



Phase transformation in solid-state reaction of MgO–V₂O₅ binary system and dissolution behavior of products

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Received 3 January 2023; accepted 18 July 2023

Abstract: The solid-state reaction behavior of MgO–V₂O₅ mixtures with different molar ratios was explored. The solubility of the solid-state reaction products (magnesium vanadates) in water at 25–55 °C was measured using the isothermal solution saturation method. The dissolution behavior and kinetics of the magnesium vanadates in dilute sulfuric acid were also investigated. The results showed that the molar ratio of MgO to V₂O₅ and roasting temperature significantly influenced the phase transformation of the solid-state reaction product. MgV₂O₆ exhibits the highest solubility in water, followed by Mg₂V₂O₇ and Mg₃V₂O₈. The dissolution rate of magnesium vanadates in dilute sulfuric acid was significantly increased with the decrease of pH from 4.0 to 2.5 and the temperature increase from 30 to 70 °C. The dissolution of magnesium vanadate can be described using a second-order pseudo-homogeneous reaction model.

Key words: vanadium recovery; MgO; V₂O₅; roasting; leaching; solubility; kinetic

1 Introduction

Vanadium, also known as “industrial monosodium glutamate”, is an important material commonly used in the manufacture of carbon steel, tool steel, and Ti–Al–V alloys [1,2]. There has been an increase in the use of vanadium as catalysts [3] and as a component of vanadium redox flow batteries [4] in recent years. Vanadium is typically extracted from vanadium slag in the form of vanadium pentoxide by salt roasting, water or acid leaching, and precipitation, followed by calcination [5,6]. When compared to sodium roasting, calcification roasting–acid leaching is a

cleaner method of obtaining vanadium from vanadium slag, with no corrosive emissions, little noxious solid waste and harmful wastewater [7], but low vanadium recovery [8].

The extraction process is reliant on two key factors: the extent of soluble vanadate conversion during roasting and the rate of dissolution in the leaching step. The formation of soluble vanadium compounds depends substantially on the composition, structure, and phase of the samples [9] as well as on the additives [10,11]. The extent of vanadium extraction largely depends on the acid concentration, particle size, and liquid/solid (L/S) ratio [12] and less on the temperature and stirring rate [13]. The kinetics of vanadium leaching from vanadium slag

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DOI: 10.1016/S1003-6326(24)66521-0

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with sulfuric acid is controlled by diffusion through the solid product layer according to the shrinking core model [14]. The slightly soluble CaSO_4 generated during leaching inhibits vanadate leaching and lowers leaching efficiency [12]. Over the past few decades, extensive research has been conducted to improve vanadium recovery during the extraction process [15–20]. However, the majority of these methods are not economically feasible for industrial production. On the other hand, laboratory research has found that replacing calcium oxide with magnesium oxide during calcification roasting could improve the vanadium recovery. It is found that $\text{MgO-V}_2\text{O}_5$ solid reactions have better kinetic conditions than $\text{CaO-V}_2\text{O}_5$, and due to magnesium vanadate being much more soluble than calcium vanadate [21], the thickness of the product layer is reduced. In any case, adding MgO alone is not sufficient to affect the extraction process, as the thermodynamic conditions for the solid reaction of $\text{MgO-V}_2\text{O}_5$ are inferior to those for $\text{CaO-V}_2\text{O}_5$ [22]. As an acidic oxide, V_2O_5 readily reacts with basic MgO , forming various magnesium vanadates depending on the composition of the mixture. In binary systems of V_2O_5 and MgO , MgV_2O_6 (metavanadate), $\text{Mg}_2\text{V}_2\text{O}_7$ (pyrovanadate), and $\text{Mg}_3\text{V}_2\text{O}_8$ (orthovanadate) are commonly found. The structure of MgV_2O_6 comprises metavanadate chains with edge-sharing VO_5 units. $\alpha\text{-Mg}_2\text{V}_2\text{O}_7$ is made up of corner-sharing VO_4 tetrahedra that forms V_2O_7 units. $\text{Mg}_3\text{V}_2\text{O}_8$ is characterized by chains of edge-sharing MgO_6 units linked by isolated VO_4 tetrahedra [23].

Magnesium vanadates are not only regarded as the key intermediate products of the vanadium extraction process but also are known to be efficient catalysts for the oxidative dehydrogenation of propane [24] and butane [25], selective oxidation of hydrogen sulfide [26], and flue gas deNO_xing [27]. Magnesium vanadates can be prepared using various techniques, such as impregnation, sol-gel, aerogel, grafting, and solid-state reactions [28].

A deep understanding of solid-state reactions and dissolution behavior of magnesium vanadate is crucial for the extraction process of vanadium and the application of V-Mg-O catalysts. The solid-phase reaction in the $\text{MgO-V}_2\text{O}_5$ mixture controls the vanadium conversion rate during the roasting of the slag, whereas dissolution behavior

and leaching kinetics of the reaction products affect the vanadium leaching rate directly. In this study, the solid-state reaction of $\text{MgO-V}_2\text{O}_5$ and the dissolution behavior of the reaction products were investigated. First, the effect of roasting temperature on the phase evolution of $\text{MgO-V}_2\text{O}_5$ mixtures with appropriate stoichiometry was investigated. Then, the solubility of the magnesium vanadate in water was measured using the isothermal solution saturation method, the dissolution behavior of magnesium vanadate in dilute sulfuric acid was studied, and its dissolution kinetics was analyzed.

2 Experimental

2.1 Materials

The raw materials, V_2O_5 and MgO , were of analytical grade with purities greater than 99.9% and were obtained from Chengdu Colon Chemical Co., Ltd., China. Deionized water was used in all experiments. Commercial sulfuric acid (H_2SO_4) with a concentration of 98% was obtained from Chongqing Chuandong Chemical Co., Ltd., China.

2.2 Experiment procedure

MgO and V_2O_5 powders were dried at 500 °C for 8 h in a blast drying oven to remove free and crystalline water. Subsequently, the MgO and V_2O_5 powders were weighed and ground thoroughly in an agate mortar using a small amount of acetone. The solid reaction experiment was performed in a muffle furnace equipped with a programmable temperature controller with a temperature control accuracy of ± 2 °C. The mixture was then loaded into an alumina crucible and placed in a furnace at a desired temperature. The heating and cooling rates were ensured to be approximately equal by placing the cold alumina crucible in a preheated muffle furnace and removing it while still hot. Next, all the mixtures were roasted at 400 °C for 40 h. The roasted samples were removed from the furnace, cooled to ambient temperature, thoroughly ground, and analyzed using an X-ray diffractometer. The roasting temperature of the samples was increased by 50 °C for another 40 h if the X-ray powder diffraction (XRD) pattern did not indicate pure magnesium vanadate. For the dissolution experiments, the final calcined samples were ground and sieved to 100% particles with sizes less

than 30 μm .

