

STUDY OF THE EVOLUTION OF CaCO₃-V₂O₅ (1:1) MIXTURE AT ROOM TEMPERATURE BY THERMAL ANALYSIS

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Reactivity of solid mixtures of crystalline V₂O₅ and basic compounds strongly increases at room temperature by means of water molecules adsorption process from a saturated atmosphere (100% RH). This is due, firstly, to a crystalline-amorphous V₂O₅ transformation and secondly to the formation of strongly acid V₂O₅ gels. In the present paper the evolution with time of the CaCO₃-V₂O₅ (1:1) mixture in the aforementioned conditions was studied by thermal analysis (TG, DTG and DSC), X-ray diffraction (XRD) and infrared spectroscopy (IR). The results confirmed the V₂O₅ gels formation which decomposed the basic CaCO₃ at room temperature through an acid-base mechanism reaction. A new crystalline compound was obtained which corresponded to a hydrated calcium metavanadate.

Keywords: CaCO₃-V₂O₅ mixture

Introduction

The reactivity of amorphous V₂O₅ towards water molecules and formation of gels have been widely studied [1-10], but information on the role played by the possible acid-base surface sites in relation to their properties and catalytic activity have not been reported.

In previous papers concerning the behaviour at room temperature of equimolecular mixtures of CdO, CdCO₃ or MgO and crystalline V₂O₅ in a water-vapour saturated atmosphere it was observed the dramatic increase of reactivity of the mixtures in such a way that cadmium metavanadate or magnesium metavanadate hydrate were obtained at room temperature [11-13]. An acid-base reaction

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mechanism was proposed which was activated by the formation of amorphous V_2O_5 and V_2O_5 gels as intermediate reactive nuclei of strong acid properties.

The aim of the present study is to achieve through a similar mechanism the $CaCO_3$ decomposition and calcium metavanadate formation at room temperature. For that an equimolecular mixture of $CaCO_3$ and crystalline V_2O_5 has been treated in the same aforementioned experimental conditions for several periods of time.

Thermal analysis (TG, DTG and DSC) have been employed to quantitatively follow the decrease of $CaCO_3$ content over time of treatment as well as the amount of water molecules adsorbed. The structural evolution of the samples has been studied by X-ray diffraction (XRD), and the kind of interaction between water molecules and solid phases by infrared spectroscopy (IR).

Experimental procedure

Mixtures of equimolecular $CaCO_3$ and crystalline V_2O_5 (grain size <0.05 mm) were prepared from Merck AR products which were previously characterized by XRD, IR and TG analyses. Samples of 1 g were kept at room temperature in small chambers at 100% of RH for various times. Before characterization studies samples were dried to constant weight in desiccators with silica gel.

For TGA and DSC a Mettler TA 3000 analysis system and a CTC10TA processor were used. The weight of samples was about 20 mg; a heating rate of $10 \text{ deg}\cdot\text{min}^{-1}$ and an air stream were employed. X-ray diffraction patterns have been performed with a Philips PW 1730 diffractometer using a graphite monochromator and $CuK\alpha$ radiation. IR study was carried out on a Perkin Elmer 305 instrument; KBr pellets contained 0.3% of sample.

Results

Thermal analysis

The information obtained from thermal analysis lets quantify both the adsorbed water molecules and the $CaCO_3$ decrease as a result of reaction advance over time of humidic treatment. The different TG, DTG and DSC curve profiles are represented in Fig. 1. The $CaCO_3$ decomposition takes place at 800°C (DTG peak) whereas in the presence of V_2O_5 is shifted to a lower value (630°C) (see curves (1) and (2) in Fig. 1 (a)). At 770°C a change of the curve slope is de-

