffraction, thermal analysis and activity measurements in combustion of *n*-butane and air mixture it was found that the presence of alumina matrix leads to improvement of thermal stability at elevated temperatures and to limitation of spinel phase recrystallization. The modified catalyst was found to show much higher activity after thermal treatment at temperatures above 773 K than pure hopcalite at the same conditions.

Keywords: Hopcalite; catalyst stabilization; post-combustion

1. Introduction

The high activity of manganese and copper oxide mixture for low temperature oxidation of CO was discovered and described by Lamb et al. in the year 1920 [1]. The catalytic properties of such a system called hopcalite were confirmed by Jones and Taylor in the year 1923 [2]; since that time hopcalite has become a well known oxidation catalyst at room temperature. It is used for the removal of air pollutants such as CO and NO_x from exhaust gases; it is also important in respiratory protection in military, mining and many other applications [3–5]. A literature survey reveals that hopcalite catalyst is highly active in the amorphous state even at room temperature but has generally been observed to lose activity after exposition at temperatures above 773 K where crystallization of the spinel $CuMn_2O_4$ occurs [6–8]. However, crystalline $CuMn_2O_4$ has also been reported by Schwab and Kanungo [6] to be active.

Some attention has been given to modification of the hopcalite catalyst in order to eliminate its faults but without significant effects, though Haruta and Sano [9] slightly enhanced the catalytic activity of such a system at elevated temperatures by adding other metallic oxides. Our previous investigations [10] have shown the possibility of thermal stabilization of hopcalite catalysts in alumina matrix. The modi-

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fied one containing 50 wt% of alumina was found to show higher activity after calcination at 1073 K than pure hopcalite under the same conditions.

In this work we tried to determine the properties of hopcalite catalyst incorporated in alumina matrix in dependence on contents of its active components.

2. Experimental

The hopcalite catalyst (H) was obtained by mixing separately precipitated copper with manganese oxides in mol ratio $CuO : MnO_2 = 1 : 2$ [11]. The hopcalite catalyst in alumina matrix (H-TA) was prepared by mixing a wet paste of hopcalite with transition aluminas (TA) obtained by flash calcination of gibbsite at 723 K [12]. After forming, a conditioning of extrudates was carried out for 48 h in the presence of H_2O, for the purpose of TA rehydration [13]. The contents of active phase (hopcalite) in alumina matrix were, respectively, 10, 20, 40, 60, 80 and 90 wt%. All the catalyst samples were dried at 380 K and then calcined for 4 h at 473, 773, 1073 and 1273 K, respectively.

Activity of catalyst samples in oxidation reaction was evaluated by combustion of 0.5 vol% *n*-butane in air mixture passed through a gradientless, circular-flow reactor with a space velocity of 10^3 h^{-1} [14]. Conversion measurements were conducted by using a gas chromatograph after attaining the reaction temperature (every 25 K) up to 650 K.

The phase and structural changes of catalysts were estimated using a X-ray diffractometer DRON-3, using Cu K_α radiation and Ni-filter. The DTA-TG analysis was made under dynamic conditions in air using a derivatograph LINSEIS GmbH.

3. Results and discussion

In fig. 1 catalytic activity curves are shown for hopcalite samples H and H-TA containing 40 wt% of active phase (for which the improvement effect of alumina matrix presence was the most visible) in dependence on calcination temperature. The *n*-butane conversion curves of pure hopcalite after thermal treatment at elevated temperatures are shifted to higher temperature range evidencing the decrease of catalyst activity. By comparison of temperatures at which the conversion of *n*-butane reaches 50%, it can be noted that the hopcalite calcined at 1073 K requires the rise of reaction temperature at least by 150 K in comparison with the same sample calcined at 473 or 773 K.

It should be noted that the H-TA sample containing 40 wt% of active phase shows different catalytic behaviour. The most visible difference is that the decrease of activity observed after thermal treatment at 1073 and 1273 K is less sharp in comparison with pure hopcalite calcined under the same condition. Moreover, after cal-

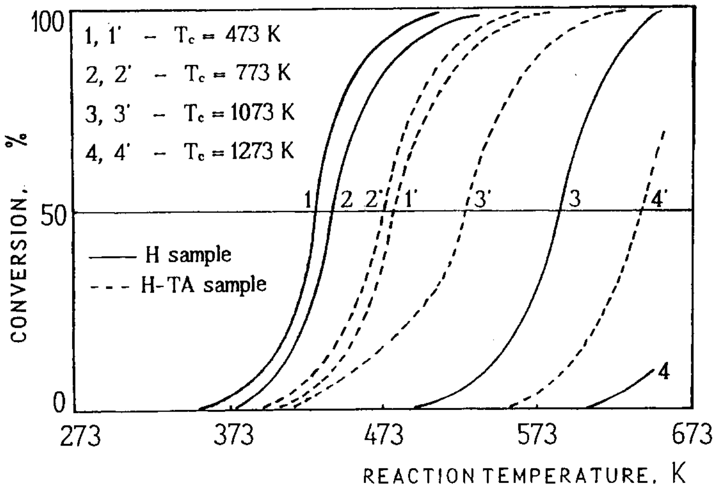

Fig. 1. The *n*-butane conversion curves as a function of reaction temperature in dependence on calcination temperature T_c for hopcalite catalyst and the hopcalite sample containing 40 wt% of active components.

