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КОМПОЗИТЫ ФУМАРАТА ЦИРКОНИЯ И ПОЛИЭЛЕКТРОЛИТОВ С УЛУЧШЕННЫМИ АДСОРБЦИОННЫМИ И МЕХАНИЧЕСКИМИ ХАРАКТЕРИСТИКАМИ

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Проблему высокой дисперсности порошков металл-органических координационных полимеров (МОКП) можно решить путем получения на их основе композитов с полиэлектролитами (ПЭ) и последующего формования в таблетки без существенного ухудшения адсорбционных свойств.

Цель работы — синтез кристаллического фумарата циркония (Zr-fum) с субмикронным размером частиц и получение на его основе композитов с ПЭ, обладающих высокой адсорбционной емкостью по водяному пару и механической прочностью в таблетированной форме.

Zr-fum синтезировали в 15% водном растворе муравьиной кислоты. Композиты Zr-fum/ПЭ, в которых массовая доля ПЭ варьируется от 1% до 50%, получили методом послойной сборки без промежуточной отмывки, а затем таблетировали под давлением. Композиты исследовали методами рентгенофазового анализа и ИК-спектроскопии. Изучили адсорбцию водяного пара композитами в зависимости от относительной влажности и массовой доли ПЭ.

Резкий рост адсорбции водяного пара Zr-fum и композитами Zr-fum/ПЭ начинается при относительном давлении менее 0,1, что меньше, чем для других изученных осушителей. В диапазоне p/p_0 = 0,2–0,75 адсорбция водяного пара композитами в два раза выше, чем молекулярными ситами 4 Å и не зависит от содержания ПЭ в них. При высокой влажности адсорбция водяного пара композитом Zr-fum/(КМЦ/ХН)$_2$ превышает соответствующие характеристики Zr-fum и Zr-fum/(ПСС/ПДДА)$_2$ и увеличивается с ростом массовой доли ПЭ. На примере композитов Zr-fum/(ПСС/ПДДА)$_2$ показано, что в процессе формования таблеток под давлением частично нарушается кристаллическая структура МОКП, причем сетка интерполиэлектролитных комплексов способствуют сохранению высокой адсорбционной емкости композитов после таблетирования.

Ключевые слова: металл-органический координационный полимер, фумарат циркония, полиэлектролиты, поливиниловый спирт, композит, сорбция водяного пара, прочность на сжатие.

COMPOSITES OF ZIRCONIUM FUMARATE AND POLYELECTROLYTES WITH IMPROVED ADSORPTION AND MECHANICAL CHARACTERISTICS

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The problem of high fineness of metal-organic coordination polymers (MOFs) powders can be solved by developing their composites with polyelectrolytes (PE) and subsequent molding them into tablets without a significant deterioration in adsorption properties.

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The purpose of the work is to synthesize crystalline zirconium fumarate (Zr-fum) with particles of submicron size and prepare its composites with PE which have a high adsorption capacity for water vapor and mechanical strength in tablet form.

Zr-fum was synthesized in a 15% aqueous solution of formic acid. Zr-fum/PE composites in which the mass fraction of PE varies from 1% to 50% were obtained with layer-by-layer assembly without intermediate washing and then were pressed in tablets. The composites were characterized by X-ray phase analysis and IR spectroscopy. The adsorption of water vapor by the composites was studied as a function of relative humidity and PE mass fraction.

A sharp increase in water vapor adsorption by Zr-fum and Zr-fum/PE composites begins at a relative pressure below 0.1; this is lower than for other studied desiccants. In the range of p/p_0 = 0.2–0.75, the adsorption of water vapor by composites is two times higher than by molecular sieves 4 Å and does not depend on PE content. At high humidity, the adsorption of water vapor by a Zr-fum/$(CMC/CH)_2$ composite exceeds the corresponding characteristics of Zr-fum and Zr-fum/$(PSS/PDDA)_2$ and increases with increasing mass fraction of PE. Using the Zr-fum/$(PSS/PDDA)_2$ composites as an example, it was shown that, during the molding of tablets with pressure, the crystal structure of MOFs is partially damaged, but the network of interpolyelectrolyte complexes supports the high adsorption capacity of the composites after tableting.

Keywords: metal-organic framework, zirconium fumarate, polyelectrolytes, polyvinyl alcohol, composite, water vapor sorption, compressive strength.

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