

Monolithic TS-1/Cordierite Catalyst Synthesized by in-situ Method

Naijia Guan and Yansong Han

*Institute of New Catalytic Material Science, Department of Chemistry, Nankai University,
Tianjin 300071, P.R. China*

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Titanium silicalite (TS-1) was in-situ synthesized on the surface of honeycomb-shaped cordierite under hydrothermal conditions for the first time. Confirmed by XRD, FTIR, UV-VIS, and SEM techniques as well as with help of a probe reaction, it has been proved that TS-1 zeolite crystals have successfully grown on the surface of cordierite.

Titanium silicalite (TS-1) was first prepared by Taramasso et al.¹ It possesses interesting catalytic properties, especially in reactions like hydroxylation of phenol, benzene, alkanes, and ammoximation of cyclohexanone involving H₂O₂ as the oxidant.² Recently, it is used for selective reduction of NO_x by NH₃.³

Honeycomb-type substrates provided with unitary structures have been widely used for catalytic support in pollution control by oxidation and reduction of automobile exhaust gases.⁴ The honeycomb-type cordierite (2MgO·2Al₂O₃·5SiO₂) is less expensive, has good mechanical strength and small thermal expansion factor, and is one of the widest applicable substrate for automotive exhaust gas converter.⁵

In this paper, titanium silicalite (TS-1) was synthesized on the surface of honeycomb-shaped cordierite. By means of a series of characterizing method and probe reaction, it is proved that TS-1 has successfully synthesized on the surface of cordierite.

This monolithic catalyst is advantageous for carrying TS-1 powder to facilitate the separation of catalysts from reaction mixture. On the other hand, it is supposed to be one of the catalysts for catalyzing reduction of NO from exhaust gas of vehicles.

Titanium silicalite (TS-1) was prepared by hydrothermal crystallization,^{6,7} using silica sol as silicium source, titanium tetrabutoxide [Ti(OBu)₄] as titanium source, and a mixture of tetraethylammonium hydroxide and tetrabutylammonium hydroxide as the template. Silica sol and the template were mixed and stirred for 1h, then [Ti(OBu)₄] was added into the mixture. The chemical composition of the gel is: 30SiO₂ : TiO₂ : 3RN : 600H₂O (RN : template). The mixture was stirred then for 5–7 h, and put into an autoclave with a piece of cordierite block. After static crystallization at 448 K for 90 h, the monolithic sample was taken out, washed by water till the residual water became neutral, then washed thoroughly by ultrasonic wave generator to remove the adhering substances. Both monolithic sample and precipitated TS-1 powder were dried at 393 K overnight.

The monolithic sample and the TS-1 powder were characterized by X-ray powder diffraction (Rigaku D/max 2500, Cu K α radiation), scanning electron microscope (HITACHI X-650 Scanning Electron Microscope), FTIR (Bruker Vector 22), and diffuse reflection UV-Vis spectroscopy (Shimadzu UV-240), to

investigate the crystallinity, the morphology, and the thickness of the zeolite on the surface of the monolithic sample. In order to prove that titanium ions have inserted into the silicalite framework, the oxidation of pyridine using of H₂O₂ as the oxidant was carried out over TS-1 powder. One g TS-1 was added into the mixed solution of 10.17 mL pyridine and 10mL water and 17.33 mL H₂O₂ (30% aqueous solution) was then added drop by drop slowly under stirring at 353 K. The reaction was kept at this temperature for 2 h. The product was separated by low-pressure distillation.

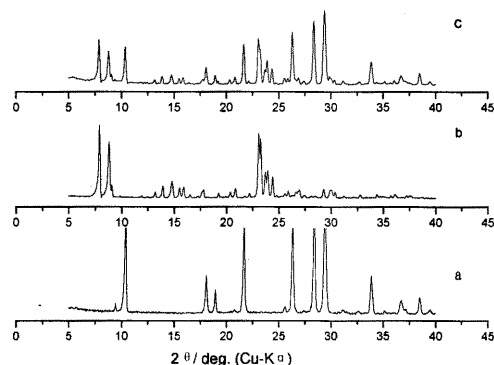


Figure 1. XRD patterns of TS-1/cordierite monolithic catalyst (c), TS-1 in powder form (b) and blank cordierite (a).