cination at 1273 K, only in the presence of H-TA sample was it possible to obtain 50% conversion of *n*-butane. The incorporation of hopcalite in alumina matrix causes therefore the significant improvement of catalyst stability with respect to its high temperature resistance.

The relationship between the temperature of 50% conversion of *n*-butane and contents of hopcalite in alumina matrix are shown in fig. 2. The activity of H-TA samples calcined at 473 and 773 K increases with the increase of hopcalite contents in alumina matrix. The H-TA samples containing no more than 40 wt% of hopcalite show a little higher activity after thermal treatment at 773 K than at 473 K but with increase of hopcalite contents above 40 wt%, this relationship becomes reverse. The advantageous effect of alumina matrix presence appears especially after calcination at 1073 K.

It can be seen that 40 wt% contents of hopcalite in alumina matrix are the most effective for thermal stability and improvement of activity in this system. It should be added that aluminium oxide used as matrix for H-TA samples shows no activity in *n*-butane conversion up to 650 K.

The results of DTA analysis of pure hopcalite catalyst and H-TA samples containing 80, 40 and 20 wt% of active components, respectively, are shown in fig. 3. The DTA analysis reveals several different thermal effects. These are: (1) loss of physically adsorbed water at 373 K, characterized by a sharp endothermic peak; (2) loss of chemically bound water at 530 K, associated with the decomposition of bayerite (formed during the rehydration of TAs); (3) endothermic effect at 770 K from the decomposition of boehmite contained in rehydration products of TAs; (4) endothermic decomposition of MnO_2 to Mn_2O_3 at 800 K; (5) well defined exother-

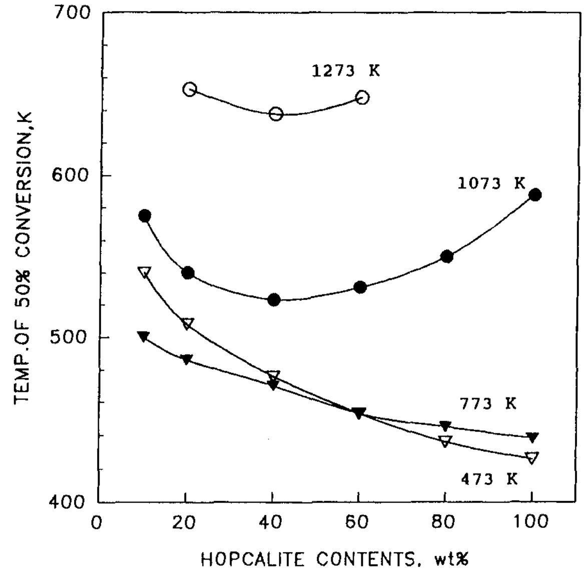

Fig. 2. The dependence of the temperature of 50% conversion of *n*-butane on hopcalite contents in alumina matrix for samples calcined at 473, 773, 1073 and 1273 K, respectively.

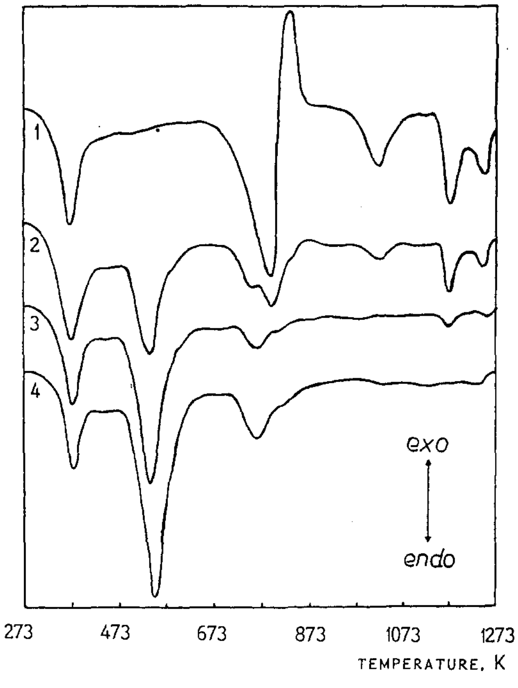

Fig. 3. DTA curves for catalytic samples in dependence on contents of hopcalite in alumina matrix. (1) 100 wt% of hopcalite, (2) 80 wt% of hopcalite, (3) 40 wt% of hopcalite, (4) 20 wt% of hopcalite.

mic peak at 850 K associated with the recrystallization of poorly crystallized spinel phase; (6) poorly defined endothermic effect from the reaction of Mn_2O_3 with excess of CuO at 1030 K; (7) endothermic decomposition of Mn_2O_3 to Mn_3O_4 at 1170 K; (8) endothermic response at 1250 K due to the decomposition of spinel phase.

