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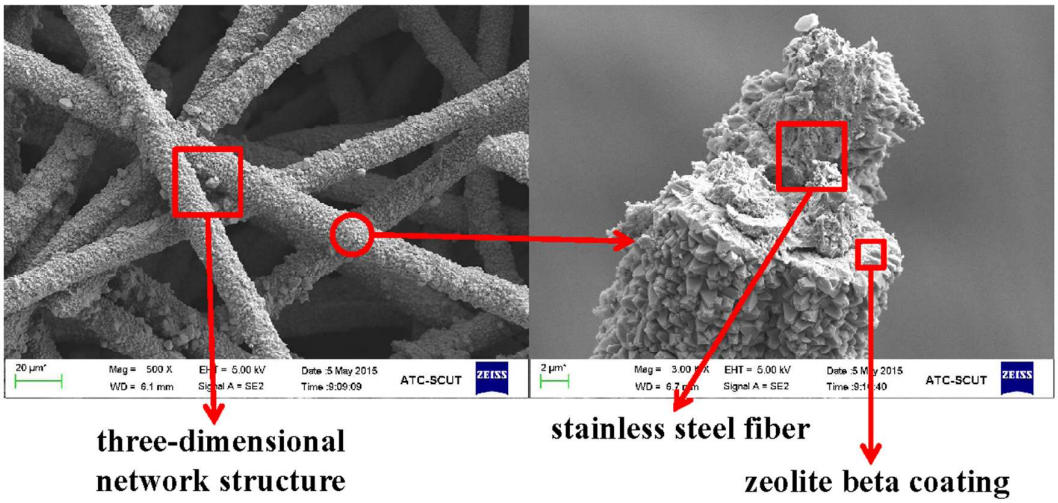

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PAPER

Preparation and characterization of novel porous zeolite beta coating/PSSF composite in fluoride media

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A novel porous zeolite beta coating/PSSF composite was prepared by secondary growth method in fluoride media. The morphology of zeolite beta coating/PSSF composite was characterized by SEM and the structural and textual properties of composite were characterized by XRD and N_2 adsorption/desorption isotherms on ASAP 2020, respectively. The thermal stability of composite was analyzed by thermogravimetry (TG) and differential scanning calorimetry (DSC). The results indicated that well-intergrown and continuous zeolite beta coating with highly crystallinity were successfully synthesized on the surface of paper-like stainless steel fibers support. The structures of zeolite beta coating/PSSF composite were three-dimensional network with large void volume and majority of microporous structure. The thickness of zeolite beta coating on stainless steel fibers is approximate 2 μm. The specific surface area (S_{BET}) and the total pore volume of composite were 118 m^2/g and 0.067 cm^3/g, respectively. The composite was stable at temperature up to 650 ℃.

1. Introduction

During the last decade, the preparation and evaluation of various types of molecular sieve coating on different porous supports composite have attracted more and more attention. A range of molecular sieves have been successfully synthesized on the surface of porous alumina,[1, 2] sintered metal fibers (SMFs)[3, 4] and porous stainless steel substrates.[5, 6] Molecular sieve fabricated on porous supports has outstanding potentials in encapsulation,[7] separation,[8, 9] adsorption[10] and catalytic processes[11, 12] due to their advantages in uniform micropores, thermal conductivity, anti-corrosion quality, mechanical strength, and chemical as well as thermal stability.

In particular, paper-like porous metal microfibers support fabricated by wet lay-up papermaking and sintering process possess the advantages of high void fractions, low cost, quick and simple preparation process and various geometries.[13] ZSM-5 coating on paper-like stainless steel (PSSF) composite can effectively improve the mass/heat transfer and contacting efficiency, reduce bed pressure drop in adsorption[14] and catalytic processes[15, 16] due to its large void volume, uniform micropore structure, entirely open structure, high thermal conductivity and permeability. However, most of the studies of zeolite coating on porous support were focused on MFI type zeolite and the application of ZSM-5 coating/PSSF composite was limited to the molecule of kinetic diameter less than 0.5 nm due to the small pore size.

