

Formation of Calcium Vanadates by Solid State Reactions of V_2O_3 with $CaCO_3$

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The chemical reactions in mixtures of solid V_2O_3 : $CaCO_3$ molar ratios of 1:1, 1:2 and 1:3 were investigated by XRD and TG-DSC. It was found that formation of calcium vanadates was dependent on the molar ratio of the starting materials and calcination temperature. Partial vanadium was transformed into the intermediate product $Ca_{0.17}V_2O_5$ at 400 °C. The V_2O_5 was produced at 500 °C. Above 600 °C, the calcium vanadates were formed. $Ca(VO_3)_2$ was formed in the mixtures with V_2O_3 : $CaCO_3$ molar ratios of 1:1 and 1:2 whereas CaV_2O_7 was formed in the mixtures with molar ratios of 1:1, 1:2 and 1:3 and $Ca_3(VO_4)_2$ was formed in the mixtures with molar ratios of 1:2 and 1:3. With increasing calcination temperature, $Ca(VO_3)_2$ was transformed into $Ca_2V_2O_7$ or even $Ca_3(VO_4)_2$.

Key Words: V_2O_3 , $CaCO_3$, Solid state reaction, Oxidation, Calcium vanadates.

INTRODUCTION

Vanadium slag is one of the important resources for recovery of vanadium, which can be obtained from vanadium titaomagnetite by different processes^{1,2}. Vanadium is present in vanadium slag as V^{3+} in spinel phases (e.g. $FeO \cdot V_2O_3$)³.

Compared with conventional sodium salt roasting technology, calcium salt roasting technology is a clean method to extract vanadium from vanadium-bearing materials, which avoid production of the harmful gases such as HCl and Cl_2 in roasting process⁴⁻⁶. The clean technology consists of calcium salts (usually $CaCO_3$ or CaO) roasting, acid or alkali leaching, purification and precipitation. It is well known that the oxidation roasting is a key stage during the process of recovery of vanadium.

According to the literatures^{7,8}, the spinel FeV_2O_4 is oxidized to the R_2O_3 (Fe_2O_3 and V_2O_3) solid solution in oxidation roasting process, then V(III) in R_2O_3 is oxidized to V(V) through intermediates such as VO_2 , V_6O_{13} . Thus, when calcium carbonate is used as additives, the calcium carbonate can react with vanadium oxides to produce calcium vanadates.

However, there are few available literatures about reactions of solid V_2O_3 with $CaCO_3$. Therefore, in this work, the reactions between V_2O_3 with $CaCO_3$ at different temperatures were investigated by XRD, TG-DSC. The formation of calcium vanadates was also discussed.

EXPERIMENTAL

The analytical grade V_2O_3 and $CaCO_3$ were used after being ground and passed through 200 mesh sieve. Power

mixtures of V_2O_3 and $CaCO_3$ were prepared in molar ratios of 1:1, 1:2 and 1:3. The mixtures were well mixed in petroleum ether for 10 h to ensure the homogeneity of the powered starting materials. Mixed samples were calcined at 300, 400, 500, 600, 700 and 800 °C for 1 h in oxidizing atmosphere.

The phase composition and microstructure of the products were analyzed using the X-ray diffraction method with X-ray diffractometer (Rigaku D/max 2500PC) and scanning electron microscope (Tescan VEGA II).

RESULTS AND DISCUSSION

Fig. 1 shows X-ray diffraction patterns of the mixtures with V_2O_3 : $CaCO_3$ molar ratios of 1:1, 1:2 and 1:3 at different temperatures for 1 h. As shown in Fig. 1a-c, raw materials (V_2O_3 and $CaCO_3$) were found at 300 °C. At 400 °C, not only product phase ($Ca_{0.17}V_2O_5$) but also raw materials (V_2O_3 and $CaCO_3$) were detected in mixtures. When calcination temperature was 500 °C, the diffraction peak of V_2O_5 appeared, indicating the V_2O_3 was oxidized to V_2O_5 .

As calcination temperature was increased to 600 °C, the diffraction peaks of major phases CaV_2O_6 and $Ca_2V_2O_7$ appeared in Fig. 1a-b, whereas diffraction peaks of major phase $Ca_2V_2O_7$ and minor phase CaV_2O_6 appeared in Fig. 1c. However, no CaO phase was detected in Fig. 1a-c at 600 °C. This suggests that $Ca(VO_3)_2$ was formed by direct solid state reaction of $CaCO_3$ with V_2O_5 , whereas formation of $Ca_2V_2O_7$ was attributed to reaction of $CaCO_3$ with V_2O_5 or transformation of $Ca(VO_3)_2$ into $Ca_2V_2O_7$ at elevated temperatures. The chemical equations can be described as:

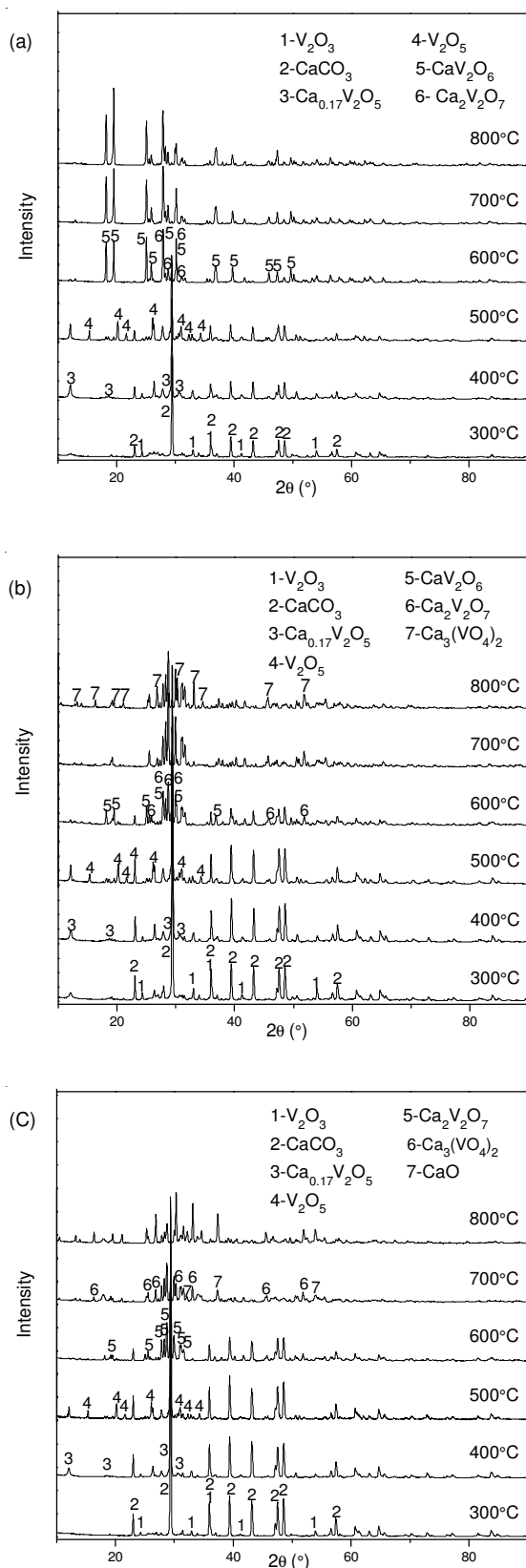
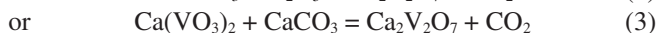
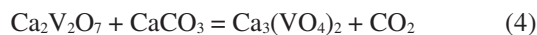


Fig. 1. X-Ray diffraction patterns of the mixtures with a $V_2O_5:CaCO_3$ molar ratio of (a) $V_2O_5:CaCO_3=1:1$; (b) $V_2O_5:CaCO_3=1:2$; (c) $V_2O_5:CaCO_3=1:3$ after calcining at different temperatures for 1 h



With increasing calcination temperature, $Ca_3(VO_4)_2$ was observed at 800 °C in Fig. 1b and at 700 °C in Fig. 1c. This indicates $Ca_2V_2O_7$ was converted into $Ca_3(VO_4)_2$ at elevated temperatures. Thus, the formation of $Ca_3(VO_4)_2$ can be represented as follows:



In addition, the characteristic peak of $CaCO_3$ disappeared at 700 °C in Fig. 1a-b and at 800 °C in Fig. 1c, suggesting the decomposition temperature of $CaCO_3$ increased when the molar ratio of $V_2O_5:CaCO_3$ was varied from 1:1 to 1:3.

Fig. 2 depicts TG and DSC curves of the mixture with a $V_2O_5:CaCO_3$ molar ratio of 1:1. It can be seen from TG curve that the weight increment was 2.4 % from 329-608 °C due to oxidation of the V_2O_5 to V_2O_5 . The weight loss was about 15.59 % from 608-687 °C due to decomposition of $CaCO_3$. According to DSC data, it was found that there were three endothermic peaks between 600 and 800 °C. Combining with XRD analysis, endothermic peaks found at 628, 658 and 757 °C can be resulted from formation of $Ca(VO_3)_2$, decomposition of $CaCO_3$ and conversion of $Ca(VO_3)_2$ to $Ca_2V_2O_7$, respectively.

