Thermochimica Acta, 85 (1985) 83–86
Elsevier Science Publishers B.V., Amsterdam — Printed in The Netherlands

THERMOGRAVIMETRIC, MASS SPECTROMETRIC AND XPS INVESTIGATION ON THE CHLORINATION REACTIONS OF V_2O_5 AND TiO_2

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ABSTRACT

Comparative studies on the kinetics and mechanism of the chlorination of V_2O_5 and TiO_2 /anatase/ with CCl_4 have been performed. The chlorination of V_2O_5 occurredto be 0.5 order in CCl_4, whereas in case of TiO_2 closely first order kinetics was observed with apparent activation energies of 77 ± 5 and 118 ± 7 $kJ.mol^{-1}$, resp. In both cases a dissociative adsorption of CCl_4 is considered to precede the reaction and the transformation of CCl_4 to CO_2 is assumed to occur via the formation of adsorbed $COCl_2$ intermediate. In case of V_2O_5, phosgene is less reactive than CCl_4, so during the chlorination of V_2O_5 by CCl_4 the gas phase concentration of $COCl_2$ might achieve a considerable level, while in the TiO_2-CCl_4 system only trace quantities of phosgene are observable. At the beginning of the reactions step by step exchange of surface O by Cl occurs, and the surface intermediates of the chlorination are V and Ti ions of lowered valence state, as it has been characterized by ESCA.

INTRODUCTION

The chlorination of V_2O_5 and TiO_2 are of great practical and scientific interest. As most of the relevant publications refer to the method using Cl_2 and C /as a reducing agent/, relatively few data are available concerning the kinetics and mechanism of chlorination by CCl_4 /refs. 1-4/ and $COCl_2$ /ref. 5/.

METHODS

Before the chlorinations V_2O_5 /$s^o = 3.1\ m^2.g^{-1}$/ and anatase-TiO_2 /$s^o = 7.0\ m^2.g^{-1}$/, both analytical grade, were oxidized for 1 h at 700 and 800 K, resp. The steady-state kinetics under flow condition was studied by TG using a METTLER semimicro recording balance. For investigating the initial stage of the reactions before the steady-state, a closed static reactor connected with BALZERS QMS 101 was employed. XPS spectra on in situ chlorinated single-crystalline V_2O_5 and powder like TiO_2 samples were run on a VG ESCA 3 MK2 and also on a KRATOS XSAM 800 instrument.

0040-6031/85/$03.30

RESULTS AND DISCUSSION

The adsorption of CCl_4 on V_2O_5 and on TiO_2 was studied by volumetric method. The kinetic and energetic features of the adsorption suggested that in both cases only a weak, physical type adsorption occurs /refs. 6-7/ at room temperatures which becomes negligible above 400 K. Therefore a first order kinetics has been expected for either gaseous or weakly adsorbed CCl_4, proposed to take part in the rate determining step, so the rate should be proportional to the pressure. While in case of TiO_2 a closely first order kinetics was found, the chlorination of V_2O_5 proved to be about half order in CCl_4, as shown in Fig.1. This suggests that in this case the reaction is preceded by a reversible dissociative adsorption of CCl_4 which probably occurs on two neighbouring exposed

$$CCl_4/g/ \rightleftharpoons [CCl_4/a/] \rightleftharpoons CCl_3/a/ + Cl/a/ \qquad /1/$$

vanadium atoms on the basal plane of V_2O_5. A detailed evaluation of the kinetic data on the TiO_2 + CCl_4 reaction /ref. 7/ has also suggested that the dissociative adsorption process in this case also should be taken into consideration.

From the temperature dependence of the initial rates apparent activation energies as 77 ± 5 $kJ.mol^{-1}$ at 450-550 K and 118 ± 7 $kJ.mol^{-1}$ at 770-920 K have been obtained for vanadia and titania, respectively.