The solubility of the samples was determined in a 200 mL flask. First, 100 mL deionized water was added to the flask and heated to the desired temperature using a thermostatic water bath. An excess quantity of solid sample was then added, and the reaction was performed at a stirring speed of 200 r/min for 12 d and then left for 1 d without stirring. The supernatant solution (1 mL) was transferred to a preheated autopipette for V and Mg content analysis. Dissolution equilibrium was assumed if the ion concentration remained unchanged for 3 d.

A 500 mL three-necked round-bottomed flask equipped with a water condenser, thermometer, magnetic stirrer, and pH meter probe was used for the dissolution experiments with acid. The flask was heated in a thermostatic water bath to maintain the desired temperature. For each run, sulfuric acid was added to reach a desired pH. Thereafter, magnesium vanadate (2 g) was added to the reactor and agitated at a stirring speed of 300 r/min. The acidity of the solution was maintained at the desired value by adding sulfuric acid during the leaching process. The dissolution rate of vanadium was determined by pipetting 2 mL of the suspension from the reactor at appropriate time intervals during each run and centrifuging. The supernatant was chemically analyzed and the solids were returned to the reactor.

2.3 Characterization

The mineralogical compositions of the samples were identified by XRD using an X-ray diffractometer (PANalytical X'Pert Powder, PANalytical B. V.) with $\text{Cu K}\alpha$ radiation ($\lambda=0.154\text{ nm}$, 40 kV, 75 mA). Phase analysis of the X-ray diffractograms was performed using the High Score Plus 5.0 software, which was applied to the ICDD powder diffraction database. Preliminary quantitative phase analyses were performed using the Rietveld method, which involved establishing an approximate model of the diffraction pattern and iteratively improving the model using the least-squares method until the best approximation of the attempted spectrum was obtained. The concentration of the suspension was determined by inductively coupled plasma optical emission spectrometry (ICAP 6000, Thermo Fisher Scientific, USA).

3 Results and discussion

3.1 Phase transformation of $\text{MgO-V}_2\text{O}_5$ mixture

3.1.1 $\text{MgO-V}_2\text{O}_5$ (molar ratio 1:1) mixture at different temperatures

The XRD patterns of the $\text{MgO-V}_2\text{O}_5$ (molar ratio 1:1) mixture after roasting at 400, 450, 500, 550, and 600 $^{\circ}\text{C}$ for 40 h are shown in Fig. 1. MgO , V_2O_5 , MgV_2O_6 , and $\text{Mg}_2\text{V}_2\text{O}_7$ were the only crystalline phases observed in the XRD patterns, and no other intermediates were identified under these experimental conditions. The diffraction peak intensities of V_2O_5 and MgO decreased sharply with increasing temperature in the range of 400–500 $^{\circ}\text{C}$ and continued to decline slightly in the range of 500–600 $^{\circ}\text{C}$. The diffraction peaks of $\text{Mg}_2\text{V}_2\text{O}_7$ almost disappeared when the roasting temperature exceeded 500 $^{\circ}\text{C}$. MgV_2O_6 was the only phase detected above 600 $^{\circ}\text{C}$.

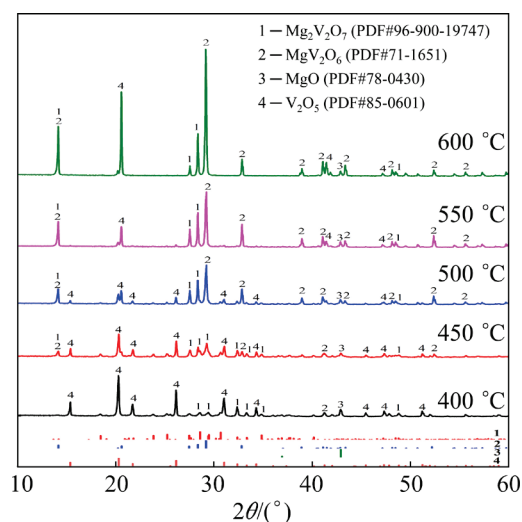


Fig. 1 XRD patterns of products of $\text{MgO-V}_2\text{O}_5$ (molar ratio 1:1) mixture roasted at different temperatures

Figure 2 shows the preliminary quantitative analysis of the X-ray spectra of the $\text{MgO-V}_2\text{O}_5$ (molar ratio 1:1) mixtures roasted at different temperatures. As shown in Fig. 2, at low temperatures ($\sim 400\text{ }^{\circ}\text{C}$), the $\text{MgO-V}_2\text{O}_5$ mixture with a $\text{MgO/V}_2\text{O}_5$ molar ratio of 1:1 formed $\text{Mg}_2\text{V}_2\text{O}_7$ rather than MgV_2O_6 , indicating that magnesium has high reactivity at the initial stage of the reaction. With increasing temperature, the $\text{Mg}_2\text{V}_2\text{O}_7$ and V_2O_5 contents gradually decreased, whereas MgV_2O_6 content gradually increased. At 600 $^{\circ}\text{C}$, the $\text{MgO-V}_2\text{O}_5$ (molar ratio 1:1) mixture

contained almost no V_2O_5 , MgO , and $Mg_2V_2O_7$, and the MgV_2O_6 content reached 100%.

3.1.2 $MgO-V_2O_5$ (molar ratio 2:1) at different temperatures

The XRD patterns of the products formed after roasting the $MgO-V_2O_5$ (molar ratio 2:1) mixture at 400, 450, 500, 550, 600, and 650 °C for 40 h are shown in Fig. 3. The transformation of $MgO-V_2O_5$ (molar ratio 2:1) involves the formation of MgV_2O_6 and $Mg_2V_2O_7$. With increasing temperature, the MgV_2O_6 diffraction peak intensity increased rapidly but then decreased sharply at higher temperatures of 500–600 °C. The intensity of the diffraction peaks of $Mg_2V_2O_7$ increased slowly at lower temperatures (400–500 °C) before increasing sharply at high temperatures (500–650 °C).