Zeolite beta with truncated bipyramidal shape has a three-dimensional 12-rings interconnected channel system with pore diameter of 0.71 × 0.73 nm. In particular, zeolite beta synthesized in fluoride media as high silica and low acidic zeolite supports shows good catalytic performance of noble metal catalysts for VOCs combustion[17] and with high hydrophobicity shows excellent affinity for linear alkanes and aromatics such as toluene.[18] However, the fabrication of zeolite beta coating on porous metal microfibers support with porosity and uniform thickness and pore size in fluoride media is still a big challenge because of the heterogenous synthesis gel with the addition of hydrofluoric acid (HF). To the best of our knowledge, there is no published work on fabrication of zeolite beta coating on the surface of paper-like stainless steel fibers in the fluoride media. The main objectives of this research were to (1) prepare a novel porous zeolite beta coating/PSSF composite in fluoride media; and (2) investigate the morphology, structural and textual properties and thermal stability of the composite by using SEM, XRD, N_2 adsorption/desorption isotherms analysis and TG-DSC analyses, respectively.

2. Experimental

2.1 Materials

The paper-like sintered stainless steel fibers (PSSF) support was prepared by the wet lay-up papermaking process and sintering process according to the previous study in our group.[19] Tetraethylammonium hydroxide (TEAOH, 35wt% in H_2O) was purchased from Alfa Aesar. Fumed silica and Ludox AS-40 were purchased from Sigma-Aldrich. Cationic polymer (poly (diallyldimethylammonium chloride), 20wt% in H_2O) was purchased from Aladdin. Hydrogen fluoride (HF, 40%), sodium

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hydroxide (NaOH, 99%), ammonia water (NH_3 aq., 25-28%), aluminum isopropoxide (AIP, 98%) and n-propyl alcohol (99%) were all purchased from Sinopharm Chemical reagent Co., Ltd. Deionized water was used in all synthesis processes. All of the chemical reagents used in this study were analytical grade without any further purification.

2.2 Seed Preparation

The seed crystals were prepared from a clear solution with the molar composition: 0.35 Na_2O:9 TEAOH:0.5 Al_2O_3:25 SiO_2:295 H_2O.[20] The mixture solution was aged for 24 h and hydrothermally treated in a 100 ml Teflon lined autoclave at 95 ℃ for 9 days. The obtained milky solution was purified by centrifugation and washed with deionized water, the procedure was repeated four times. After that the seed solution (2 wt%) was prepared by adjusting the pH value to 10 using 0.1M NH_3 aq..

2.3 Synthesis of zeolite beta coating on PSSF support

The PSSF support was calcined in air at 550 ℃ for 4 h to create an oxide layer on the fibers surface. After that, the PSSF support was immersed in a 1wt% aqueous solution of the cationic polymer for 30 min so as to reverse its surface charge, rinsed in 0.1M NH_3 aq. and air dried. The pretreated PSSF was immersed in the seed solution (2 wt%, pH=10) for 30 min to adsorb zeolite beta seeds on the surface, rinsed in 0.1M NH_3 aq. with sonification and air dried.

The secondary growth synthesis gel molar composition was 1 SiO_2:0.6 TEAOH:0.6 HF:10.5 H_2O:2 n-propyl alcohol. First, fumed silica was added to TEAOH solution under vigorously stirring until complete dissolution of silica, then HF was added dropwise and a viscous solidified-gel was formed, the solidified-gel was aged for 24 h without stirring. Thereafter, the solidified-gel was dissolved in n-propyl alcohol under vigorously stirring until a uniform gel was formed. Finally, a vertically fixed seeded PSSF support was immersed into the gel and placed into a 100 ml Teflon lined autoclave. The static hydrothermal synthesis was carried out at 140 ℃ for 4 d. After crystallization, the as-synthesis zeolite beta coating/PSSF composite was dipped in deionized water with ultrasonic treatment to remove the loose zeolite beta crystals, air dried and calcined at 550 ℃ for 6 h under air atmosphere to remove the organic template.

2.4 Characterization

X-ray diffraction (XRD) patterns of samples were performed on a D8 Advance (Bruker Co.) diffractometer using Cu Kα radiation (40 kV, 40 mA) with 2θ range of 5-60°. N_2 adsorption/desorption isotherms of the samples at 77 K were measured to investigate the pore textural properties by using Micromeritics' Accelerated Suface Area and Porosimetry Analyzer 2020 (ASAP 2020) equipped with commercial software of calculation and analysis. The morphologies of the composite were observed by Zeiss Merlin scanning electron microscopy (SEM). All of the samples were coated with an ultra-thin film of gold to make them conductive before analysis. Thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses were performed on a NETZSCH STA 449C instrument from room temperature to 650 ℃ (heating rate: 5K/min) in a dry air atmosphere at a flow rate of 50 ml/min. Before measurements, all of the samples were out-gassed at 523 K for 8 h.