The initial stage of the chlorination was studied in detail at lower temperatures. Fig.2 shows the sequence of product formation when CCl_4 is brought to contact with V_2O_5 /A/ and with TiO_2 /B/ in a closed reactor. As seen in Fig.2A,

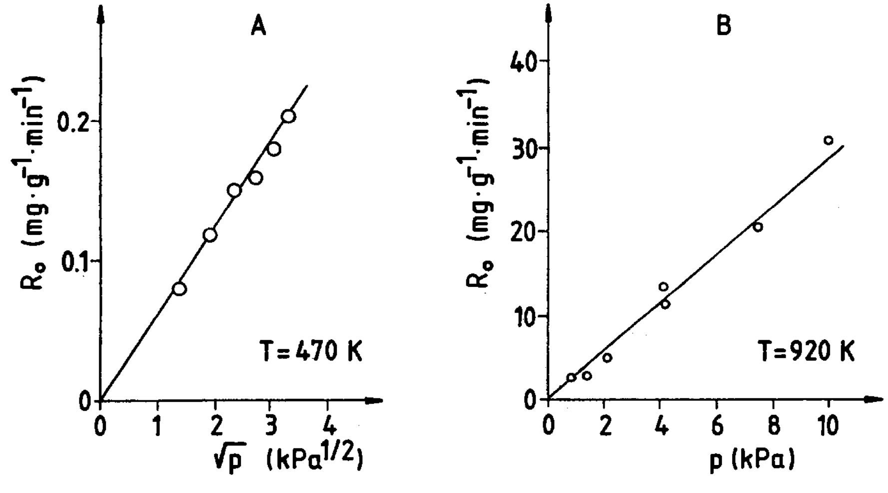

Fig.1. The dependence of the initial rate of chlorination /R_o/ on p_{CCl_4} in case of V_2O_5 /A/ and TiO_2 /B/

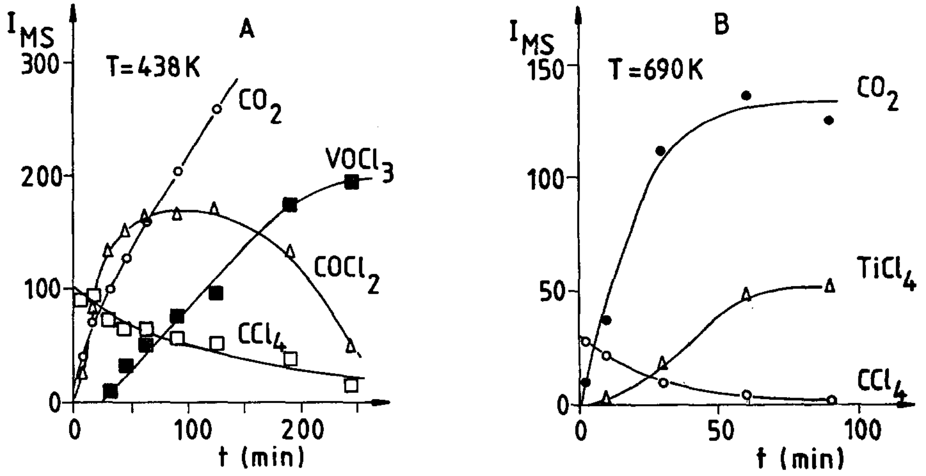

Fig.2. The MS-intensities of the major ions a.u. vs. reaction time: /A/-V_2O_5, /B/-TiO_2

the gas phase concentration of $COCl_2$ exhibits a wide local maximum, while in case of TiO_2 /Fig.2B./ phosgene was not detected in the gas phase. We do consider that in the latter case the formation of CO_2 also occurs via adsorbed phosgene, however the probability /i.e. the rate constant/ of its desorption is much lower than its further reaction. A brief comparison of the reactivities of phosgene and CCl_4 /Fig.3./ also suggests that the formation of adsorbed phosgene intermediate should be the rate determining step in the TiO_2 - CCl_4 re-

