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In-situ Synthesis of Binderless ZSM-5 Zeolitic Coatings on Aluminum

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Abstract: ZSM-5 zeolitic coatings on aluminum have been prepared successfully by *in-situ* hydrothermal synthesis method and ZSM-5/Al monolith was formed. The effects of pH value and crystallization time on the *in-situ* synthesis were discussed.

Keywords: ZSM-5, *in-situ*, synthesis, aluminum.

The potential of ZSM-5 zeolite for catalytic processes can hardly be overestimated. The direct use of ZSM-5 zeolite causes some problems such as high pressure drops and difficult separation and operation. To solve these problems, it has been proposed to make ZSM-5 zeolitic coatings on structured substrate. The most elegant way is to grow ZSM-5 crystals on the substrate through *in-situ* hydrothermal synthesis[1]. Under the right conditions, zeolites grow preferentially on the substrate surface rather than in liquid phase, yielding a binderless film of chemically bonded zeolite crystals[2]. By this method, ZSM-5 zeolite has been successfully synthesized on very different substrates, including metals[3], ceramics[4] and carbon materials[5].

In this study, aluminum was chosen as the new metal substrate. The formation of firm ZSM-5 zeolitic coatings on aluminum substrate without additional aluminium source was studied and the synthesis conditions were discussed. At last, the catalytic ability of copper ion-exchanged ZSM-5/Al monolith was investigated by SCR deNOx reactions.

Aluminum plate was pretreated in 1 mol/L HCl for two hours to remove the aluminum oxide on the surface. Silica sol was used as silicon source and the aluminum source was from the aluminum substrate. Template was dispensed. Silica sol, sodium hydroxide and water were mixed with proportion of $84SiO_2$: 10NaOH: 3500 H_2O. The pH value of the mixture was adjusted by 1 mol/L H_2SO_4. After two hours' strenuous stiring, the gained transparent liquid and pretreated aluminium plate were put into PTFE lined stainless steel autoclaves for static crystallization at 453 K. After crystallization, the samples were taken out, washed with distilled water ultrasonically, and then dried at 373 K over night.

The crystallinity of the synthesized ZSM-5/Al was given by powder X-ray diffraction

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(XRD) using Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using Cu Kα radiation. The Si/Al ratio of synthesized Na-ZSM-5 zeolite was gained by the method of comparing the average lattice plane distance reported in reference [6]. The method is based on the expectation that the crystal cell dimensions of Na-ZSM-5 vary with the Si/Al ratio due to the larger T–O bond length for T=Al instead of Si.

Cross sections and external surfaces of ZSM-5/Al were observed by scanning electron microscopy (SEM) in a HITACHI X-650 microscope. The SCR reaction of NO by propane was carried out in fixed-bed reactor. The reactant gas mixture contained NO (1000 ppm), C_3H_8 (1000 ppm), H_2O (10 %) and O_2 (5.0 %) balance with He to 100%. The total flow of the inlet gas was set at 60 mL min^{-1}. The space velocity is about 72 000 $mLgcat^{-1}h^{-1}$ (1.0 g sample containing about 5% catalyst powder and 95% cordierite substrate.)

The products were analyzed on-line using the GC (HP 6890 series) equipped with TCD detector. A molecular sieve 5A column served for separation of N_2, O_2 and CO, and a Porapak Q column for separation of CO_2, C_3H_8, N_2O, NO and H_2O.

The pH value in the system has great effect on the synthetic results and the XRD patterns in different pH values were shown in **Figure 1**. In our synthetic course, the aluminum source was the surface atoms of aluminium plate, so the ionization of aluminum atom on the surface was essential. The ionization of aluminum in the alkali circumstance is as follows.

$$2Al + 2H_2O + 2OH^- \rightarrow 2AlO_2^- + 3H_2$$

In weak alkali circumstance (pH=8), nearly no ionization of aluminum atom occurred. So it tended to form silicalite in the liquid phase and there was no ZSM-5 formed on the surface of aluminum substrate. In the condign alkali circumstance (pH= 11), ionization of outer layer aluminum atoms proceeded. Thus the ZSM-5 zeolitic coatings formed on the aluminum substrate. Besides, for the existence of the interaction between aluminum atoms in the outer layer and inter layer, ZSM-5 coatings were attached firmly to substrate. In the strong alkali circumstance (pH=14), a lot of alumi- num atoms leaked from the substrate to the liquid phase accompanied with the ionization of out layer aluminum. Then, zeolites grew not only in the liquid phase but also on the substrate surface. Affected by the Si/Al ratio in the liquid phase, the zeolite formed on surface of the substrate was most mordenite with impurity. The optimal pH value is 11.

The crystallization time has great effects on the synthesis, especially the thickness of zeolite phase. **Figure 2** showed the XRD patterns of samples with different crystallization time. From **Figure 2** we can see that after crystallization for 12 hours, there was almost no crystal grew on the aluminum substrate. After 24 hours, the surface was already completely covered with ZSM-5 crystals. When crystallization for 48 hours, the layer of ZSM-5 zeolite became thicker, which could be obtained by comparing the peak intensity of MFI structure and aluminum substrate. The further thickness increase is to be attributed to both the growth of the size of the crystals already present and to the nucleation of new crystals on already existing ones. To prepare a layer of ZSM-5 zeolite on aluminum substrate with strong interaction, the optimal crystallization time is 24 hours.

