

Inorganic Ion Exchanger $\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$ and Its Ion-exchange Ability

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Keywords: spinel-type metal oxides ion-exchange Solid state reaction mechanism $\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$

Abstract. Spinel-type metal oxides, magnesium-manganese- titanium oxide ($\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$), was prepared by a solid state reaction crystallization method. The Li^+ extraction/insertion with this material were investigated by X-ray and K_d measurement. The results showed that the Li^+ extraction/insertion be progressed mainly by an ion-exchange mechanism. The acid treated samples had an ion exchange capacity of 9.7mmol/g for Li^+ .

Introduction

The chemical analysis showed that the Li^+ extraction/insertion be progressed mainly by an ion-exchange mechanism. The inorganic ion-exchange preparation has the advantage of thermo-stability and radiation resistance, synthesis simple and good selectivity etc. Apart from that, it appears the fine speciality in dealing with nuclear waste, gathering and separating of metal ions and chromatogram analysis[1-2]. The experimental result have proved that the inorganic material has better selectivity and higher capacity of exchange for Li^+ in the solution removed Li^+ previously. Moreover, the cost is cheap and its application prospect is significant.

Experimental Section

Reagent and Instruments. MgO and TiO_2 were all analytical reagents; pure ethanol; D/max-A type X-ray diffraction instrument; Dx-170 type ion chromatogram instrument; XQM planetary ball mill; AA-670 atom absorption spectrum instrument; tubular-furnace.

Synthesis and Identifiable of $\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$. The pure ethanol was dropped into a XQM planetary ball mill mixed powder of MgO and TiO_2 with a Mg/Ti mole ration of 1.5:1.25 at the condition of constant rate churning. After 8 hours, the mixture was mixed completely. After mixing fully, the mixture was pressed to tablet by tablet press machine. Then the tablet was heat-treated for 4.5h at 900°C to obtain the Mg-Ti metal compound, the sample was designed as MgTi-900 , whose theoretical formula was $\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$. Then it was analysed of x-ray diffraction and compared to literature[3-4].

Composition analysis: A 0.2g portion of sample was dissolved with acid. The Mg and Ti contents were determined by atomic absorption spectrometry.

The Cation Extraction of Mg-Ti metal compound and Acid Modification. Four 0.200g portions of sample (MgTi-900 compound) were immersed in a HNO_3 solution (50ml) of 0.01M, 0.1M, 1M and 10M respectively with shaking in constant temperature water at 25°C . After 3 days, take the supernatant solution to determine the cation concentration, test its acid proof ability and the extraction ration of Ti^{4+} .

A 5g portion of sample (MgTi-900) was immersed in a 1M HNO_3 solution (500mL) with intermittent shaking in constant temperature water at 25°C . After 7 days, remove the supernatant solution and add new HNO_3 solution. Repeating that for twice, then the initial sample was transformed to H-type sample, washed with water and air-dried. The sample obtained by thermal crystallized at 900°C and acid modified was designated as MgTi-900 (H) .

Saturation Capacity of Exchange. Weigh five 0.5g portions of MgTi-900 (H) , then each portion was immersed in a 0.1M solution (10mL), containing Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ respectively,

diluted to 100mL, shaken in constant temperature water at 25°C. After saturation exchanging (namely, after 10 days by literature[3-5]) the solutions were filtered by subminiature aperture sieve, and the cation concentration was determined. At the same time, do vacant experiment. Last, the inorganic exchanger saturation capacity of exchange for alkali-metal-ions obtained by decrease quantity.

Distribution Coefficient (Kd). After weighing four 0.100g portions of MgTi-900 (H), each portion of sample was immersed in a 0.05M mixed solution (0.200mL) containing Li^+ , Na^+ , K^+ , Rb^+ and Cs^+ (Cl^-/OH^- ratios are different in each solution, $\text{C}(\text{Cl}^-)+\text{C}(\text{OH}^-)=0.1\text{M}$, $\text{C}=\text{Li}^+$, Na^+ , K^+ , Rb^+ and Cs^+). The alkali-metals ions total concentration all was $1.0\times 10^{-3}\text{M}$ by adding 9mL distilled water. After the samples were shaken for 7 days in constant temperature water at 25°C and were filtered, cation concentrations in each samples were obtained.