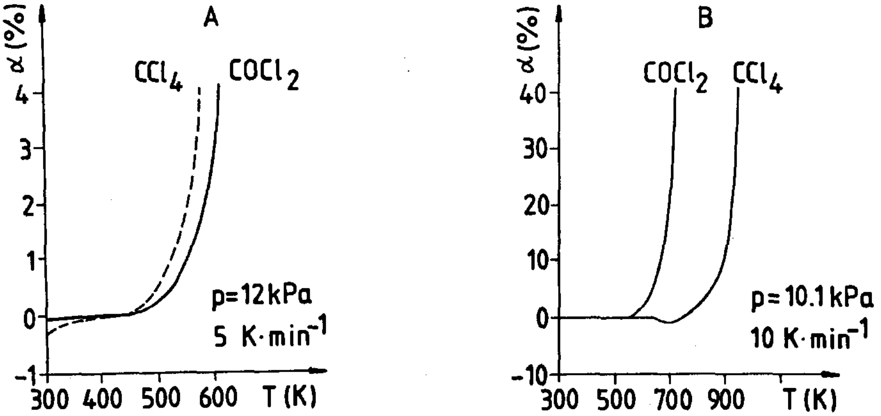

Fig.3. Anisothermal TG curves of the chlorination of V_2O_5 /A/ and TiO_2 /B/ with CCl_4 and $COCl_2$; α : mass loss

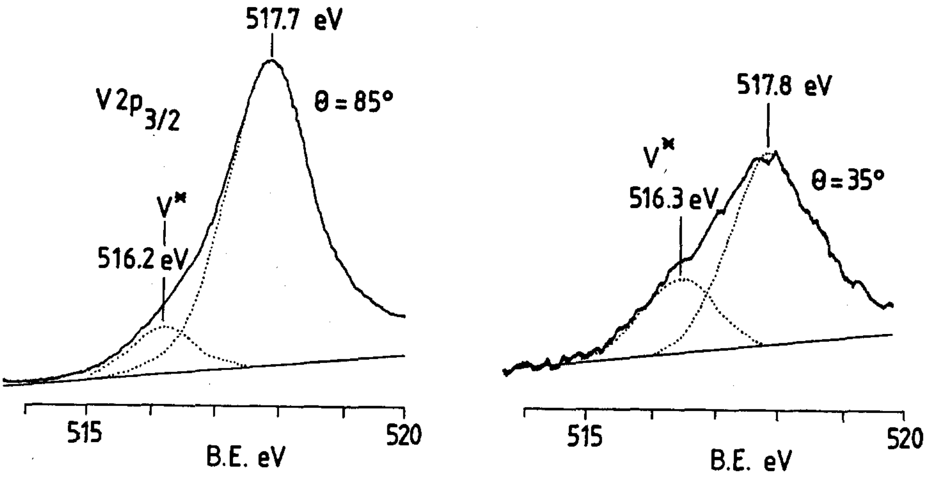

Fig.4. The angular dependence of the intensity ratio of the V 2p 3/2 lines on chlorinated V_2O_5 single crystal

action. It is worthwhile to note that in the experiments in static reactor /see Fig.2./ molecular Cl_2 has not been observed by MS. Therefore in both reactions the formation of CO_2 and $COCl_2$, i.e. the removal of the surface oxygens should correspond to their exchange by chlorine, as it was proposed previously /ref. 3,4/ for TiO_2+CCl_4. In fact, during this reaction a step by step accumulation of chlorine atoms on the surface was observed by ESCA. Moreover, in the XPS spectra of the chlorinated samples a shift of the V 2p and Ti 2p lines towards the lower binding energies has been found. To all probability these new lines refer to V^{4+} /or V^{3+}/ and Ti^{3+} ions as intermediates of the chlorination reactions. Angular dependence studies on chlorinated single-crystalline V_2O_5 have rendered it probable that V in this lower valence state forms an overlayer on the pure V_2O_5 substrate /Fig.4./.

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