Figure 1(a)–(c) presents the comparison of monolithic sample, pure TS-1 and blank cordierite. In the monolithic sample's XRD patterns, the typical MFI structure peaks of TS-1 are clear and show a highly crystallinity of the zeolite growing on the surface of the cordierite. TS-1 can be considered to transform from silicalite-1 when Ti atoms get into its framework by isomorphous replacement. To determine whether titanium got into the framework of the zeolite on its surface, the monolithic sample had been calcined at 823 K for 4 h. It is found from its XRD pattern, that the peak $2\theta = 24.4^\circ$ does not divide. Upon calcination at 823 K in air, silicalite-1 is transformed into a material with monoclinic symmetry. So in its XRD pattern, the peak $2\theta = 24.4^\circ$ split, while TS-1 retains its orthorhombic symmetry.⁷ The cell parameters are calculated from XRD pattern of Figure 1-c. The unit cell parameters (a , b , c) of TS-1 are 20.106, 20.085 and 13.504 Å, larger than the cell parameters of silicalite-1 (20.087, 19.885, 13.381 Å).⁸ It is because that the incorporation of Ti⁴⁺ in the MFI-type framework causes an increase in its unit cell dimensions.⁸

Further characterization was achieved by IR and UV-Vis spectroscopy. The zeolite powder obtained from the same autoclave with monolithic sample was calcined in the air at 823 K for 4 h, and then investigated by FTIR (Figure 2) and UV-Vis.

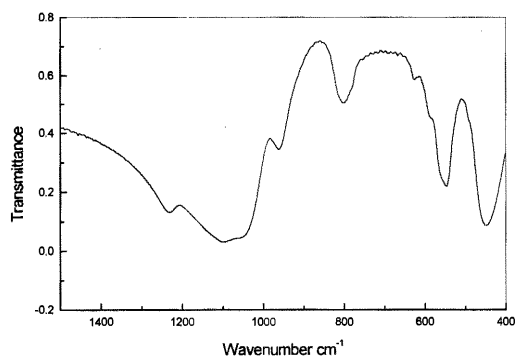


Figure 2. FTIR Patterns of TS-1 powder from the monolithic catalyst.

The band at 960 cm^{-1} in FTIR, belongs to one of the important characteristics of TS-1, which confirmed the incorporation of titanium in the lattice framework.^{7,8} The absence of any other heterophase of titanium oxide was further probed by UV-Vis. The presence of a dominant peak at 213 nm (The onset wavelength of the absorption is 400 nm) is an indication of the tetrahedral titanium isomorphously substituted in the zeolite framework.⁹

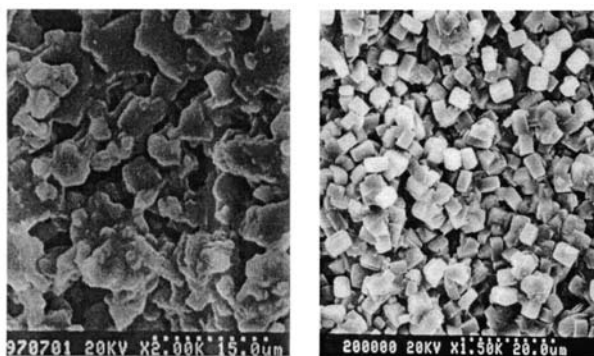


Figure 3. SEM photos of cordierite before (left) and after (right) in-situ synthesis.

SEM photos are shown in Figure 3. From the comparison between the blank cordierite and the monolithic sample, we can see TS-1 crystals of uniform size (about $2\mu\text{m}$) and shape (cuboid) are well distributed on the surface of cordierite, with good accumulation morphology. In the cross section photo (Figure 4, $\times 150$), three layers can be seen. The thick middle layer is the wall of cordierite and the upper and bottom layers are TS-1 films. It is shown that more than $50\mu\text{m}$ thick zeolite membrane is growing on the both sides of the cordierite piece.

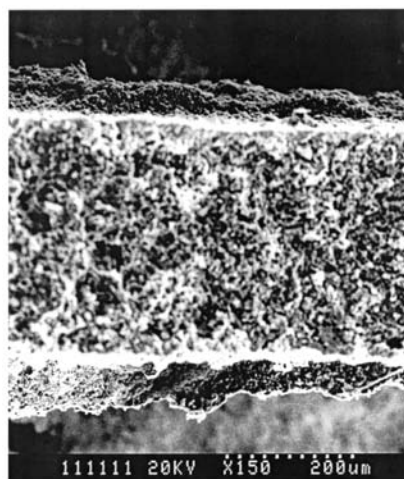


Figure 4. The cross section SEM photo of the monolithic sample.

The catalytic oxidation of pyridine was carried out as the probe reaction to confirm the TS-1 growing on the cordierite. In this reaction, pyridine was oxidized to dark yellow *N*-oxidized pyridine by H_2O_2 . Above 60% yield were obtained over TS-1/cordierite monolithic sample. For comparison, this catalytic reaction was also carried out over silicalite-1 and ZSM-5 ($\text{SiO}_2/\text{Al}_2\text{O}_3 = 50$) under the same condition. The results indicate that this selectively oxidative reaction can not be carried out without TS-1 catalyst. It firmly confirms that Ti has successfully entered into the framework of the zeolite on the surface of cordierite.

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