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THERMAL ANALYSIS OF THE EFFECT OF SAMARIUM OXIDE ON THE REDUCTION OF PRECIPITATED AMMONIA SYNTHESIS CATALYST

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ABSTRACT

The effect of samarium oxide on reduction kinetics of the precipitated ammonia synthesis catalyst was investigated by thermal methods. The reduction was carried out with purified hydrogen. The kinetic parameters were calculated from the nonisothermal DTA and TG plots. Results obtained were complementary to the previous kinetic measurements and indicate that the addition of Sm_2O_3 changed the velocity of reduction and has some but no remarkable effect on the activation energy of the catalyst reduction.

INTRODUCTION

Many efforts were done to elucidate the effect of various compounds on the properties and activity of the ammonia synthesis catalyst, with the aim of developing the more efficiant promoters. In that scope rare earths are of interest, too. In this work thermal analysis has been applied to follow the reduction of the precipitated ammonia synthesis catalyst with Sm_2O_3 added instead of aluminium or calcium oxides as a common promoters.

EXPERIMENTAL

Catalysts were synthetized by coprecipitation of iron and samarium hydroxide and addition of potassium, the procedure being described elsewhere(1). To one of the samples (F-4) aluminium and silicium oxide were added in order to obtain a composition corresponding to the industrial type of catalyst. Contents of the promoters in the investigated samples is shown in table 1.

Table 1. Contents (wt%) of the promoters in the investigated samples

Sample	K_2O	Sm_2O_3	Al_2O_3	SiO_2
F-0	-	-	-	-
F-1	0.67	1.38	-	-
F-2	0.62	1.87	-	-
F-3	1.20	2.65	-	-
F-4	0.78	2.15	3.50	1.20

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Phase composition of the samples was determined by X-ray diffraction. Reduction of catalysts, ground to -0.1 mm and dried at 383K, has been performed in a stream of purified hydrogen and followed nonisothermally, till completion, with the Linseis L 81/22 thermobalance. Energy of activation of the reduction was calculated from thermogravimetric data following the method of Coats and Redfern(2).

RESULTS AND DISCUSSION

In all the unreduced samples the phase of hematite was detected, only. Results of thermal analysis are shown in table 2, where temperatures of the beginning (T_b) and the end (T_e) of the reduction, the maximum of the effects (T_m) detected by DTA, degrees of reduction (d) and energy of activation of the reduction from 700K to 933K (630K-815K for sample F-0) calculated from TG data are listed. On figure 1 characteristic thermograms of the catalyst with samarium oxide were compared to the sample without promoters.

Table 2. Results of thermal analysis

Sample	DTA				TGA				Ea
	T_b	T_{m1}	T_{m2}	T_e	T_b	d_{T1}	d_{T2}	T_e	KJ/mol
F-0	635	700	810	869	593	0.19_{688}	0.34_{734}	875	55,2
F-1	677	708	759	869	621	0.13_{698}	0.34_{759}	973	75,6
F-2	684	718	779	846	646	0.12_{708}	0.31_{779}	1011	61.9
F-3	677	714	800	343	624	0.10_{696}	0.33_{759}	1088	64.4
F-4	664	715	729	873	648	0.18_{775}	0.39_{873}	1166	36.8

Adding of samarium effected the shifting both the beginning and the end of the reduction toward higher temperatures than in the case of the pure iron oxide. Sample F-4 which contains two promoters besides potassium and samarium oxides was reducted most slowly which may be ascribed to the superposition of the effect of the present oxides.

Energy of activation of the reduction was higher in samples with samarium oxide.