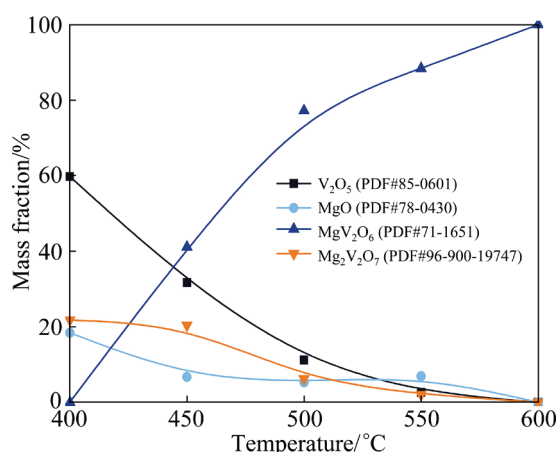


Fig. 2 Variation of phase composition for $MgO-V_2O_5$ (molar ratio 1:1) mixture as function of roasting temperature

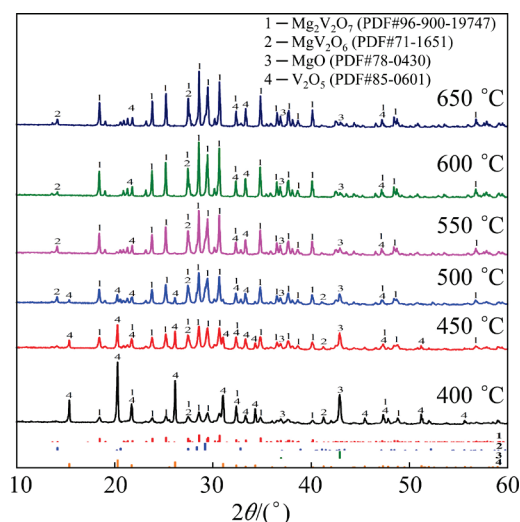


Fig. 3 XRD patterns of products of $MgO-V_2O_5$ (molar ratio 2:1) mixture roasted at different temperatures

The preliminary quantitative analysis results of the X-ray spectra of the $MgO-V_2O_5$ (molar ratio 2:1) mixture roasted at different temperatures (Fig. 4) show a dramatic decrease in MgO and V_2O_5 contents with increasing temperature, reaching zero at 650 and 550 °C, respectively. A rapid increase in MgV_2O_6 content with temperature occurred up to 500 °C, then dropped gradually at higher temperatures of 500–600 °C, and finally zero was achieved at 650 °C due to a solid-state reaction between MgV_2O_6 and V_2O_5 . Meanwhile, the content of $Mg_2V_2O_7$ increased steadily with the increase in temperature, reaching approximately 100% at 650 °C.

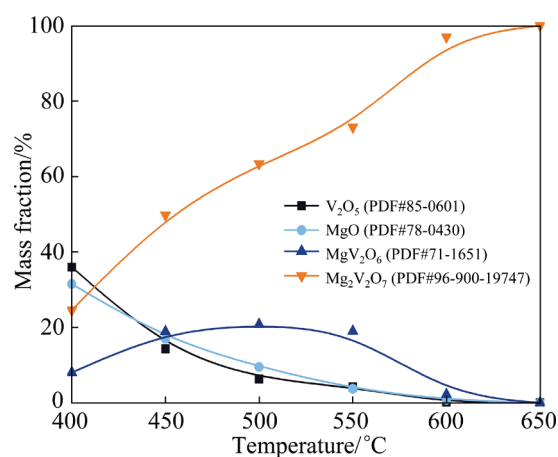


Fig. 4 Variation of phase composition for $MgO-V_2O_5$ (molar ratio 2:1) mixture as function of roasting temperature

3.1.3 $MgO-V_2O_5$ (molar ratio 3:1) at different temperatures

In the XRD patterns of the $MgO-V_2O_5$ (molar ratio 3:1) mixture after 40 h of roasting at 400, 450, 500, 550, 600, 650, 700, and 750 °C (Fig. 5), only MgO , V_2O_5 , $Mg_2V_2O_7$, and $Mg_3V_2O_8$ were observed. Under these experimental conditions, no crystalline phase of MgV_2O_6 could be observed. The intensity of the diffraction peaks of $Mg_2V_2O_7$ rapidly increased as the temperature increased from 400 to 500 °C and then dramatically decreased at higher temperatures (550–700 °C). Above 550 °C, $Mg_3V_2O_8$ diffraction peaks became visible.

According to the preliminary quantitative analysis of the X-ray spectra of the $MgO-V_2O_5$ (molar ratio 3:1) mixture roasted at different temperatures, $Mg_2V_2O_7$ content rapidly increased from 400 to 500 °C (Fig. 6), reaching a maximum value at 500 °C before dramatically decreasing. In

contrast, the content of $\text{Mg}_3\text{V}_2\text{O}_8$ almost linearly increased with increasing temperature from 500 to 750 °C. Accordingly, it appears that in the $\text{MgO}-\text{V}_2\text{O}_5$ (3:1) mixture, MgO first reacts with V_2O_5 at low temperatures to form a large amount of $\text{Mg}_2\text{V}_2\text{O}_7$ and a small amount of $\text{Mg}_3\text{V}_2\text{O}_8$. The remaining MgO reacts with $\text{Mg}_2\text{V}_2\text{O}_7$ to form $\text{Mg}_3\text{V}_2\text{O}_8$ at high temperatures.

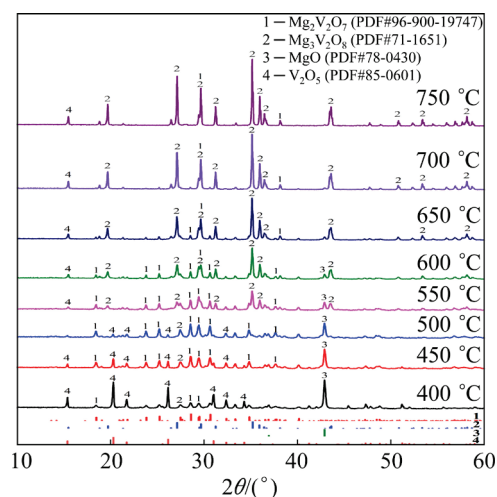


Fig. 5 XRD patterns of products of $\text{MgO}-\text{V}_2\text{O}_5$ (molar ratio 3:1) mixture roasted at different temperatures

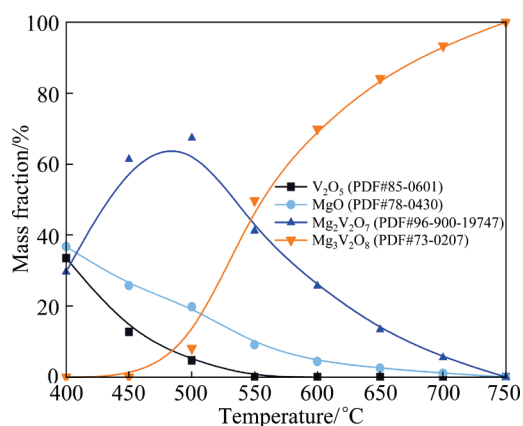


Fig. 6 Variation of phase composition for $\text{MgO}-\text{V}_2\text{O}_5$ (molar ratio 3:1) mixture as function of roasting temperature