Figure 1 XRD patterns of ZSM-5/Al synthesized in different pH values

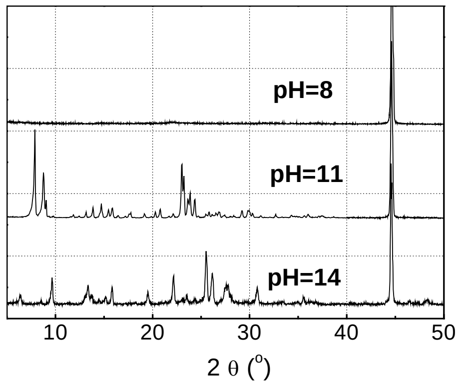

Figure 2 XRD patterns of ZSM-5/Al from different synthetic time

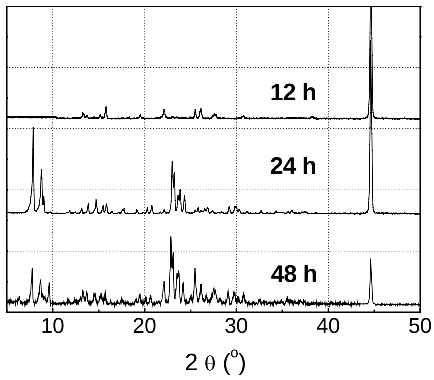

Figure 3 SEM photos of the surface (left) and the cross-section (right) of ZSM-5/Al

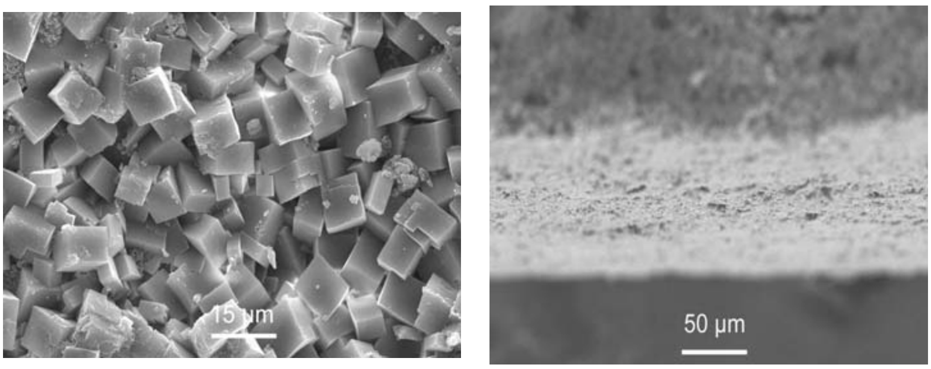

Figure 4 Relation between average lattice plane distance and the Si/Al ratio of Na-ZSM-5

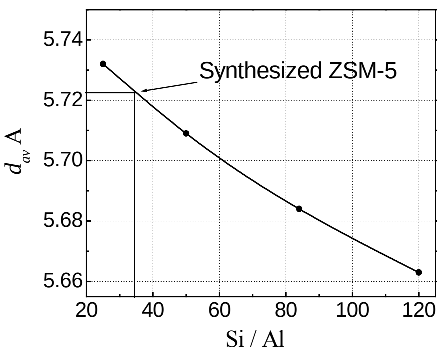

Figure 5 Selective catalytic reduction of NO by propane over Cu-ZSM-5/Al monolith

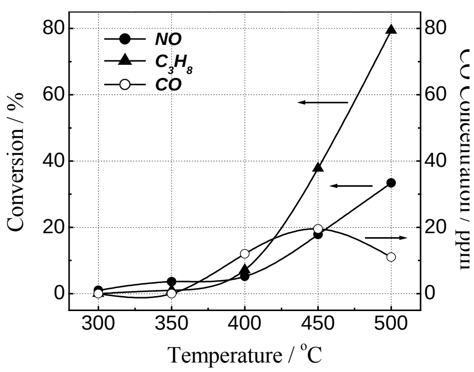

Figure 3 shows the SEM photograph of ZSM-5/Al prepared in the optimal synthetic conditions mentioned above. From the surface image, we can see that ZSM-5 crystal grain in the size of about 10 μm grew on the surface of aluminum substrate compactly and homogeneously. The thickness of coatings on the substrate was determined by studying the monolith cross-section. In the cross-section image, a layer of about 100 μm homogeneous ZSM-5 crystalloid grown on the wall of aluminum substrate can be observed. The crystal grain and the substrate phases coupled tightly.

Figure 4 shows the relation between Si/Al ratio and average lattice plane distance d_{av} employed to determine the Si/Al ratio of the aluminum supported Na-ZSM-5. When d_{av} was 5.723 Å, the calibration curve yields the Si/Al ratio of 34.

In-situ synthesized binderless ZSM-5 zeolitic coatings on structured substrates have been applied in the laboratory-scale processes for the selective catalytic reduction nitrogen oxides, catalytic distillation, methanol conversion, and so on. To prove the results of synthesis, copper ion-exchanged ZSM-5/Al monolith was used as catalyst to reduce NO by propane in the presence of oxygen. As shown in **Figure 5**, Cu-ZSM-5/Al showed high deNOx activity increasing with temperature. The only product was nitrogen; neither N_2O nor NO_2 was formed in the whole reaction process. Simultaneity, there was only a little CO (<20 ppm) formation in the reaction and most product from propane is CO_2. Cu-ZSM-5/Al showed superior selectivity to both N_2 and CO_2, partially attributed to the symmetrical distribution of ZSM-5 coatings on the aluminum.

ZSM-5 coatings have been successfully synthesized on the aluminum substrate by *in-situ* hydrothermal method. The aluminum resource was the outer layer aluminum atom of aluminum substrate instead of any aluminum salt. The optimal synthetic conditions were in the pH value of 11 and crystallization for 24 hours. Under these conditions, homogeneous ZSM-5 coatings of about 100 μm attached firmly to the substrate. Copper ion-exchanged ZSM-5/Al was used as the catalyst for HC-SCR deNOx reactions and good results were gained, which also proved the synthetic results.

Acknowledgments

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