Results and Discussion

Compound and Appraisalment of $\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$. The X-ray diffraction pattern of compound metal oxide ($\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$), crystallized was shown in figure 1. The structure of compound metal oxide $\text{Mg}_{1.5}\text{Ti}_{1.25}\text{O}_4$ crystallized at 900°C was much perfect.

We know from chemical analysis, the composition of MgTi-900 is $\text{Mg}_{1.47}\text{Ti}_{1.23}\text{O}_{3.96}$, whose chemical component is basically corresponded with the composition of inverse spinel-type metal oxides.

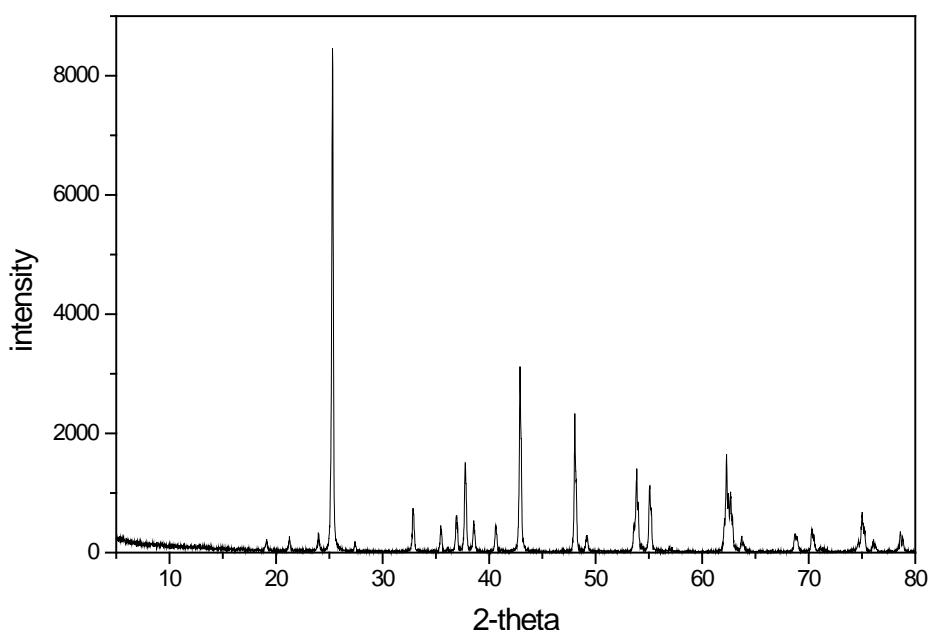


Fig.1 The powder's X-ray figures of $\text{Mg}_{1.47}\text{Ti}_{1.23}\text{O}_{3.96}$ crystal

Cation Extraction of Metal Compound Mg-Ti and Acid Modification. The extraction ration of Mg^{2+} and Ti^{4+} from MgTi-900 in different concentration HNO_3 solution is shown in Figure2. we know from Figure2, the extractabilities of Mg^{2+} are 34%~77% and Ti^{4+} are 2.5%~8.2%. Those indicate that the extractabilities of Mg^{2+} are higher than those of Ti^{4+} when exchanger was immersed in 1M acid solution, correspondding with the exchanger condition was better.(1N, Mg^{2+} 72%, Ti^{4+} 6.1%)

X-ray diffraction of MgTi-900 (H), which is the acid modification product, is shown in Figure1. As shown, the structure of MgTi-900(H) is nearly constant, which is spinel oxide type too. It indicate that the exchanger is steady. The analysis indicate the composition of MgTi-900 (H) was $\text{H}_{2.11}\text{Mg}_{0.41}\text{Ti}_{1.13}\text{O}_{3.57}$, whose component of 72% Mg^{2+} transformed to H^+ compared with the composition $\text{Mg}_{1.47}\text{Ti}_{1.23}\text{O}_{3.96}$ before acid-treated. Then the specific Mg^{2+} of exchanger were extracted fulfill basically and remained the H-type identified with initial type.