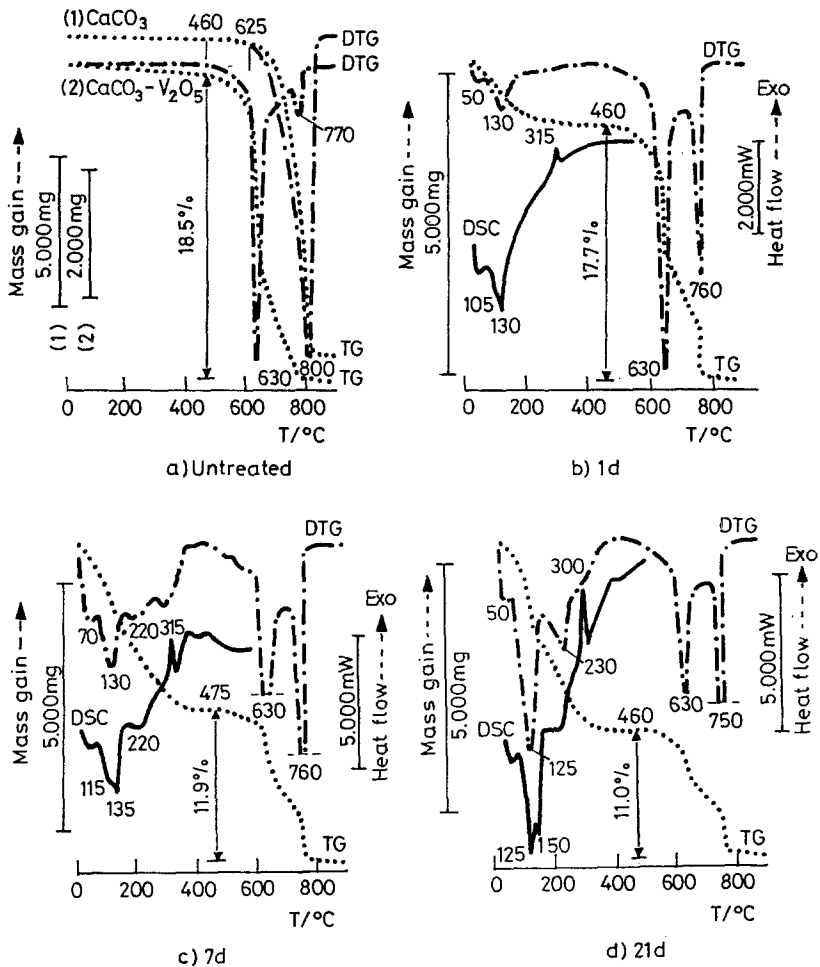


Fig. 1 TG, DTG and DSC curves at different times of treatment

tected which is due to the CaV_2O_6 fusion what favours the release of the rest of CO_2 . The V_2O_5 fusion takes place at 630°C which also favours the CaCO_3 decomposition. Once the samples are submitted to the humidic treatment the profile of the curves mainly changes in the $25^\circ\text{--}350^\circ\text{C}$ range of low temperature in which the adsorbed water molecules are released at different steps: 50° , 130° , 220° and 300°C depending on the time of previous treatment. The release of these different water molecules produces the corresponding endothermic peaks in the DSC curves at the same temperature ranges than those of DTG curves. The endothermic peak centered at 130°C and the shoulder at 105°C (Fig. 1(b))

becomes in a very strong endothermic double peak with maxima at 125° and 150°C (Fig. 1(d)). It should be mentioned the appearance of a narrow exothermic peak at 300°–315°C which is due to an amorphous-crystalline V₂O₅ transformation what has been constated from the XRD analyses of the samples taken off before and after the peak.

The CaCO₃ content mainly decreases at the earlier ages of previous treatment, practically stopping thereafter seven days (compare Fig. 1(c) and (d)). The fusion of free V₂O₅ and CaV₂O₆ take place at the same temperatures than those observed in the untreated mixture.

In Table 1 the mmols of the different kinds of water molecules per mmol of total V₂O₅ as well as the CaCO₃ content and reaction advance degree (α) are illustrated. From seven days of treatment (α) increases and decreases what seems to indicate the stop of the reaction.

Table 1 Data obtained from TG curves

Samples CaCO ₃ -V ₂ O ₅	wt. loss / mmol H ₂ O per total V ₂ O ₅				CO ₂ / % 630°C	Reaction advance degre (α)	
	total (Δn)	50°-70°C (Δn_1)	130°-150°C (Δn_2)	220°C (Δn_3)			300°C (Δn_4)
untreated	—	—	—	—	—	18.5	0.0
1 day	0.5	—	0.32	0.18	—	17.7	0.04
2 days	0.75	0.25	0.25	0.25	—	15.8	0.15
4 days	1.2	0.41	0.32	0.49	—	12.8	0.31
7 days	1.7	0.25	0.65	0.57	0.25	11.9	0.35
10 days	2.2	0.42	0.50	0.59	0.33	10.8	0.41
14 days	1.9	0.48	0.58	0.58	0.25	9.9	0.46
21 days	2.0	—	1.05	0.67	0.26	11.0	0.40

X-ray diffraction analysis

The evolution of the X-ray diffraction patterns with reaction time is shown in Fig. 2. After one day (Fig. 2(b)) some new lines appear whose intensities increase over reaction time showing the formation of a new crystalline phase which does not correspond to any calcium metavanadate anhydrous or hydrate X-ray data up to now published [14–23]. The intensity of the V₂O₅ and CaCO₃ lines progressively decreases disappearing totally the formers after seven days (Fig. 2(d)). This fact seems to indicate that crystalline V₂O₅ undergoes into amorphous what is in good agreement with the aforementioned DSC data.