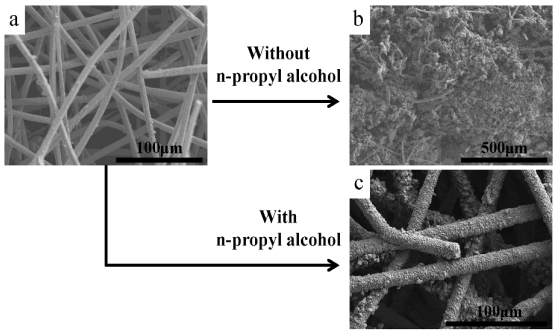

Fig. 1. SEM images of paper-like stainless steel fibers support (a); secondary synthesis of zeolite beta coating on stainless steel fibers without (b) and with (c) n-propyl alcohol in fluoride media.

3. Results and discussion

3.1 Effect of n-propyl alcohol

Zeolite beta crystals prepared from a near-neutral gel in fluoride media often exhibited high hydrophobicity and high thermal stability. However, the low solubility of the silicon species in the near-neutral media resulted in a heterogeneous synthesis gel. The gel prepared with fumed silica was uniform that enabled the synthesis of extended zeolite layers on flat and non-porous support, such as silicon wafers[21] and stainless steel substrate.[22] Nevertheless, the gel was lack of fluidity to cover each stainless steel fiber in this study. As can be seen in Fig. 1b, the three-dimensional network structure of paper-like stainless steel fibers support was blocked after secondary growth process caused by the heterogeneous gel with addition of hydrofluoric acid. Fortunately, it was shown that n-propyl alcohol could dissolved a part of silicon species (TEOS) and accelerated the crystal growth in Chen's research,[23] the homogeneity and fluidity of the reaction mixture with n-propyl alcohol became much better than the synthesis gel without n-propyl alcohol and made it possible for the three-dimensional network of paper-like stainless steel fibers support retained after secondary growth process in fluoride media (Fig. 1c). In this study, to avoid the formation of amorphous material resulted from the incomplete evaporation of ethanol when TEOS was used,[24] fumed silica was selected as the silicon species and the final composition of the secondary growth synthesis gel was set up to 1 SiO_2:0.6 TEAOH:0.6 HF:10.5 H_2O:2 n-propyl alcohol.

3.2 The morphologies of the composite

The morphologies of the zeolite beta coating/PSSF composite were observed by scanning electron microscopy (SEM). As can be seen in Fig. 2a, stainless steel fibers support presents a three-dimensional network structure with large void volume, which make the support possess good permeability. The SEM image in Fig. 2b show that the zeolite beta seeds were uniformly dispersed on the surface of stainless steel fibers and

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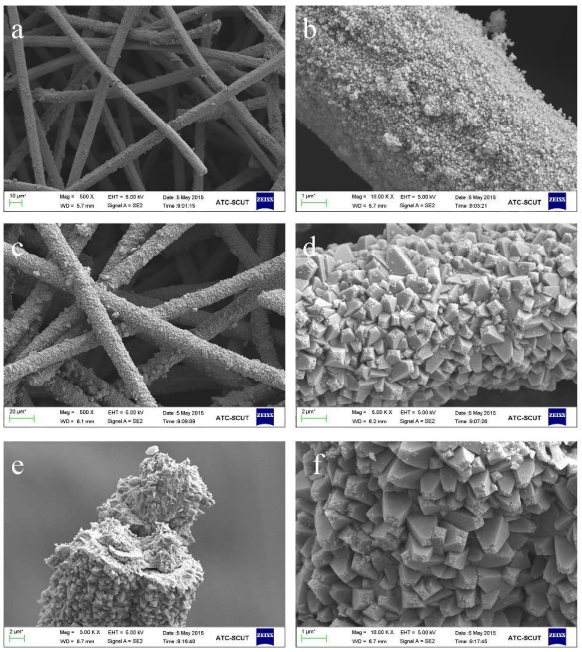

