

# Thermal and hydrothermal stability of monolithic TS-1/cordierite catalyst

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## Abstract

Monolithic TS-1/cordierite catalyst has the practical prospect for cleaning  $\text{NO}_x$  from vehicle exhaust gas. In order to elucidate whether the 10–14% water vapor in the exhaust gas would destroy the catalyst structure under the high circumstance temperature, the TS-1 and monolithic TS-1/cordierite catalyst were steam-treated at 1073 K for 3 h. XRD and SEM results indicated that both the TS-1 zeolite itself and the TS-1 zeolite on the cordierite substrate remained their structure, crystallinity and surface dispersion. In addition, FTIR results also showed that little amount of Ti atoms was separated from the TS-1 zeolite frameworks. Therefore, the monolithic TS-1/cordierite catalyst suggested a good thermal and hydrothermal stability. © 2002 Elsevier Science B.V. All rights reserved.

*Keywords:* Monolithic TS-1/cordierite catalyst; Thermal and hydrothermal stability

## 1. Introduction

Titanium silicalite (TS-1) was first prepared by Taramasso et al. [1]. It possesses interesting catalytic properties in the environmental protection fields, such as to catalyze the hydroxylation of phenol, benzene, alkanes, and ammoxidation of cyclohexanone involving  $\text{H}_2\text{O}_2$  as the oxidant, etc. [2]. Especially it is recently used for the selective catalytic reduction (SCR) of  $\text{NO}_x$  by  $\text{NH}_3$  and CO [2–6]. On the other hand, the honeycomb-shaped cordierite ( $2\text{MgO} \cdot 2\text{Al}_2\text{O}_3 \cdot 5\text{SiO}_2$ ) providing with

unitary structures has good mechanical strength and a small thermal expansion factor. It is widely used as substrate for automotive exhaust gas converters [7]. Usually one loads the active component TS-1 on the cordierite substrate by impregnation or doping, etc. However, due to the weak component–substrate interaction by this preparation method, the coated TS-1–cordierite catalyst may not be stable enough and disassembles under some extreme conditions, for example under the high space velocity of exhaust gas, etc., which shall cause the loss of catalyst active components from the substrate. In addition, the loss of active metals may also result in the secondary environmental pollution.

In our former work [8], for the first time TS-1 was synthesized on the surface of honeycomb-

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shaped cordierite to form monolithic catalyst by in situ method in order to overcome the above-mentioned catalyst preparation disadvantages, since the in situ synthesis of monolithic TS-1/cordierite can lead the TS-1 zeolite to grow on the cordierite surface tightly and hence a strong interaction is obtained. The in situ synthesis of zeolite on honeycomb-shaped cordierite can also take advantages of the superior thermal conductivity, lower mass transfer resistance and higher mechanical strength of the carrier. Recently, it was reported that this monolithic catalyst could be used as monolithic reactor, an attractive alternative to replace the conventional multi-phase reactors, such as slurry reactor and trickled-bed reactor [9]. Therefore, this novel catalyst preparation method will broaden the applied fields of TS-1 zeolite greatly.

Actually the exhaust gas from the automotive vehicles contains about 10–14% water. Containing water vapor commonly acts as both a main poison for the catalyst and a factor to collapse the catalyst

structure. Therefore, either acting as catalysts for catalyzing the reduction of  $\text{NO}_x$  from vehicle exhaust gas or as the monolithic reactor, monolithic TS-1/cordierite catalyst must possess certain stability against the high temperature with vapor in its operation conditions. In this study, the in situ synthesized monolithic TS-1/cordierite catalyst was steam-treated at 1073 K and then determined by XRD, FTIR, and SEM techniques with the aim to investigate the thermal and hydrothermal stability.