3.2 Solubility of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$

3.2.1 Determination of solubility

The solubilities of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$, expressed as the mass of the solute (magnesium vanadate) dissolved in 100 g of solvent (deionized water), are listed in Table 1. Among these three kinds of magnesium vanadates, metavanadate (MgV_2O_6) has the highest solubility in water, reaching 7.118–9.576 g, whereas pyrovanadate ($\text{Mg}_2\text{V}_2\text{O}_7$) and orthovanadate ($\text{Mg}_3\text{V}_2\text{O}_8$)

have lower solubilities, 0.178–0.360 g, and 0.014–0.052 g, respectively. The solubilities of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ in water increase slightly with increasing temperature. When the temperature increased from 25 to 55 °C, the solubilities of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ in water gradually increased from 7.118, 0.178, and 0.014 g to 9.576, 0.360, and 0.052 g, respectively.

Table 1 Solubilities of different vanadates in water at different temperatures (g relative to 100 g solvent (H_2O))

Temperature/°C	MgV_2O_6	$\text{Mg}_2\text{V}_2\text{O}_7$	$\text{Mg}_3\text{V}_2\text{O}_8$
25	7.005	0.181	0.012
	7.130	0.170	0.015
	7.219	0.183	0.015
Average	7.118	0.178	0.014
35	8.964	0.257	0.024
	8.910	0.249	0.033
	8.817	0.265	0.027
Average	8.897	0.257	0.028
45	9.410	0.325	0.047
	9.426	0.313	0.045
	9.505	0.310	0.040
Average	9.447	0.316	0.044
55	9.618	0.355	0.048
	9.540	0.362	0.054
	9.570	0.363	0.054
Average	9.576	0.360	0.052

3.2.2 Modelling of solubility data

Experimental measurements can only give limited solubility data at specific experimental temperatures. Therefore, Van't Hoff and modified Apelblat models were used to fit the experimental solubility data of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ in water between 25 and 55 °C to gain a comprehensive understanding of their solubilities. These equations and mathematical expressions were consistently employed to correlate the solubility data of other compounds.

The measured solubility of the solute in g/100 g H_2O was first converted to the molar fraction solubility x (mol/mol) using Eq. (1):

$$x = \frac{m_B/M_B}{(m_B/M_B) + (m_A/M_A)} \quad (1)$$

where m_B is the mass of the solute, M_B is the relative molecular mass of the solute, m_A is the mass of the solvent, and M_A is the relative molecular mass of the solvent.

The ideal solution equation can describe the relationship between the temperature and mole fraction solubility of magnesium vanadate in water. The Van't Hoff equation relates the logarithm of the mole fraction of a solute to a linear function of the reciprocal of the thermodynamic temperature T , according to Eq. (2) [29]:

$$\ln x = A + B/T \quad (2)$$

where A and B are model constants calculated by the least-squares analysis. The modified Apelblat model is a widely used semi-empirical model that relates the solubility of a solute to its thermodynamic temperature T according to Eq. (3) [30]:

$$\ln x = A + B/T + C \ln T \quad (3)$$

where A , B , and C are semi-empirical parameters.

The relative deviation (RD) of the experiment from the calculated values is described by Eq. (4):

$$RD = (x_e - x_c) / x_e \times 100\% \quad (4)$$

where x_e and x_c are the experimental and calculated mole fraction solubilities of magnesium vanadate, respectively.

The relative average deviation (RAD) method was adopted to determine the accuracy of the mathematical model and evaluate the correlation

results. The RAD is obtained according to Eq. (5):

$$RAD = \frac{1}{N} \sum_{i=1}^N \left(\left| \frac{x_{e,i} - x_{c,i}}{x_{e,i}} \right| \right) \times 100\% \quad (5)$$

where N is the number of data points.

The model fitting results for the solubilities of MgV_2O_6 , $Mg_2V_2O_7$, and $Mg_3V_2O_8$ in water are presented in Tables 2 and 3. Relative deviations of the experimental data from the values calculated using the Van't Hoff were evident. For MgV_2O_6 , the RD values for Van't Hoff model and Apelblat models varied between -5.43% and 6.47% , and between -1.32% and 1.80% , respectively. The RAD for the modified Apelblat model was much lower (1.00%) than that for the Van't Hoff model (4.89%), indicating that the modified Apelblat model was suitable for the simulation of MgV_2O_6 solubility in water.

However, for $Mg_2V_2O_7$ and $Mg_3V_2O_8$, the RADs for the Van't Hoff model were much lower than those for the modified Apelblat model. This indicated that the Van't Hoff model was suitable for correlating the solubilities of $Mg_2V_2O_7$ and $Mg_3V_2O_8$ in water. However, it is worth noting that the RDA values for $Mg_2V_2O_7$ and $Mg_3V_2O_8$ using the Van't Hoff model (5.17% for $Mg_2V_2O_7$ and 11.77% for $Mg_3V_2O_8$) are not so ideal, which may be caused by an increase in analysis and detection errors owing to the low solubility.

Table 2 Model fitting results for solubility of vanadate in water

Solute	T/K	x_e	Van's Hoff model		Apelblat model	
			x_c	RD/%	x_c	RD/%
MgV_2O_6	298.15	5.74×10^{-3}	6.05×10^{-3}	-5.43	5.75×10^{-3}	-0.13
	308.15	7.16×10^{-3}	6.70×10^{-3}	6.47	7.03×10^{-3}	1.80
	318.15	7.60×10^{-3}	7.37×10^{-3}	3.06	7.70×10^{-3}	-1.32
	328.15	7.70×10^{-3}	8.06×10^{-3}	-4.61	7.65×10^{-3}	0.76
$Mg_2V_2O_7$	298.15	1.22×10^{-4}	1.29×10^{-4}	-5.54	1.02×10^{-4}	16.91
	308.15	1.77×10^{-4}	1.65×10^{-4}	6.28	1.44×10^{-4}	18.17
	318.15	2.17×10^{-4}	2.09×10^{-4}	3.79	1.81×10^{-4}	16.58
	328.15	2.47×10^{-4}	2.60×10^{-4}	-5.09	2.03×10^{-4}	17.90
$Mg_3V_2O_8$	298.15	8.34×10^{-6}	9.32×10^{-6}	-11.69	1.49×10^{-5}	-78.81
	308.15	1.67×10^{-5}	1.49×10^{-5}	10.59	3.03×10^{-5}	-81.77
	318.15	2.62×10^{-5}	2.32×10^{-5}	11.56	4.67×10^{-5}	-77.93
	328.15	3.10×10^{-5}	3.51×10^{-5}	-13.23	5.61×10^{-5}	-81.03