Fig. 2. SEM images of paper-like stainless steel fibers (a); the zeolite beta seeds layer (b); morphology of zeolite beta coating/PSSF composite (c); morphology of zeolite beta coating on stainless steel fibers (d), (e) and (f).

the size of the seeds is approximately 100 nm, which make them suitable for seeding purpose. And the SEM image in Fig. 2c reveals that a three-dimensional network structure with large void volume was retained after secondary synthesis resulting from the homogeneous and fluid synthesis gel. Moreover, it can been found that well-intergrown and continuous zeolite beta cover on the stainless steel fibers with truncated bipyramidal shape and the orientation is random (Fig. 2d and 2f). The thickness of the coating observed from the Fig. 2e is approximate 2 μm.

3.3 X-ray diffraction

The crystal phases of the zeolite beta coating/PSSF composite and the excess zeolite beta crystals deposited on the bottom of autoclave were detected by means of X-ray diffraction and the results are shown in Fig. 3. The diffraction peaks in Fig. 3a (*) were related to the paper-like stainless steel fibers (PSSF) support and the hematite (Fe_2O_3, 2θ=33.4° and 2θ=35.3°)[25] was detected on the surface of the PSSF support after calcination. Moreover, there were two strong diffraction peaks appear at the ranges of 2θ = 7-9° and 2θ = 21-22.5° in both the XRD patterns, which matching well with the standard pattern of zeolite beta synthesized in fluoride media according to the literature.[26]

3.4 N_2 adsorption/desorption isotherm analysis

The pore volume, pore size distribution and specific surface area were obtain by analyzing the N_2 adsorption/desorption isotherm at 77 K. The micropore volume and mesopore volume of composite were calculated by HK (Horvath-Kawazoe)
method and BJH (Barrett-Joyner-Halenda) theory respectively. The micropore pore size distribution of composite was analyzing via HK method. The specific surface areas (S_{BET}) was

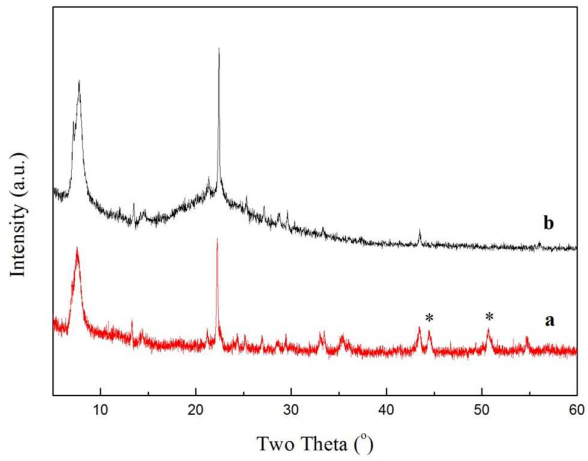

Fig. 3. X-ray diffraction patterns of different samples: (a) zeolite beta coating/PSSF composite; (b) samples deposited on the bottom of the autoclave.

calculated from adsorption braches in the relative pressure range of 0.06-0.3 using the BET (Brunauer-Emmett-Teller) method. As can be seen in Fig. 4, the volume absorbed of nitrogen increase remarkably at low relative pressure resulted from the presence of micropores of zeolite beta coating. As the relative pressures keep increasing, the volume absorbed of nitrogen increase slightly as well. There is a small hysteresis loop at a high relative pressure P/P_0 of 0.8-0.95, which was attributed to the existence of mesopores and macropores of PSSF support. Correspondingly, the pore size distribution of composite in Fig. 5. clearly indicates that a narrow peak centered at ca. 0.79 nm. Moreover, for the composite, the percentage of micropores was very high, the volume was 0.055 cm^3/g which was 82% of the total pore volume. The above N_2 adsorption/desorption results reveal that the composite was porous structure with majority of micropores and minority of mesopores and macropores, attributing to the highly crystallinity and the uniformly growth of zeolite beta on

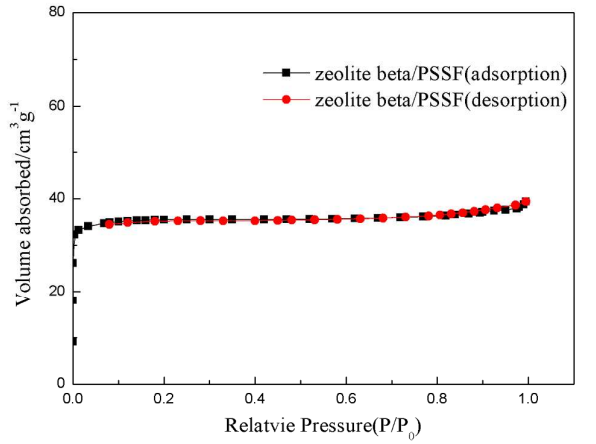

Fig. 4. N_2 adsorption/desorption of the zeolite beta coating/PSSF composite at 77K.

