In-situ synthesis of SAPO-34@kaolin composite catalyst for methanol to olefins

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Abstract: In this article, we describe a novel strategy for in-situ synthesizing SAPO-34@kaolin composites via using hexadecyltrimethyl ammonium bromide (CTAB) surfactants as the inductive agent. The results show that as compared with the conversional synthesized SAPO-34@kaolin composite, the as-synthesized SAPO-34@kaolin composite using CTAB showed excellent MTO catalytic performances with the lifetime increased significantly and the yield of light olefins including ethylene and propylene increased by 15 wt.%, due to its relatively high content and small crystal size of SAPO-34 in the composite.

Keywords: Kaolin, SAPO-34, In-situ synthesis, CTAB.

1. Introduction

In recent years, with the ever-increasing of market demand of light olefins, such as ethylene and propylene, and the decreasing of crude oil which is the major source of the light olefins. Developing new alternative non-oil route to produce light olefins becomes much urgent. The methanol to olefins (MTO) process coupled with transformation of coal or natural gas to methanol has been proved a promising alternative one [1,2]. SAPO-34 with a CHA topology has relatively moderate acid strength and small pores (0.38 nm) so that it obtains extensive investigation and using in MTO process [3]. Unfortunately, in the industrial practice, the SAPO-34 based MTO catalyst is prepared by spray-drying the mixture consisting of SAPO-34, a matrix (usually kaolin) and a binder (usually silica or alumina sol) in proper proportion. In this semi-synthesis technology, the active component SAPO-34 will be wrapped in the binder or matrix leading to the internal diffusion limitations and relatively lower accessibility of the active centers, thus resulting the decrease of catalytic efficiency.

Here we propose a novel approach to synthesize SAPO-34@kaolin MTO catalyst via in-situ synthesis method by using calcined kaolin microsphers (KMS) as the materials and matrix, and using triethylamine (TEA) as the template and CTAB as the introductive agent to tuning the pore structure and crystal size of SAPO-34.

2. Experimental

SAPO-34@kaolin catalysts were synthesized via conventional hydrothermal crystallization process. The mass compositions of starting gels were 1KMS: 1H_3PO_4: 1TEA: 6H_2O: xCTAB (x=0~2). In a typical synthesis, 5.0 g of H_3PO_4 was mixed with 30 g of deionized water stirring at 40 ^oC for 30 minutes, then added 5.0 g TEA as the zeolite template, 5.0 g calcined KMS, and 1 g CTAB. At last, after the temperature increasing from 40 ^oC to 70 ^oC, the mixture was transferred into 100 ml stainless-steel autoclave lined with polytetrafluoroethylene. Then put the autoclave into 200 ^oC rolling oven for 48 h. The thus-obtained solid product was centrifugated and washed three times, then dried at 120 ^oC. At last we got the SAPO-34@kaolin catalyst after calcining at 550 ^oC for 4 h in air to decompose the organics, named S@KMS-C. In addition, S@KMS which synthesized without CTAB surfactants was for comparison.

The phase structure, crystal morphology and pore structure of S@KMS and S@KMS-C were characterized by X-ray powder diffraction (XRD), scanning electron microscope (SEM) and N_2 adsorption-desorption techniques, respectively.

3. Results and discussion

3.1 Characterizations

The XRD patterns, SEM images and N_2 adsorption-desorption curves of S@KMS and S@KMS-C are presented in Figure 1. Both of the XRD patterns (Figure 1A) of S@KMS and S@KMS-C show the characteristic diffractions ascribed to SAPO-34, demonstrating the existence of SAPO-34 crystallization structure in the composites. According to calculating, the content of SAPO-34 in S@KMS-C is 34 wt.%, which is much higher than that of S@KMS (11.2 wt.%). From the low magnification SEM images shown in Figure 1B (a, c), we can see that after crystallization the micro-spherical morphologies of kaolin are maintained in both of S@KMS and S@KMS-C. Interestingly, from the high magnification SEM images of Figure 1B (b, d), it can be seen that the two samples look distinctly different. S@KMS-C is composed of the lamellar crystals rather than cubic particles of S@KMS. Figure 1C shows that the N_2 adsorption-desorption curves of S@KMS and S@KMS-C belong to Langmuir I and IV types, demonstrating the coexistence of micropores and mesopores. Hierarchical factor (HF) is an important index for measuring the hierarchical structure, which is defined as $(V_{micro}/V_{pore}) \times (S_{meso}/S_{BET})$. From Table 1, we can see that the HF of S@KMS-C is 0.122, which is much higher than that of S@KMS (0.097). This can further conform that the existence of hierarchical structure of as-synthesized S@KMS-C. By combining the results of XRD, SEM and N_2 adsorption-desorption characterizations, we can conclude that introduction of CTAB surfactant in synthesis gel can promote produce small crystal size and high content of SAPO-34 in kaolin microspheres.

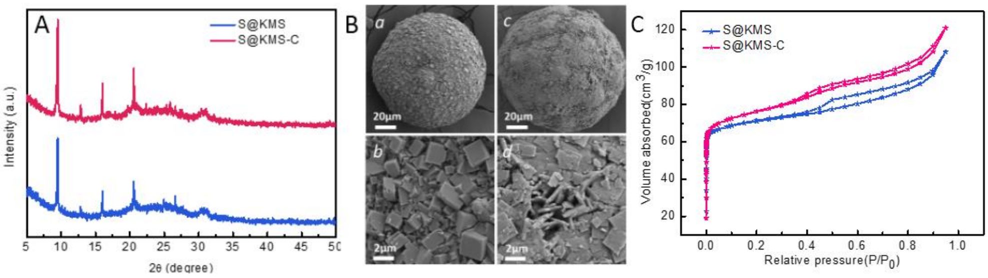

Figure 1.XRD patterns (A), SEM images (a,b S@KMS; c,d S@KMS-C) (B) and N_2 adsorption-desorption isotherms

3.2 Catalytic test

The MTO catalytic evaluation results of S@KMS and S@KMS-C are listed in table 1. As seen, S@KMS-C gives the higher selectivity of ethylene than S@KMS, while they give the same propylene selectivity. The catalytic life time of S@KMS-C (123 min) is much longer than S@KMS (10 min). The small crystal of SAPO-34 facilitates the accessibility of the reactant molecules to the acid sites and shortens the diffusion paths, which can explain the better catalytic performance of S@KMS-C.

Table 1. Catalytic performance of the samples.

Catalysts	Selectivity of products[a] (wt.%)					Lifetime[b] (min)	The hierarchical factor (HF)
	C_2H_4	C_3H_6	C_2H_4+C_3H_6	C1-C3	C4+		
S@KMS	30	35	65	24	12	10	0.097
S@KMS-C	45	35	80	11	10	123	0.122

Reaction conditions: T=743 K, WHSV=2.5 h^{-1}*. Reaction material: 95 wt.% methanol-water solution.*

4. Conclusions

In conclusion, we have successfully synthesized high content and small crystal size of SAPO-34@kaolin MTO catalyst via in-situ synthesis method by using CTAB as the inductive agent. As compared with the conventional synthesized SAPO-34@kaolin composite, this catalyst showed excellent MTO catalytic performances with the lifetime increased dramatically and the yield of light olefins including ethylene and propylene increased 15 wt.%.

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