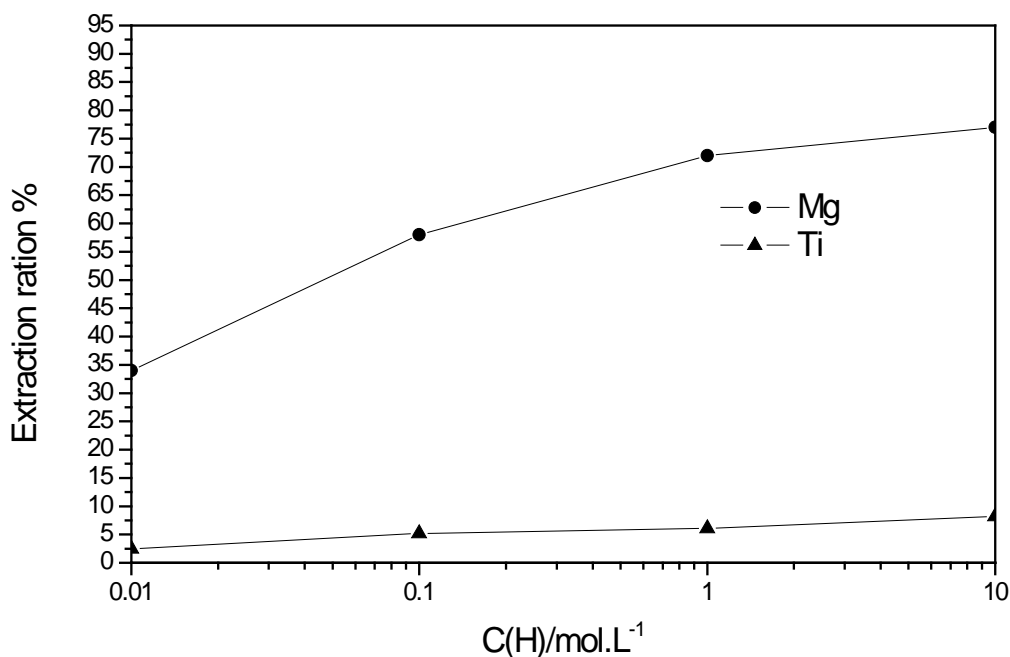


Fig.2 Extraction ration of cations from MgTi-900 in nitric acid solution

Saturation Capacity of Exchange. The relation between radius and saturated ion exchange capacity of MgTi-900 (H) for alkali was shown in figure 3. Known from figure 3, the capacity of exchange for Li^+ was much higher than those for other alkali ions. The capacity for Li^+ is $9.7 \text{ mmol} \cdot \text{g}^{-1}$. It proved that the ion exchange synthesized has higher capacity of exchange, and better remembering of exchange for Li^+ . The effect factors of saturation capacity of exchange of MgTi-900 (H) are: 1) The Li^+ in exchange solution must be removed previously, because Li^+ exchanged with exchanger vacancy site when existing too much Li^+ ; 2) The experimental results shown that the exchange capacity of ion exchanger for Li^+ is much higher than those for other alkali ions in thin solution, which indicate that the ion-exchange reaction is carried out between and bare ions; 3) At the time of exchange, a Li^+ was replaced by one H^+ . Li^+ not only entered the vacancy site but also exchanged with the H^+ of surface. Therefore, MgTi-900 (H) has a higher exchange capacity for Li^+ .