It should be mentioned that neither CaO nor Ca(OH)_2 have been detected along the time of treatment what would logically be produced from CaCO_3 decomposition and posterior CaO hydration.

Infrared Spectroscopic Analysis

The results obtained from IR analysis (Fig. 3) confirm the abovementioned XRD conclusions and also provide important information related to the water molecules and amorphous V_2O_5 interactions.

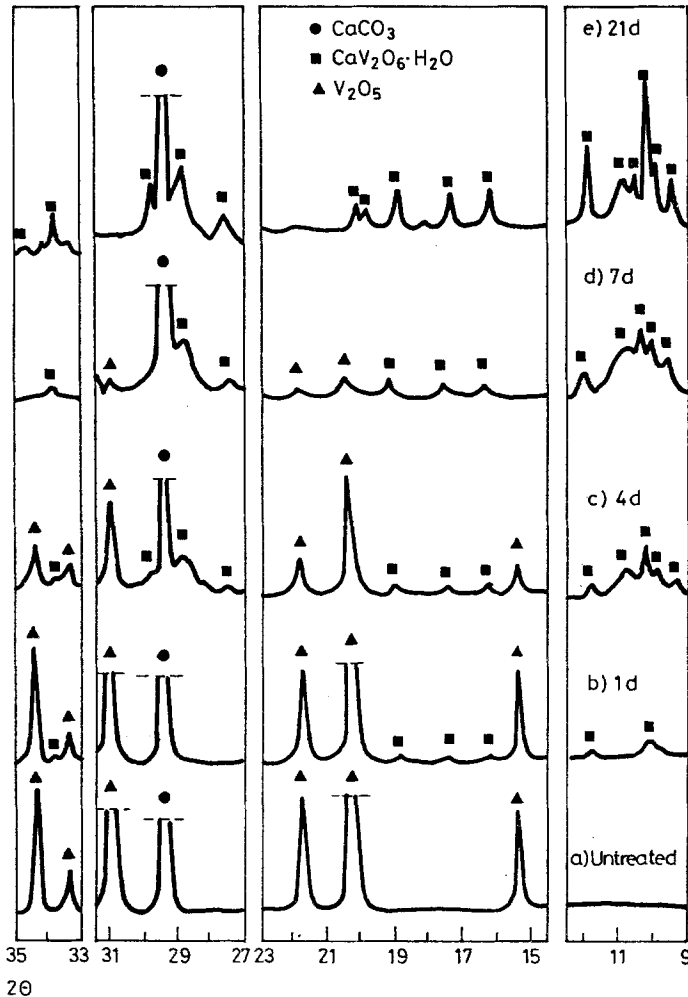


Fig. 2 Evolution of the X-ray diffraction patterns with time

As can be seen, in the 400–1100 cm^{-1} zone, V_2O_5 absorption bands at 1025, 825 and 600–475 cm^{-1} (Fig. 3(a)) decrease in intensity with reaction time practically disappearing at the end of treatment (Fig. 3(e)). On the contrary, the following new bands are developed at 1000, 950, 740 and 550 cm^{-1} (Fig. 3(e)).

In the 3000–4000 cm^{-1} zone a very broad band centered at 3460 cm^{-1} with two shoulders at 3590 and 3200 cm^{-1} can be seen, becoming the later in a band at 3150 cm^{-1} (Fig. 3(e)).