The most important difference in thermal analysis of pure hopcalite catalyst and samples containing alumina besides active components is the lack of the sharp exothermic peak at 850 K associated with the crystallization of spinel phase for samples in alumina matrix. The lack of the exothermic effect at 850 K indicates that alumina matrix significantly impedes recrystallization of poorly crystallized and well dispersed spinel phase.

The X-ray diffraction investigations have shown that after activation of catalyst at 473 K all the H and H-TA samples consist of highly dispersed phases of initial oxides. The poorly crystalline spinel phase appears at 573 K. The increase of calcination temperature causes a decrease in the dispersion of the spinel phase according to the initial hopcalite contents in alumina matrix.

It has been noted that for the H-TA sample containing 40 wt% of active phase the average spinel particle size (derived from line broadening of the diffraction peak corresponding to $d = 2.9595$ Å) changes little after calcination in the temperature range 773–1273 K from 120 to 240 Å. At the same time the dispersion of the pure hopcalite sample becomes explicitly smaller and the average particle size of the spinel phase increases to 870 Å after calcination at 1273 K.

It was also found from X-ray diffraction study that lattice parameter a of the spinel phase in investigated samples, was strongly dependent on hopcalite contents in alumina matrix as well as on calcination temperature. These changes are shown in fig. 4.

For pure hopcalite catalyst the lattice parameter a of the spinel phase is 8.33 Å which is very similar to the literature value [15]. In the case of hopcalite in alumina matrix catalyst (H-TA) the spinel lattice parameter a changes dramatically with the increase of the hopcalite contents in alumina matrix particularly for samples calcined at temperatures above 1073 K. For the sample containing 20 wt% of hopcalite and calcined at 1273 K, the lattice parameter a of the spinel phase reaches 8.12 Å which suggests a partial incorporation of smaller aluminum ions into the structure of spinel phase and the creation of a mixed Cu–Mn–Al spinel.

It is obvious from our investigations that the presence of alumina matrix leads to improvements of the thermal stability of hopcalite at elevated temperatures and significantly impedes recrystallization of dispersed spinel phase. Therefore, it can still show high catalytic activity at high temperatures.

The mechanism of stabilization of hopcalite-alumina catalyst may result, on the one hand, in the fact that alumina matrix formed by rehydration of transition aluminas creates a porous aluminum oxide system containing dispersed active components. Such a system may exhibit better thermal stability at elevated temperatures by being restraint on sintering and recrystallization of active components. Or,

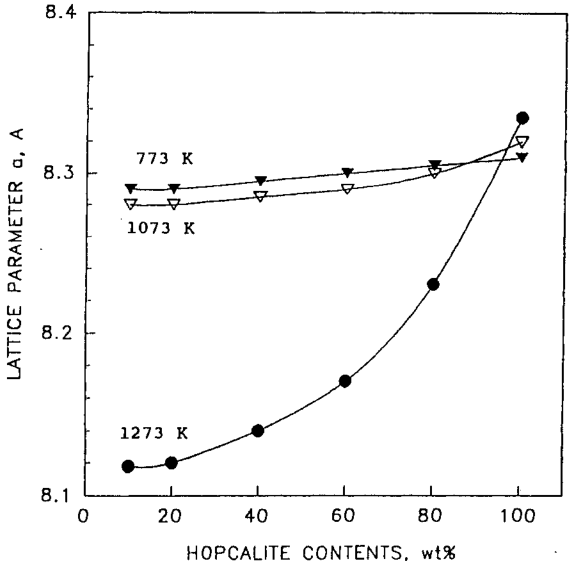

Fig. 4. Effect of calcination temperature T_c on relationship between lattice parameter a of spinel phase and hopcalite contents in alumina matrix (numbers on curves denote T_c in K).

on the other hand, in the creation of mixed aluminum–manganese spinel whose recrystallization at temperatures above 773 K, may be inhibited.

The hopcalite catalyst in alumina matrix shows besides high mechanical strength and low abrasiveness. Sometimes it would be a good substitute of catalysts containing noble metals used for the purification of various industrial and automotive exhaust gases.

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