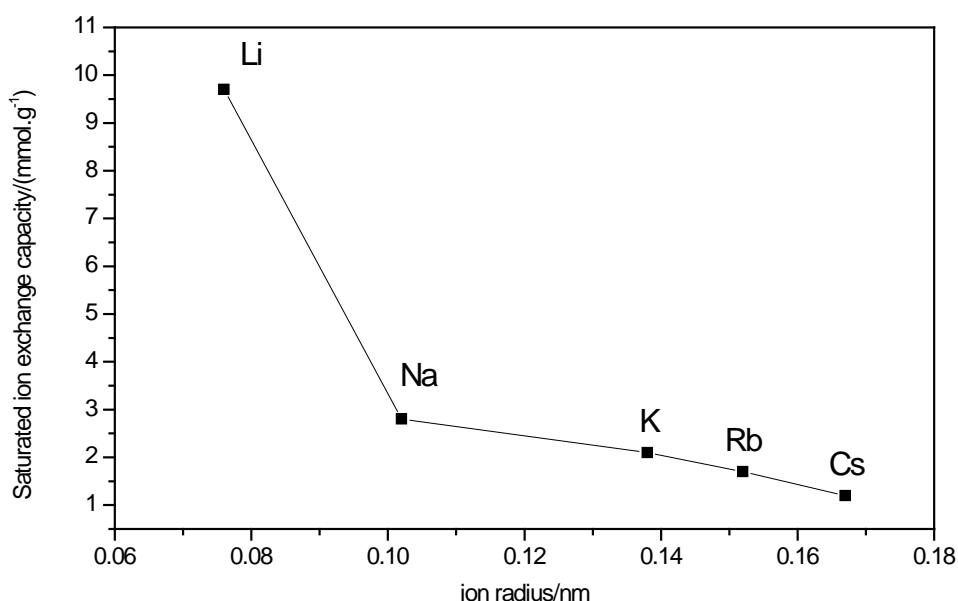


Fig.3 Relation between ion radius and saturated ion exchange capacity of MgTi-900 for alkali ions

Distribution coefficient(Kd). Kd values can be the token of exchange selectivity of MgTi-900 (H) for correlate ions. Shown in figure 4, Kd values of MgTi-900 (H) for alkali ions are larger and larger with an increase pH over the pH region studied. The selectivity sequence of MgTi-900 for alkali metal ions as follows:

$$Li^+ > Cs^+ > Rb^+ > K^+ > Na^+ \quad (1)$$

It indicates that MgTi-900 (H) has a better ion selectivity for Li^+ . Ion-exchange reaction is reversible reaction. The reaction of H^+ in ion-exchanger with alkali metal ions in solution as follows(example for Li^+):

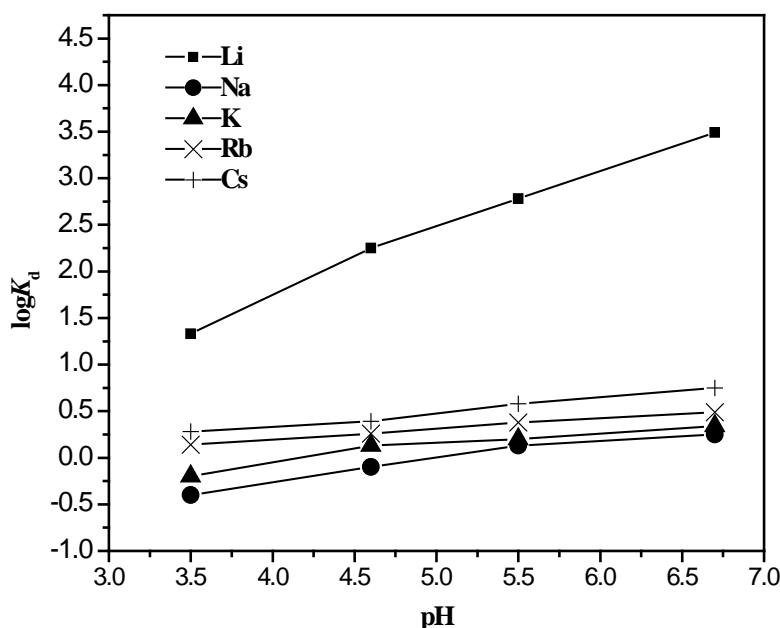


Fig.4 Distribution coefficient of MgTi-900(H)for alkali ions

Conclusions

$Mg_{1.5}Ti_{1.25}O_4$ is an ion-memory inorganic ion exchanger for Li^+ . The comprehensive results indicate that the $Mg_{1.5}Ti_{1.25}O_4$ of spinel-type metal oxide show a capacity extraction/insertion of Li^+ in the aqueous phase. The Li^+ -extracted samples show a high selectivity and a large capacity for Li^+ among alkali metal ions.

Acknowledgments

This research was supported by the Chinese National Nature Science Foundation (51541205), The national Spark Program (2014GA740047) and Nature Science Foundation of Shandong Province(ZR2013BL016).

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