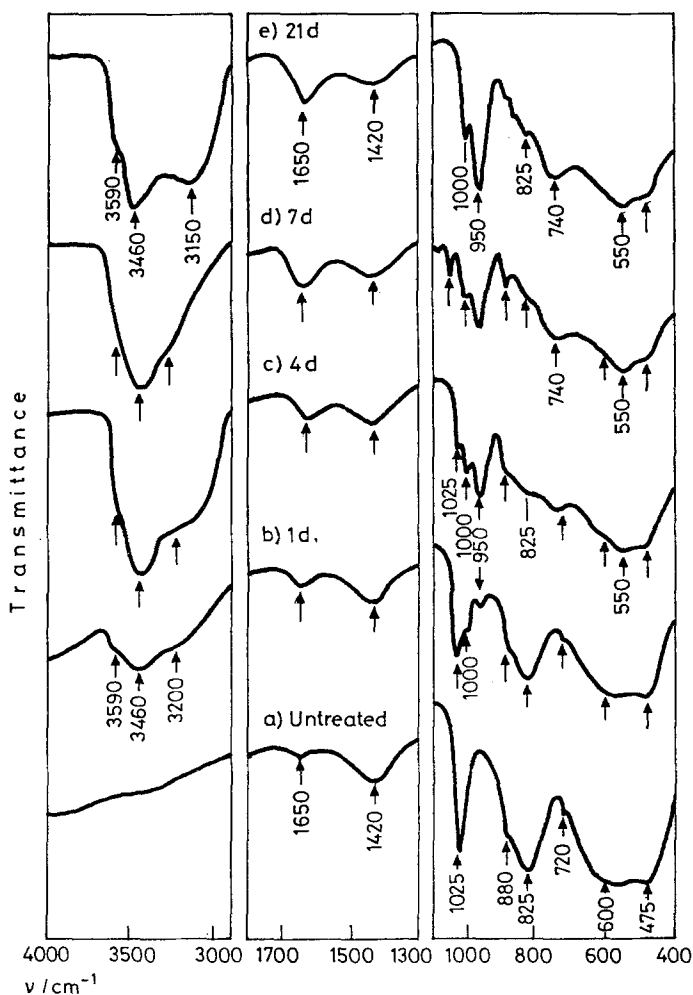


Fig. 3 Evolution of the IR spectra with time

Discussion

The CaCO_3 (calcite form) is one of the most stable compounds whose decomposition from a dry heating starts at 625°C , nevertheless mixed with an acid compound as crystalline V_2O_5 , its decomposition is shifted to 460°C . Once the mixture is submitted to the humidic treatment, the CaCO_3 decomposition is produced at room temperature.

As was earlier mentioned in the Introduction, in similar previous studies carried out on the equimolecular $\text{CdCO}_3\text{-V}_2\text{O}_5$ mixture, the total CdCO_3 decomposition and CdV_2O_6 formation were achieved at room temperature. The dramatic increase of reactivity of the mixture was attributed to the formation of V_2O_5 gels of very strong acid catalytic properties. So, a hypothetic acid-base mechanism of reaction was proposed [11].

The results herein obtained show a great parallelism to respect those of $\text{CdCO}_3\text{-V}_2\text{O}_5$ mixture. So, a similar crystalline-amorphous V_2O_5 transformation takes place which has been observed from XRD and DSC data as well as the formation of V_2O_5 gels evidenced from the new absorption bands appeared. Identical bands were found in the $\text{CdCO}_3\text{-V}_2\text{O}_5$ samples (Fig. 4 on Ref. [11]). Besides, the release of the different kinds of water molecules is produced at the practically same temperature zone (Fig. 5 on Ref. [11]). Therefore it seems obvious that a similar acid-base reaction mechanism may be applied in the case of the $\text{CaCO}_3\text{-V}_2\text{O}_5$ mixtures. The V_2O_5 gels are the catalytic nuclei which act through surface acid sites. The reaction does not totally advance probably due to the crystalline interface located on the unreacted CaCO_3 particles and in this sense further studies are needed.

As far as the new crystalline phase is concerning, it may correspond to a calcium metavanadate hydrate because anhydrous CaV_2O_6 is formed on heating the sample at 200°C (after the strong double endothermic peak). The number of water molecules of the hydrate has not been possible to determine due to the presence of V_2O_5 gels.

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Zusammenfassung — Die Reaktivität von Feststoffgemischen aus V_2O_5 und basischen Verbindungen nimmt bei Raumtemperatur durch die Adsorption von Wassermolekülen aus einer gesättigten Atmosphäre (rel.LF 100 %) stark zu. Dies erfolgt einerseits wegen einer kristallin/amorph Phasenumwandlung von V_2O_5 und andererseits wegen der Bildung stark saurer V_2O_5 -Gele. Mittels TG, DTG, DSC, Röntgendiffraktion und Infrarotspektroskopie wurde der Werdegang eines 1:1 Gemisches aus $CaCO_3$ - V_2O_5 unter den obengenannten Bedingungen untersucht. Die Ergebnisse bestätigen die Bildung von V_2O_5 -Gelen, die das basische $CaCO_3$ bei Raumtemperatur über eine Säure-Basen-Reaktion zersetzen. Als Endprodukt erhält man eine neue kristalline Verbindungen, das Hydrat von Calciummetavanadat.