## 2. Experimental

The synthesis of monolithic TS-1/cordierite was reported elsewhere in detail [8]. The monolithic catalyst or the TS-1 powder was, respectively, put in the ceramic boats, which were then placed in a long quartz tube heated outside by a tube furnace. The steam treatment was carried out by flowing water vapor through the quartz tube at 1073 K for

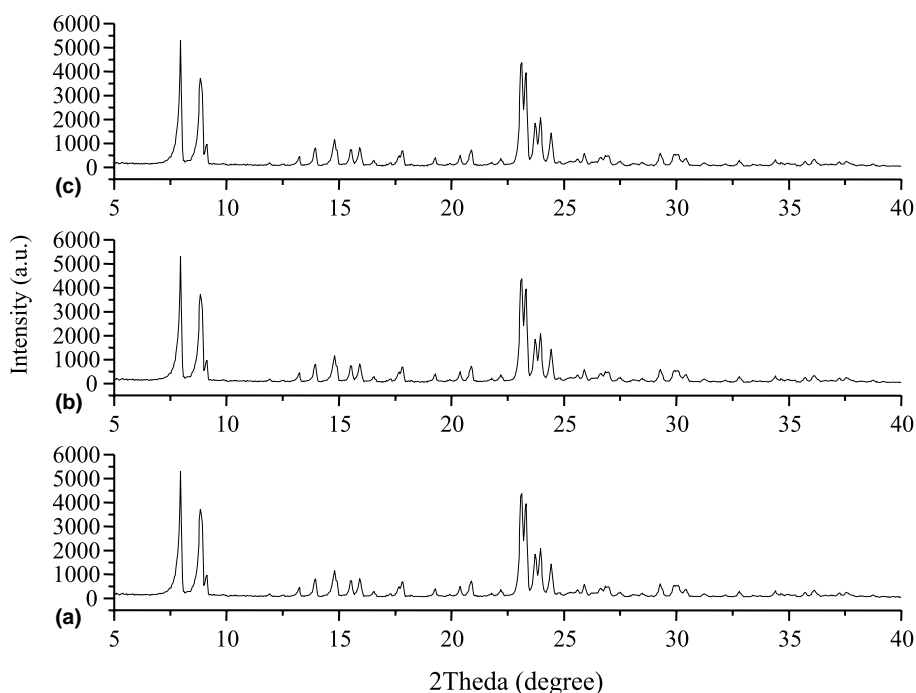


Fig. 1. XRD patterns of TS-1 powders (a) without any treatment, (b) after calcination at 1073 K and (c) after steam treatment at 1073 K.

3 h, where the water flow was generated by a water distillation set ( $SV = 3000 \text{ h}^{-1}$ ). Finally the obtained samples were taken out and dried.

The monolithic catalyst and the TS-1 powder after thermal and hydrothermal treatment were characterized by X-ray powder diffraction (Rigacu

D/max 2500,  $\text{CuK}_\alpha$  radiation), scanning electron microscope (HITACHI X-650), and FTIR (Bruker Vector 22) to investigate the textual changes.

### 3. Results and discussion

In order to determine the thermal and hydrothermal stability of the monolithic TS-1/cordierite catalyst, the TS-1 itself must be investigated in advance. XRD patterns give the comparison of the effect of different treatment on the TS-1 zeolite (Fig. 1). Clearly none of the distinct peaks in patterns b and c are different from those in the curve a, which means that, even after the calcination and steam treatment up to 1073 K, the TS-1 samples kept their zeolite morphology.

Further characterization was performed by FTIR technique. Fig. 2 shows the comparison of the TS-1 zeolite powder before (a) and after (b) the steam treatment. The existence of the band at  $960 \text{ cm}^{-1}$ , one of the important characteristics of TS-1 zeolite, has confirmed the incorporation of

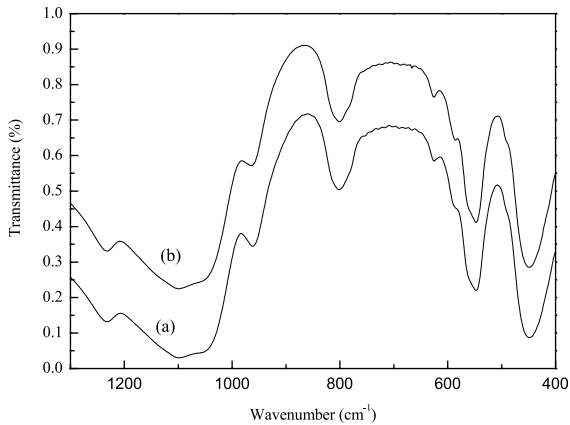


Fig. 2. FTIR profiles of TS-1 powders (a) before and (b) after steam treatment at 1073 K.