Table 3 Model fitting parameters and relative average deviations

Solute	Model	<i>A</i>	<i>B</i>	<i>C</i>	RAD/%
MgV ₂ O ₆	Van't Hoff	−1.97	−935.61	−	4.89
	Apelblat	650.4	−31170	−96.71	1.00
Mg ₂ V ₂ O ₇	Van't Hoff	−1.30	−2282.53	−	5.17
	Apelblat	686.5	−34150	−102	17.39
Mg ₃ V ₂ O ₈	Van't Hoff	2.92	−4323.80	−	11.77
	Apelblat	1553	−76140	−229.7	79.88

To visually compare the correlation between the selected model and measured solubility data, scatter plots of the measured solubility values of MgV₂O₆, Mg₂V₂O₇, and Mg₃V₂O₈ in water and the corresponding line plots of the calculated solubility values were drawn simultaneously, as shown in Fig. 7. Almost all the measured solubility data points fell on the calculated solubility curves, indicating that the selected model and calculated parameters *A*, *B*, and *C* can be correlated with the solubility of MgV₂O₆, Mg₂V₂O₇, and Mg₃V₂O₈ in water.

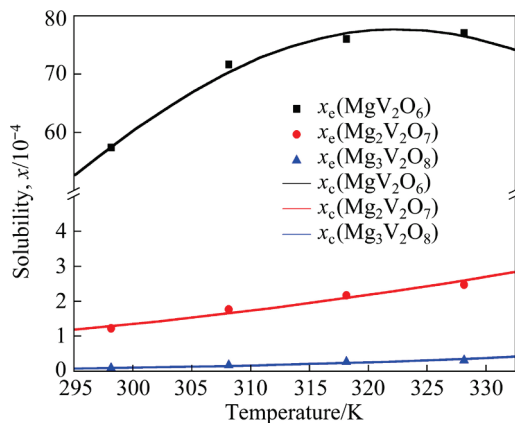


Fig. 7 Comparison of measured and calculated solubilities of MgV₂O₆, Mg₂V₂O₇, and Mg₃V₂O₈ in water

3.3 Dissolution behavior of MgV₂O₆, Mg₂V₂O₇, and Mg₃V₂O₈ in sulfuric acid

3.3.1 Effect of pH

The effect of the pH value of the solution on the dissolution rate of magnesium vanadates was investigated in the pH range of 2.5–4.0 at a liquid/solid ratio of 150:1 (mL/g), temperature of 50 °C, and time of 10 min. The dissolution curves of MgV₂O₆, Mg₂V₂O₇, and Mg₃V₂O₈ in dilute sulfuric acid at different pH values are shown in Fig. 8.

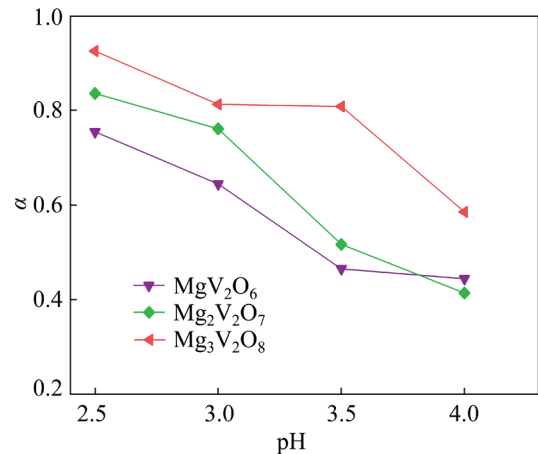


Fig. 8 Effect of pH value on dissolution rate (α) of magnesium vanadates

As shown in Fig. 8, Mg₃V₂O₈ shows a higher dissolution rate than Mg₂V₂O₇ and MgV₂O₆ in dilute sulfuric acid with a pH of 2.5–4.0. With an increase in pH from 2.5 to 4.0, the dissolution rates of MgV₂O₆, Mg₂V₂O₇, and Mg₃V₂O₈ gradually decreased from 0.75, 0.84, and 0.93 to 0.44, 0.41, and 0.59, respectively. It has been reported that the optimum acidity of leaching solution for recovering vanadium from vanadium slag by composite roasting with CaO/MgO or pure CaO is approximately at a pH of 2.5 [31]. When the pH of the solution was in the range of 3.0–4.0, the dissolution rate of vanadium decreased significantly with an increase in pH, whereas when the pH was lower than 2.0, vanadium ions were easily hydrolyzed [32]. Therefore, a sulfuric acid solution with a pH value of 2.5 is the most suitable solution for dissolving magnesium vanadate, as it can ensure a higher dissolution rate.

3.3.2 Effect of temperature

Figure 9 shows the isothermal dissolution curves of magnesium vanadates in dilute sulfuric acid (pH 2.5). The dissolution of the magnesium vanadates involves a rapid stage and a slow stage. As shown in Fig. 9(a), the reaction temperature significantly affected the dissolution of MgV₂O₆. The dissolution rate of MgV₂O₆ increased significantly in the first 10 min; thereafter, it increased slightly with a further extension of time up to 120 min. When the temperature was increased from 30 to 70 °C, the dissolution rate of MgV₂O₆ increased from approximately 0.5 to 0.9 within 10 min. However, the reaction temperature had a

mild effect on the dissolution of $\text{Mg}_2\text{V}_2\text{O}_7$ and $\text{Mg}_3\text{V}_2\text{O}_8$, as shown in Figs. 9(b) and (c), respectively. The dissolution rate of $\text{Mg}_2\text{V}_2\text{O}_7$ in the first 10 min was much lower than that of $\text{Mg}_3\text{V}_2\text{O}_8$ and increased only from 0.49 to 0.64 with increasing the reaction temperature from 30 to 70 °C.