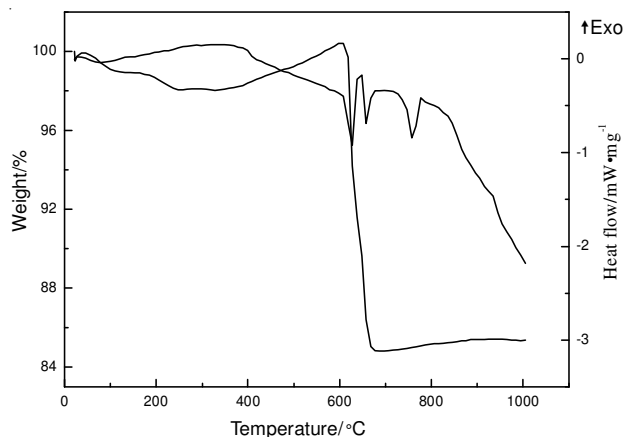


Fig. 2. TG and DSC curves of the mixture with a $V_2O_5:CaCO_3$ molar ratio of 1:1

Fig. 3 presents the SEM images of samples with $V_2O_5:CaCO_3$ molar ratios of 1:1, 1:2 and 1:3 after calcining at 800 °C for 1 h. As shown in Fig. 3a, calcined samples presented lump, irregular shape and relatively smooth surface. According to XRD results, the sample was mainly the mixture of $Ca(VO_3)_2$ and $Ca_2V_2O_7$. As the molar ratio of $V_2O_5:CaCO_3$ was 1:2 or 1:3, petaloid crystals were embedded in a continuous matrix, as shown in Figs. 3b-c. Combining with XRD analysis, the samples were the mixture of $Ca_2V_2O_7$ and $Ca_3(VO_4)_2$. This suggests that the starting materials with different $V_2O_5:CaCO_3$ molar ratios had a significant influence on the morphologies of the products.

Conclusion

Based on the results obtained in this work, formation of calcium vanadates was dependent on the molar ratio of the starting materials and calcination temperature. Partial vanadium was transformed into the intermediate product $Ca_{0.17}V_2O_5$ at 400 °C. The V_2O_5 was produced at 500 °C. At temperatures above 600 °C, the calcium vanadates were formed. $Ca(VO_3)_2$ was formed in the mixtures with $V_2O_5:CaCO_3$ molar ratios of

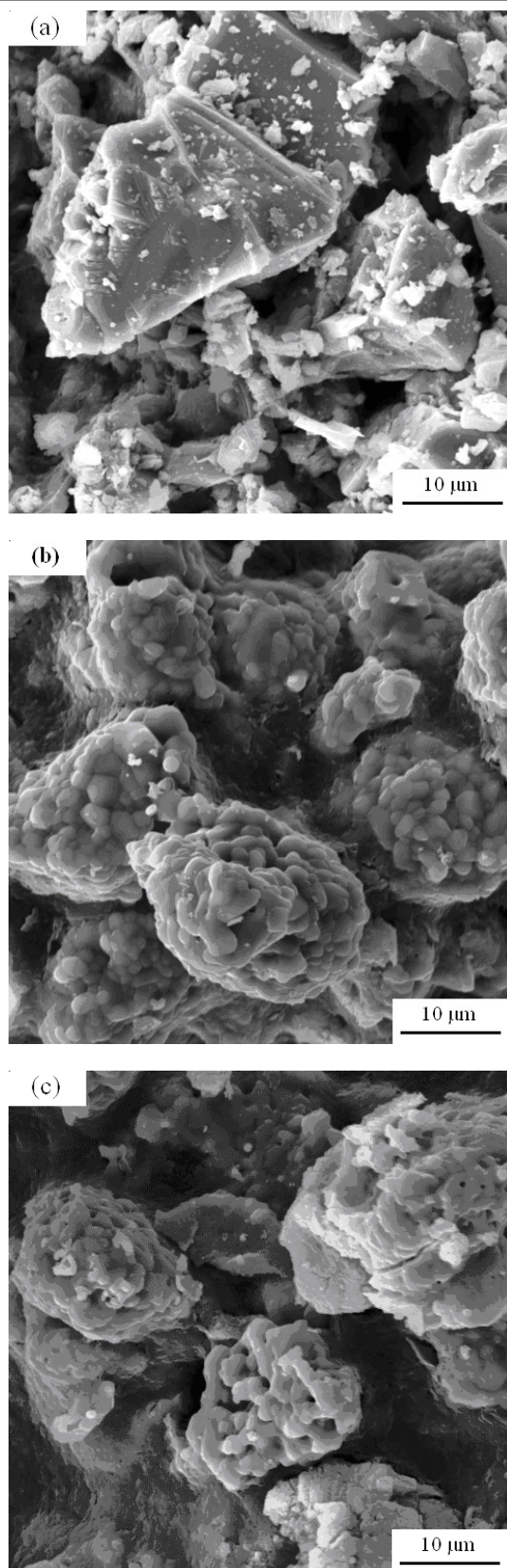


Fig. 3. SEM-SE images of the mixtures of $V_2O_5:CaCO_3$ with different molar ratios after calcining at $800\text{ }^\circ\text{C}$ for 1 h. (a) $V_2O_5:CaCO_3 = 1:1$; (b) $V_2O_5:CaCO_3 = 1:2$; (c) $V_2O_5:CaCO_3 = 1:3$

1:1 and 1:2 whereas CaV_2O_7 was formed in the mixtures with molar ratios of 1:1, 1:2 and 1:3 and $Ca_3(VO_4)_2$ was formed in the mixtures with molar ratios of 1:2 and 1:3. With increasing calcination temperature, $Ca(VO_3)_2$ was transformed into $Ca_2V_2O_7$ or even $Ca_3(VO_4)_2$.

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