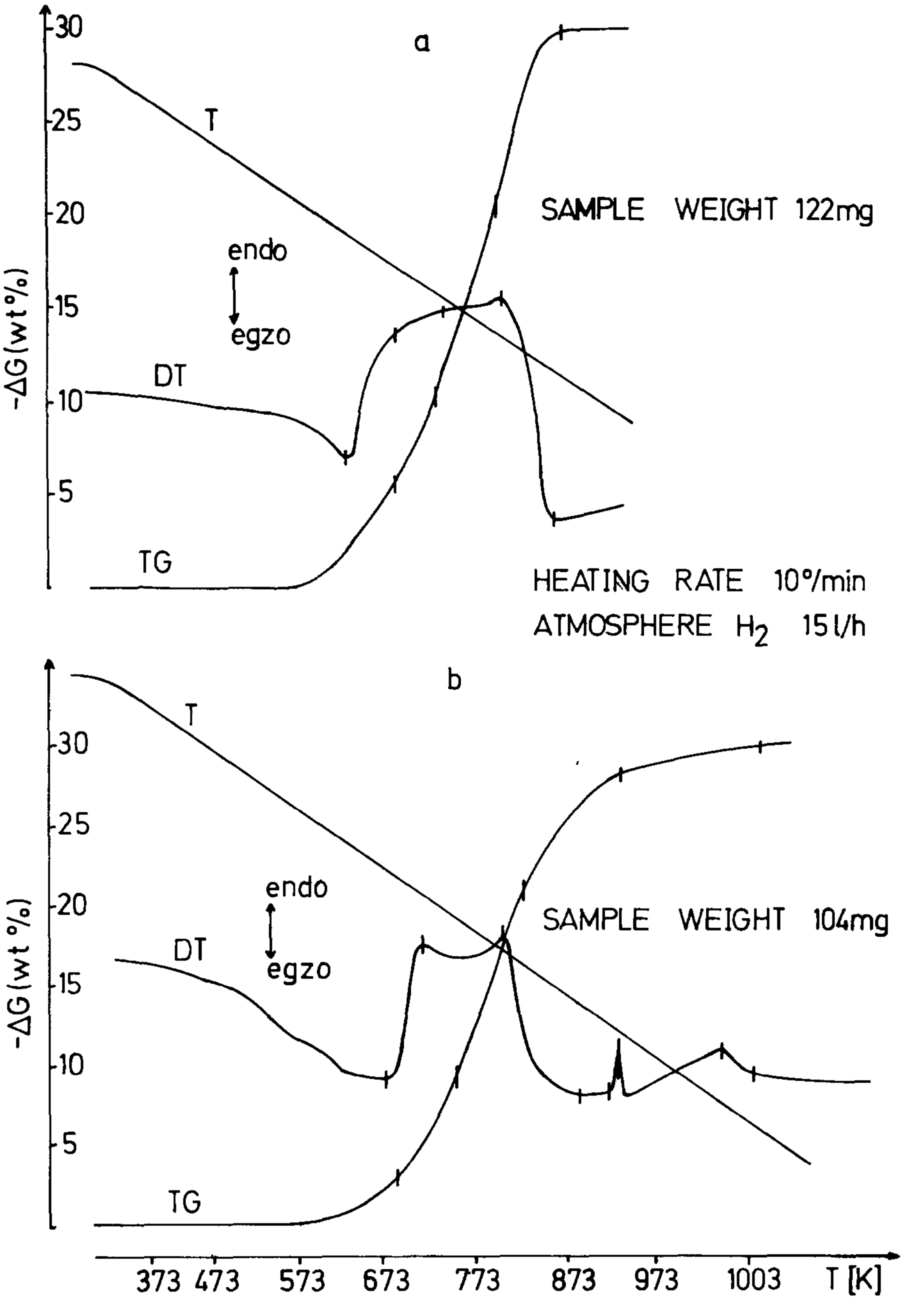

Figure 1. DTA and TG curves of the samples F-0 (a) and F-3 (b)

All the samples show the stepwise reduction. Some discripience between the characteristic temperatures of the reduction steps observed by DT and TG analysis may be ascribed both to the higher sensitivity of thermogravimetric measurements and the law thermal effects of some sequences of the reaction especialy near the end of the reduction. On the basis of the results obtained it may be assumed that the reduction in the applied conditions passes through all of the steps of ferric oxide reduction(3). Our previous investigations of the reduction kinetics of the same catalyst by the gas-volumetric method(4) have confirmed the existence off all these steps. The accumulation of the wustite was detected by Mossbauer spectroscopy in the samples with oxide promoters even at temperatures some what lower than the limit of thermodynamic stability of pure wustite phase. In this work, wustite was detected by X-ray analysis in samples with samarium oxide reduced at temperatures higher than 710K.

CONCLUSIONS

Addition of samarium oxide to the precipitated ammonia synthesis catalyst shiftsthe beginning and the end of reduction toward the higher temperatures, loweres the rate of reduction and in a small extent increased the energy of activation of the reduction. The effect of the samarium oxide concentration was not observed.

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