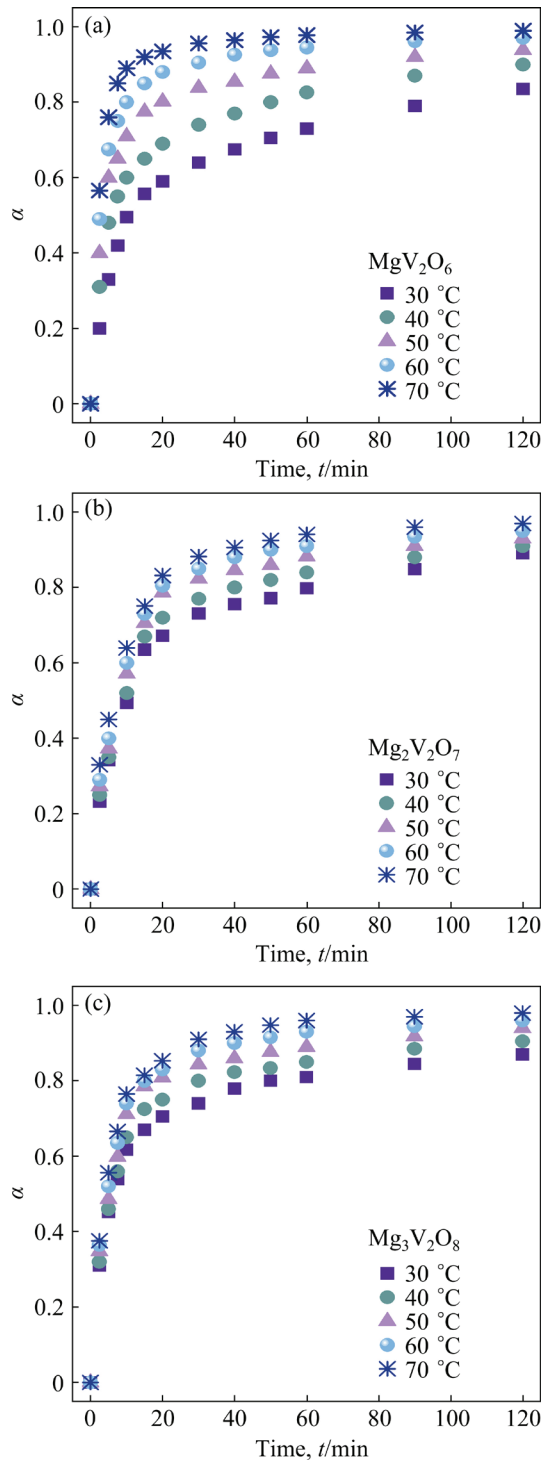


Fig. 9 Isothermal dissolution curves of magnesium vanadates at pH 2.5 and different temperatures: (a) MgV_2O_6 ; (b) $\text{Mg}_2\text{V}_2\text{O}_7$; (c) $\text{Mg}_3\text{V}_2\text{O}_8$

Plots of the derivative of the dissolution rate ($d\alpha/dt$) versus the dissolution rate α for the magnesium vanadates are shown in Fig. 10. The derivative dissolution rate $d\alpha/dt$ was defined as the rate of dissolution at time t . As shown in Fig. 10(a), initially, with increasing dissolution rate, the derivative dissolution rate for MgV_2O_6 decreased

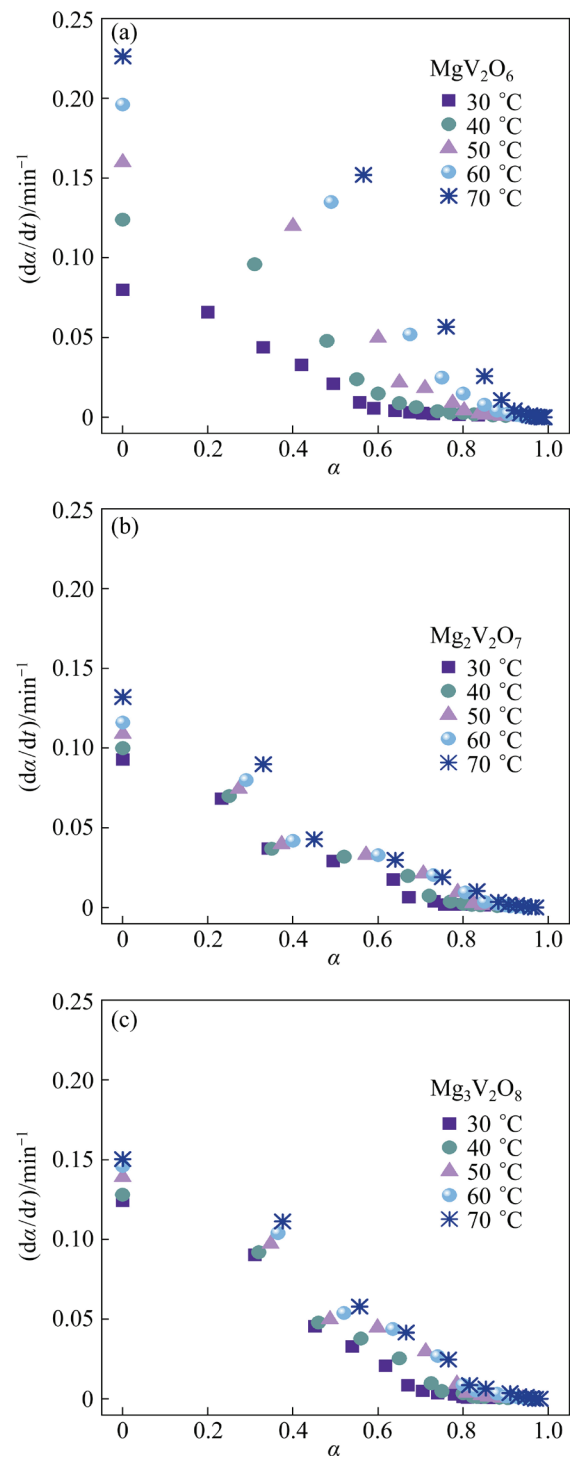
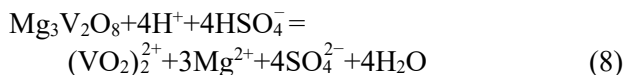
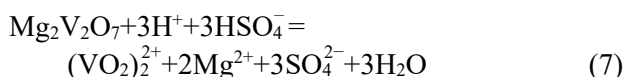
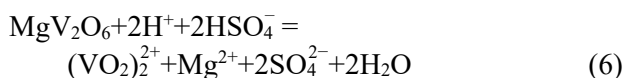


Fig. 10 Plots of derivative dissolution rate ($d\alpha/dt$) versus dissolution rate (α) for magnesium vanadates at different temperatures: (a) MgV_2O_6 ; (b) $\text{Mg}_2\text{V}_2\text{O}_7$; (c) $\text{Mg}_3\text{V}_2\text{O}_8$

significantly, reached a turning point, and then became almost constant, indicative of the two-stage mechanism of the magnesium vanadate dissolution. The dissolution rate was also significantly increased by increasing the reaction temperature. A rapid diffusion of ions in the solution caused by the increase in temperature accelerates the dissolution rate. As shown in Fig. 10(b), the differences in the rate of dissolution with respect to temperature for $\text{Mg}_2\text{V}_2\text{O}_7$ were significantly smaller than those for MgV_2O_6 , particularly when the temperature was higher than 30 °C. In addition, the rate of dissolution of $\text{Mg}_2\text{V}_2\text{O}_7$ was much lower than that of MgV_2O_6 . As shown in Fig. 10(c), the dissolution behavior observed for $\text{Mg}_3\text{V}_2\text{O}_8$ showed a trend similar to that of $\text{Mg}_2\text{V}_2\text{O}_7$, except that the dissolution rate of $\text{Mg}_3\text{V}_2\text{O}_8$ was slightly higher than that of $\text{Mg}_2\text{V}_2\text{O}_7$.

