INITIAL ACTIVITY OF ACIDIC, BASIC AND AMPHOTERIC OXIDES IN THE REACTION OF CO$_2$ WITH CS$_2$ TO FORM COS

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Received March 22, 1999
Accepted June 11, 1999

Abstract

Among various acidic, basic and amphoteric oxides La$_2$O$_3$ and ThO$_2$, both having strong ionic character and peculiar acid-base properties, exhibited outstanding initial catalytic activity in the CO$_2$ + CS$_2$ = 2COS reaction.

Keywords: Oxide catalysts, acid-base properties, COS formation, initial activity

INTRODUCTION

Carbonyl sulfide is an important reagent in organic synthesis, in particular in the manufacture of substituted thiocarbamic acid type herbicides. One of the methods of producing COS is the catalytic O/S exchange reaction between CO$_2$ and CS$_2$. Apart from its practical importance, the reaction is a good example of the catalytic activation of CO$_2$ at moderate temperatures (500-700 K).

The reaction can be catalyzed by charcoal, zeolites and metal oxides. Sugioka et al. [1] have shown that on a catalytic activity per catalyst weight basis, gamma-Al$_2$O$_3$ is superior to other oxides. Since then, most of the investigations have been made on alumina [2-6]. It has been shown that the loss of catalytic activity upon long term loading is roughly proportional to the loss of surface basic sites [4] and is primarily caused by the deposition of carbon and sulfur in C-S, C=S and C-C environment [5]. Donor type additives (alkali, pre-adsorbed ammonia or pyridine) resulted in an increased surface basicity, increased CO$_2$ and CS$_2$ adsorption and better catalytic performance [6], suggesting that catalytic activity is closely related to the energy and population of surface acidic and basic sites.
This paper will be restricted to the study of the acid-base properties and the initial catalytic activity of metal oxides ranging from strongly basic to strongly acidic, and kinetic results referring to steady state conditions will be discussed in paper [7].

EXPERIMENTAL

The population and energy of the surface acidic and basic sites were characterized with the differential adsorption heats of NH$_3$ (at 423 K) and CO$_2$ (at 296 K) by a combined volumetric-calorimetric method [8], in the pressure range of 0 - 1 mbar. The specific surface area was determined by the BET method. The adsorption of CO$_2$ at temperatures overlapping with those of the catalytic tests was studied by thermogravimetry.

Catalytic tests were done by a pulse method in a fixed bed microreactor connected to a GC. Crushed catalysts were layered upon the quartz filter inside a vertical quartz reactor of 5 mm I.D. The gas entered the reactor from the top. In all experiments the catalyst charge was 0.100 g. The carrier gas was high purity He with a flow rate of 60 cm$^3$/min. Reagent grade CS$_2$ was introduced to the pulsing valve by a continuous stream of CO$_2$ through a thermostated bubbler kept at 294 K. Thus, the partial pressure of CO$_2$ and CS$_2$ entering the pulsing valve was 0.59 and 0.41 bar, respectively. The pulse volume was 1.0 cm$^3$.

Catalysts, pretreatment and the state of oxides after pretreatment

Alumina (type CK 300) was manufactured by Ketjen. MoO$_3$ and WO$_3$ were supplied by REANAL. The other 13 oxides under study were purchased from other manufacturers or prepared in the laboratory from high purity precursors. For more details, the interested reader is directed to the papers by Auroux and Gervasini [8, 9].

Prior to calorimetric study the samples have been heated overnight at 673 K under an oxygen atmosphere and then evacuated at the same temperature for 2 h. Before kinetic and thermogravimetric measurements the samples were kept at 773 K in flowing O$_2$ for 2 h, and then in high purity He flow, also for 2 h.

We assume the first stage of the pretreatment (O$_2$ at 663 or 773 K) results in the formation of full oxides and the removal of carbonaceous impurities. However, it was questionable whether any of the well known lower oxides of titanium, niobium, tantalum, molybdenum or tungsten can be formed or not in the second stage of pretreatment under high vacuum or in high purity He stream. For the assumed reactions and for 800 K, the equilibrium conditions calculated by utilizing the data of the JANAF Thermochemical Tables [10] are given below.