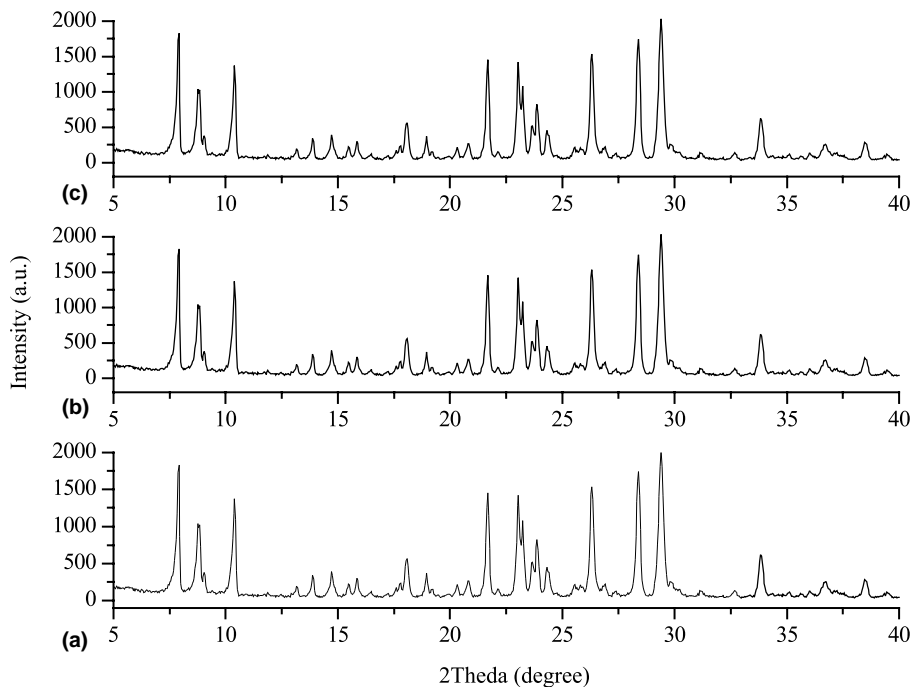


Fig. 3. XRD patterns of monolithic TS-1/cordierite catalysts (a) without any treatment, (b) after calcination at 1073 K and (c) after steam treatment at 1073 K.

titanium into the lattice framework [6,10]. It is also known that the intensity of this band increases when Ti content in the zeolite framework increases. The band at  $550\text{ cm}^{-1}$  is the characteristic of the MFI structure. And the ratio of band intensity of  $960\text{ cm}^{-1}$  to that of  $550\text{ cm}^{-1}$  represents the change of Ti content in the zeolite [10]. Comparing the two ratios obtained from curve (a) and curve (b), respectively, in this work, the ratio of the intensity of the  $960\text{--}550\text{ cm}^{-1}$  bands after hydrothermal treatment (b) was very close to the ratio that before the hydrothermal treatment (a), which

indicates the hydrothermal treatment did not result the separation of Ti atoms from the TS-1 zeolite framework. The TS-1 zeolite should possess a high thermal and hydrothermal ability.

XRD technique also was applied to investigate the effect of thermal and hydrothermal treatment on the monolithic TS-1/cordierite catalyst (Fig. 3). Clearly as same as the pure TS-1 powders in Fig. 1, no distinct peak changes were observed on the monolithic TS-1/cordierite samples after the calcination treatment and the steam treatment up to  $1073\text{ K}$ . In patterns b and c, the five typical MFI