3.4 Dissolution mechanism of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ in sulfuric acid

The dissolution of magnesium vanadates in dilute H_2SO_4 solution is a solid–liquid heterogeneous reaction. The basic chemical reactions that occur during the dissolution are as follows:



In homogeneous reaction models, it is assumed that the liquid penetrates the solid particles and reacts throughout the particle. These models are known as first-order and second-order pseudo-homogeneous models. However, the particle size of the magnesium vanadate decreased over time, and no ash or product layers were formed. Therefore, diffusion through the product layer (ash) was not the rate-controlling step.

The heterogeneous reaction model provides rate equations for each control mechanism, where the step with the highest resistance is the rate-controlling step. Both the heterogeneous and homogeneous models were applied to the experimental data to determine the kinetics of the reaction between magnesium vanadate and sulfuric acid. The applied models and regression coefficients obtained for these models are summarized in Table 4. According to the statistical analysis, the second-order pseudo-homogeneous model with the highest regression coefficient value was considered suitable for describing the kinetics in this study. The rate equation is as follows:

$$(1-\alpha)^{-1} = kt \quad (9)$$

where k is the reaction rate constant (min^{-1}).

The plots of $(1-\alpha)^{-1}$ versus time t for the dissolution of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ were expected to be straight lines, as there was a

Table 4 Integrated rate equations used in process and regression coefficients

Rate equation [33,34]	Rate-controlling step	Sample	R^2				
			30 °C	40 °C	50 °C	60 °C	70 °C
$1 - (1-\alpha)^{1/3} = kt$	Surface chemical reaction control model	MgV_2O_6	0.765	0.728	0.627	0.577	0.510
		$\text{Mg}_2\text{V}_2\text{O}_7$	0.735	0.710	0.667	0.672	0.689
		$\text{Mg}_3\text{V}_2\text{O}_8$	0.538	0.580	0.609	0.684	0.835
$1 - (1-\alpha)^{2/3} = kt$	Fluid film diffusion control model	MgV_2O_6	0.537	0.764	0.694	0.414	0.298
		$\text{Mg}_2\text{V}_2\text{O}_7$	0.640	0.610	0.564	0.560	0.556
		$\text{Mg}_3\text{V}_2\text{O}_8$	0.467	0.491	0.492	0.528	0.568
$-\ln(1-\alpha) = kt$	First-order pseudo-homogeneous model	MgV_2O_6	0.841	0.831	0.762	0.744	0.728
		$\text{Mg}_2\text{V}_2\text{O}_7$	0.826	0.807	0.772	0.787	0.821
		$\text{Mg}_3\text{V}_2\text{O}_8$	0.736	0.741	0.749	0.769	0.815
$(1-\alpha)^{-1} = kt$	Second-order pseudo-homogeneous model	MgV_2O_6	0.979	0.991	0.987	0.997	0.993
		$\text{Mg}_2\text{V}_2\text{O}_7$	0.980	0.986	0.982	0.993	0.998
		$\text{Mg}_3\text{V}_2\text{O}_8$	0.941	0.960	0.979	0.992	0.992

linear relationship between $(1-\alpha)^{-1}$ and time t , as seen in Eq. (9), with the slopes of the straight lines indicating the rate constants. Figure 11 presents plots of $(1-\alpha)^{-1}$ versus time t for the dissolution of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ at different temperatures.

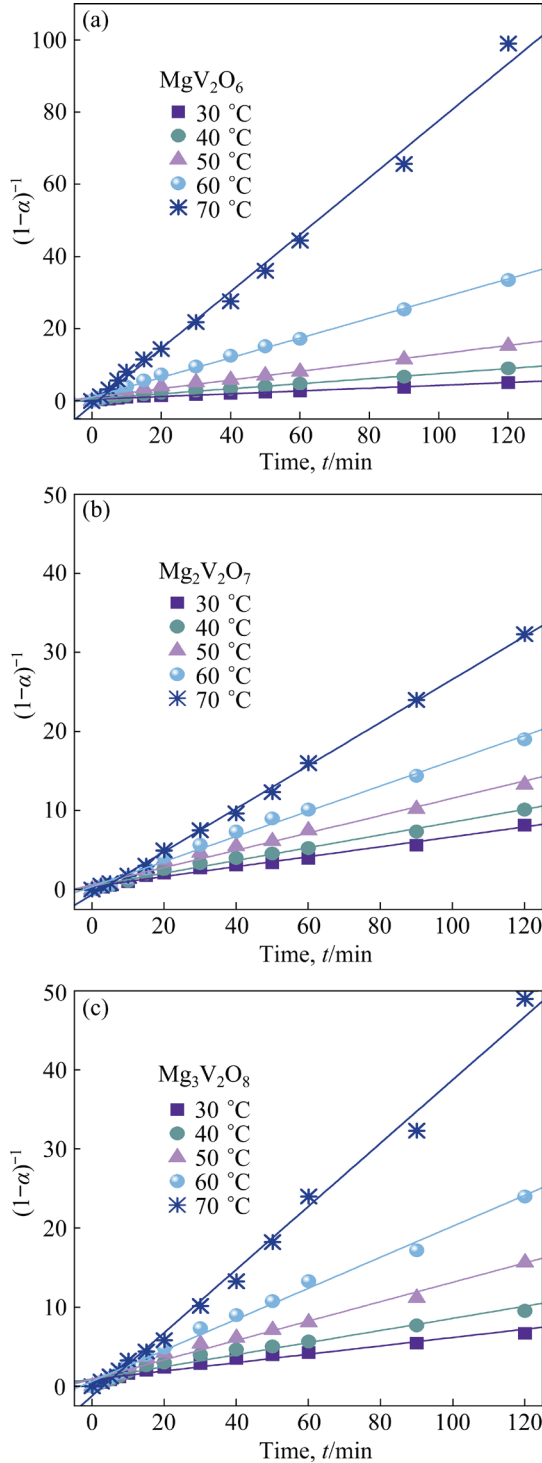


Fig. 11 Plots of $(1-\alpha)^{-1}$ versus time t at different temperatures for magnesium vanadates: (a) MgV_2O_6 ; (b) $\text{Mg}_2\text{V}_2\text{O}_7$; (c) $\text{Mg}_3\text{V}_2\text{O}_8$