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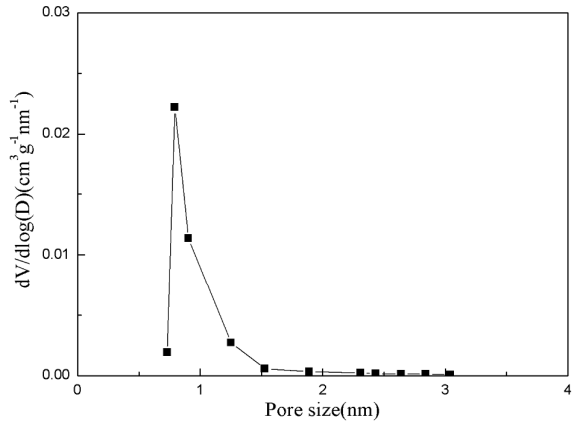

Fig. 5. Pore size distribution of the zeolite beta coating/PSSF composite.

Table 1. Pore structure characteristics of zeolite beta coating/PSSF composite and PSSF.

Samples	$V_{Micro\text{-}pore}$ (cm^3/g)	$V_{Meso\text{-}pore}$ (cm^3/g)	V_{total} (cm^3/g)	S_{BET} (m^2/g)
PSSF[a]	-	-	-	12
Zeolite beta/PSSF[b]	0.055	0.003	0.067	118

[a] Relative to paper-like sintered stainless steel fibers support

[b] Relative to the zeolite beta coating/PSSF composite

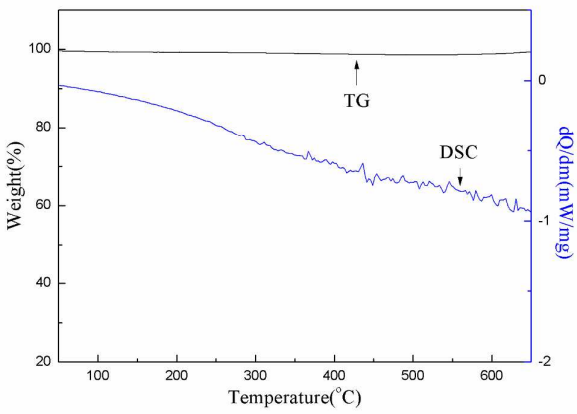

Fig. 6. TG-DSC curves of the zeolite beta coating/PSSF composite.

zeolite beta on PSSF surface significantly increase the BET specific surface area of PSSF from 12 m^2/g to 118 m^2/g, which was beneficial to dispersing the catalyst and improving the contacting efficiency.

3.5 Thermogravimetric analyses

The thermal stability of the zeolite beta coating/PSSF composite was characterized by using thermogravimetry (TG) and differential scanning calorimetry (DSC) analyses. The results are shown in Fig. 6. The composite exhibits almost 0% weight loss from room temperature to 650 ℃ on TG curve and there is no obvious endothermic or exothermic peak on DSC curve. The results reveal that the composite exhibit good thermal stability at temperature up to 650 ℃ and there are no organic templates and impurities left in the composite after calcined process and out-gassed pretreatment process, respectively.

4. Conclusion

In this study, well-intergrown zeolite beta coating was successfully fabricated on the surface of porous paper-like stainless steel fibers in fluoride media via secondary growth method. The zeolite beta coating/PSSF composite presented large void volume property, majority of microporous structure and a good thermal stability. The addition of n-propyl alcohol produced homogeneous and fluid reaction mixture, which in favor of the growth of intergrown and continuous zeolite beta coating on the fibers surface. On the other hand, the preparation of a controlled thickness zeolite beta coating and the application of zeolite beta coating/PSSF composite in adsorption and catalytic process are currently in progress.

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