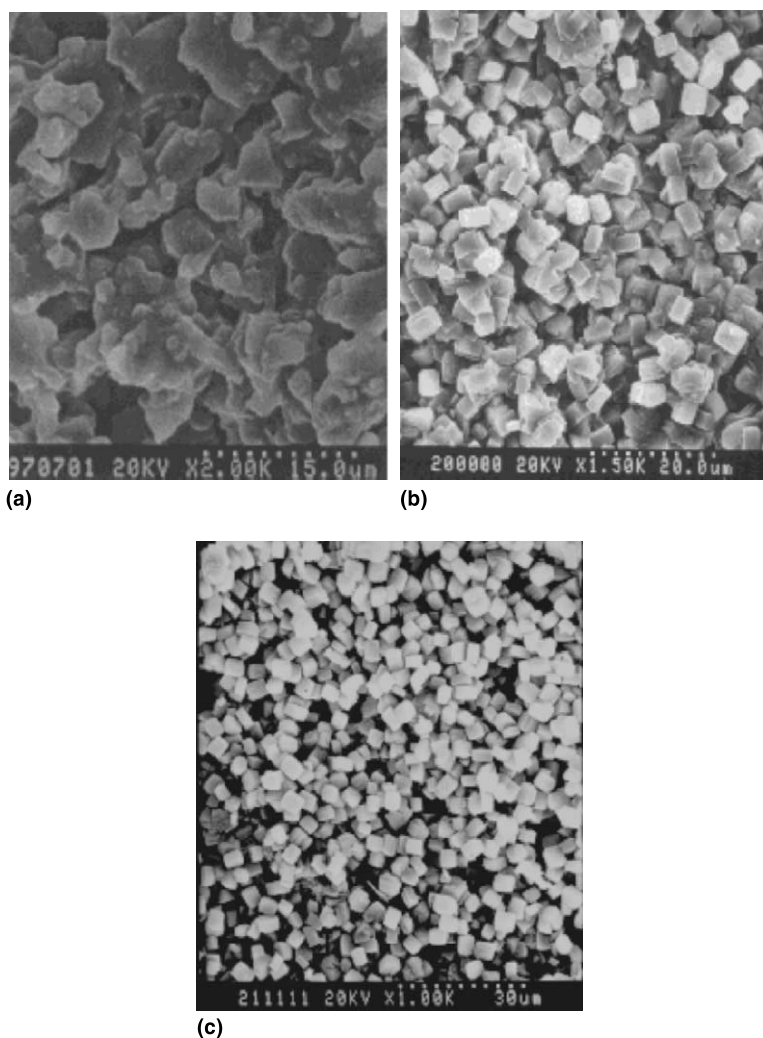


Fig. 4. TEM photographs of (a) cordierite, monolithic TS-1/cordierite catalysts, (b) before and (c) after steam treatment at  $1073\text{ K}$ .

structure peaks ( $2\theta = 7.92^\circ, 8.84^\circ, 23.16^\circ, 23.92^\circ, 24.36^\circ$ ) of TS-1 are still distinct and strong. If comparing the ratios of the peak intensities of TS-1 to those of cordierite carrier, it can be known that a high crystallinity of the zeolite dispersing on the cordierite substrate surface remained even after the thermal and hydrothermal treatment.

In addition, the characteristic peaks  $2\theta = 24.4^\circ$  in patterns b and c did not split into two peaks, which demonstrates that the symmetry of TS-1 zeolite crystal cells did not change and TS-1 remained its orthorhombic symmetry even after the thermal and hydrothermal treatment. If the TS-1 had decreased its symmetry from orthorhombic to lower monoclinic symmetry, for example to form the silicalite-1, a possible splitting of peak  $2\theta = 24.4^\circ$  would have happened [6]. Therefore, this observation proves that the thermal and hydrothermal treatment of the TS-1 zeolite (Fig. 1) or the monolithic TS-1/cordierite catalyst (Fig. 3) did not destroy the existing state of the Ti atoms in the frameworks.

The cell parameters were calculated from XRD patterns [10]. The unit cell parameters (a, b, c) of TS-1 sample after hydrothermal treatment in this study are 20.367, 20.081 and 13.414 Å, respectively, which are completely consistent with the cell parameters of the TS-1 zeolite before hydrothermal treatment [10,11].

The SEM images of the surface of the cordierite, monolithic TS-1/cordierite catalyst before and after hydrothermal treatment are shown in Fig. 4. From picture b, it is clearly shown that the in situ synthesized TS-1 crystals were regularly grown on the cordierite substrate surface. They are cuboid and have the uniform size about 1  $\mu\text{m}$ . Even after the hydrothermal treatment, the TS-1 crystals are still well dispersed on the surface of cordierite with

good accumulation morphology. No aggregations or sintering happened.

#### 4. Conclusions

All of these obtained results completely support that both the TS-1 zeolite and the monolithic TS-1/cordierite catalyst possess good thermal and hydrothermal ability. The containing water vapor in the automotive vehicle exhaust gas would not destroy both the active catalyst component and strip off the TS-1 zeolite from the substrate even under high operation temperature (1073 K). From this point of view, the practical application of the monolithic TS-1/cordierite as both catalyst and reactor is prospective.

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