The temperature dependence of the reaction rate constant (k) was calculated using the Arrhenius equation to determine the activation energy of the reactions [35]:

$$k = A \exp[-E/(RT)] \quad (10)$$

Taking the natural logarithm on both sides yields:

$$\ln k = \ln A - \frac{E}{RT} \quad (11)$$

where A is the frequency factor (min^{-1}), E is the activation energy of the reaction (J/mol), and R is the molar gas constant ($8.314 \text{ J/(mol}\cdot\text{K)}$). The reaction rate constants k at various temperatures were calculated from the linearized plots shown in Fig. 11. Figure 12 shows the Arrhenius plots (i.e., $\ln k$ versus $1/T$) used to determine the dissolution activation energy of the magnesium vanadates. From the slopes of the straight lines, the apparent activation energies for the dissolution of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ were found to be 63.36, 31.01, and 42.85 kJ/mol, respectively. Such activation energy values indicated that the dissolution of MgV_2O_6 and $\text{Mg}_3\text{V}_2\text{O}_8$ is a chemically controlled reaction, which is consistent with the values obtained in a similar study on fluid–solid reaction systems [36]. The moderate activation energy for the dissolution of $\text{Mg}_2\text{V}_2\text{O}_7$ is due to the mixed chemical diffusion-controlled nature of the reaction since the activation energy of a diffusion-controlled process typically ranges from 4 to 12 kJ/mol, whereas that of a chemically controlled process is often greater than 40 kJ/mol [37].

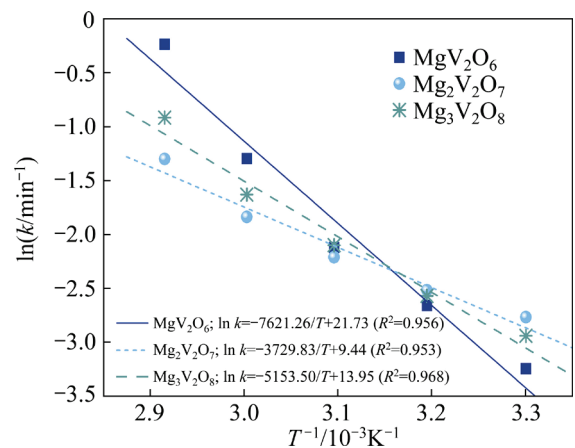


Fig. 12 Arrhenius plots for dissolution of magnesium vanadates

4 Conclusions

(1) The $\text{MgO}/\text{V}_2\text{O}_5$ molar ratio and reaction temperature significantly influenced the phase transformation of the solid-state reaction products. The transformation of magnesium vanadate proceeded via a step-by-step solid-state reaction of $\text{MgO}-\text{V}_2\text{O}_5$. The final products of the solid-state reaction of the $\text{MgO}-\text{V}_2\text{O}_5$ mixture with $\text{MgO}/\text{V}_2\text{O}_5$ molar ratios of 1:1, 2:1, and 3:1 were MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$, respectively.

(2) The solubilities of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ in water slightly increased with increasing temperature. MgV_2O_6 had the highest solubility in water (7.118–9.576 g/100 g H_2O), followed by $\text{Mg}_2\text{V}_2\text{O}_7$ (0.0178–0.360 g/100 g H_2O) and $\text{Mg}_3\text{V}_2\text{O}_8$ (0.014–0.052 g/100 g H_2O) at 25–55 °C. The solubility of MgV_2O_6 could be explained using the modified Apelblat model, whereas those of $\text{Mg}_2\text{V}_2\text{O}_7$ and $\text{Mg}_3\text{V}_2\text{O}_8$ could be described using the Van't Hoff model.

(3) The dissolution rates of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ in dilute sulfuric acid significantly increased with the decrease of pH from 4.0 to 2.5 and the temperature increase from 30 to 70 °C. The dissolution of magnesium vanadate in sulfuric acid (pH 2.5) followed a second-order pseudo-homogeneous reaction model. The apparent activation energies for the dissolution of MgV_2O_6 , $\text{Mg}_2\text{V}_2\text{O}_7$, and $\text{Mg}_3\text{V}_2\text{O}_8$ were calculated as 63.36, 31.01, and 42.85 kJ/mol, respectively.

CRedit authorship contribution statement

Jun-yi XIANG: Conceptualization, Methodology, Formal analysis, Resources, Investigation, Writing – Review and editing; **Ming-shuai LUO:** Formal analysis, Software, Investigation, Writing – Original draft preparation; **Lu-wei BAI:** Data curation; **Xi LU:** Validation; **Zhong-peng ZHU:** Validation; **Qing-yun HUANG:** Data curation; **Kui-song ZHU:** Formal analysis; **Gui-shang PEI:** Validation; **Xue-wei LÜ:** Conceptualization, Methodology, Formal analysis, Resources, Supervision, Project administration, Financial support. All authors have read and agreed to the published version of the manuscript.

Declaration of competing interest

The authors declare that they have no known competing financial interests or personal relationships that could have appeared to influence the work reported in this paper.

Acknowledgments

This work was financially supported by the National Natural Science Foundation of China (No. 52004044), the Natural Science Foundation of Chongqing, China (No. CSTB2022NSCQ-MSX0801), the Foundation of Chongqing University of Science and Technology, China (No. ckrc2022030), the Graduate Research Innovation Project of Chongqing University of Science and Technology, China (No. YKJCX2220214), the Science and Technology Innovation Training Program of Chongqing University of Science and Technology, China (No. 2022046), and the College Students' Innovation and Entrepreneurship Training Program of Chongqing University of Science and Technology, China (No. 2022007).

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MgO–V₂O₅ 二元系固相反应相变及产物溶解行为

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摘 要: 研究不同摩尔比 MgO–V₂O₅ 混合物的固相反应行为。采用等温溶解平衡法测定 25~55 °C 下反应产物(钒酸镁)在水中的溶解度, 并研究其在稀硫酸中的溶解行为和动力学。结果表明, MgO 与 V₂O₅ 的摩尔比和焙烧温度对固相反应产物的相变有较大影响; MgV₂O₆ 在水中溶解度最大, 其次是 Mg₂V₂O₇ 和 Mg₃V₂O₈; 随着 pH 值从 4.0 降低到 2.5, 温度从 30 °C 增加到 70 °C, 钒酸镁在稀硫酸中的溶解率显著增加, 其在稀硫酸中的溶解符合二级伪均相反应模型。

关键词: 提钒; MgO; V₂O₅; 焙烧; 浸出; 溶解度; 动力学

(Edited by Wei-ping CHEN)