Selective catalytic reduction of nitrogen oxides from exhaust of lean burn engine over in situ synthesized monolithic Cu–TS-1/cordierite

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Abstract

Titanium silicalite (TS-1) zeolite was in situ synthesized successfully on the surface of honeycomb cordierite substrate, which was certified by XRD and SEM techniques. The in situ synthesized monolithic TS-1/cordierite showed superior thermal and hydrothermal stabilities. Cu–TS-1/cordierite prepared with ion-exchange and impregnation methods were studied as catalysts for selective catalytic reduction (SCR) of nitrogen oxides (NO_x). For practicality, the evaluation experiments were carried out in exhaust of a real lean burn engine without any other additive. Cu–TS-1/cordierite prepared with two methods both exhibited similar high activities, and at about 715 K, the max NO_x conversion could reach 58% in the space velocity (SV) of $12000\,h^{-1}$. Ion-exchanged Cu–TS-1/cordierite had superior duration and anti-poison properties while impregnated Cu–TS-1/cordierite not. Cooper is the main active component in the catalyst and Cu(I), which was found in the catalyst during the proceeding of reaction by XPS, is thought to be essential.
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1. Introduction

The emission of nitrogen oxides from automobile source is a serious environmental problem. A lean burn engine is invented both to reduce fuel consumption and to prevent greenhouse effect [1,2]. The lean burn engine is run under the rich oxygen condition. This causes the invalidation of the three-ways catalysts (TWC), which are up to now the best and widely used means to treat the exhaust [3]. Selective catalytic reduction (SCR) of NO_x by hydrocarbons in the presence of excess oxygen is a potential method to remove NO_x from exhausts [4]. Ion-exchanged ZSM-5 was reported as high activity catalyst in the SCR reaction [5,6]. Because titanium silicalite (TS-1) has the similar structure as ZSM-5 [7], ion-exchanged TS-1 is supposed to have high activity in SCR reaction. Moreover, for practical purpose, zeolite powders have to be shaped by using binder materials, which often affects the activity of the resulting catalyst. To avoid these problems, it has been proposed to prepare the catalytic zeolite component from crystallites grown on substrate surfaces [8,9] called in situ synthesis. In our previ-

ous work, we have successfully in situ synthesized TS-1 on the honeycomb substrate cordierite ($2MgO\ 2Al_2O_3\ 5SiO_2$) [10]. The main advantages of in situ synthesis come from these: the substrate is used as a base for nucleation; and under specific conditions a chemical bonding between crystals and substrate layer is formed and no binder or glue is needed. Thus, under the condition of high space velocity, it decreases the loss of catalyst, which causes the second pollution. It is believed that in situ grown zeolite can be applied to form a structured catalyst that provides good flow characteristics [11]. At the same time, the interaction of zeolite and cordierite substrate can improve the anti-poison characteristic of the monolithic catalyst.

We applied Cu–TS-1/cordierite prepared from ion-exchange and impregnation methods in treating the exhaust of lean engine and got good results.

2. Experiment

2.1. Preparation of catalysts

2.1.1. In situ synthesis of TS-1/cordierite
Silica sol was used as silicon resource and tetrabutylorthotitanate (TBOT) as titanium resource. Tetrapropyl-

Table 1
Preparation process of Me-TS-1/cordierite

Precursor	Ion resources	pH	Time	Products
TS-1/cordierite	0.05 M Cu(AC)$_2$	6.5	30 h 15 h × 3	Cu–TS-1/cordierite
TS-1/cordierite	1.0 M Cu(AC)$_2$	6	25h	Cu–TS-1/cordierite

ammonium hydroxide (TPAOH) was used as template. Silica sol, template and water were mixed together and stirred for an hour before TBOT was dropwise added in. The molar composition of the reagent: $30SiO_2:TiO_2:3TPAOH:600H_2O$. After 6 h strenuous stir, the gained transparent liquid and cordierite ($\Phi 24$ mm × 50 mm, 60 cells/cm^2) were put into high-pressure polytetrafluoroethylene lined autoclave for static crystallization at 453 K for 90 h together. Then the samples were taken out, washed by distilled water, dried at 373 K and then calcined at 823 K in the air for 4 h to remove the template.

2.1.2. Ion-exchange and impregnation

Cu–TS-1/cordierite was prepared from TS-1/cordierite by the solution ion-exchange [12] and impregnation method at the room temperature. The concrete process is shown as below (Table 1):

The gained catalysts were washed five times by ultrasonic generator, 10 min each time, to remove the copper appendiculating on the surface of catalysts and then calcined at 823 K in the air for 4 h.

2.2. Characterization methods

The crystallinity of the synthesized TS-1/cordierite was checked by XRD. Data were collected with a Rigaku D/max 2500 diffractometer provided with a graphite monochromator and using Cu Kα radiation. SEM from a HITACHI X-650 Scanning Electron Microscope detected the surface feature and degree of accumulated homogeneity.

Chemical valence states of copper in the catalysts before and in reaction was measured by XPS with a PHI-5300 instrument with Mg Kα X-ray excitation source. Accurate ±0.1 eV binding energies were determined with respect to the position of the adventitious C 1 s peak at 284.8 eV. The residual pressure in the analysis chamber was maintained below 10^{-7} Pa during data acquisition.

The concentration of metal cation in the synthesized catalysts was mensurated by ICP (IRIS Advantage, TJA solution).

2.2.1. Evaluation of catalysts

The catalytic evaluation experiment was carried through on a four-valve S.I. engine. The controllable quasi-homogenous mixture inside cylinder made by the controllable injection on this engine realized the fast quasi-homogenous mixture combustion. The air fuel ratio (A/F) was controlled
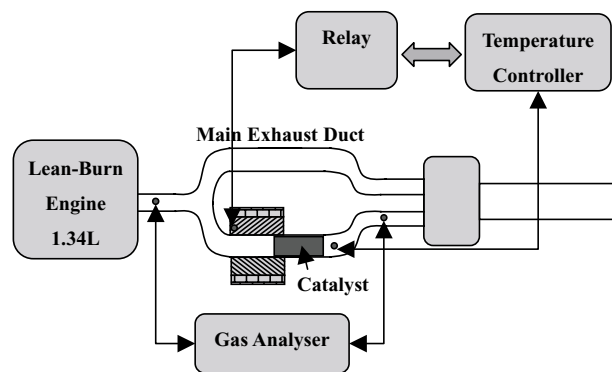

Fig. 1. Equipment of catalytic assessment experiments. Basic status of the engine in the evaluation experiment: load = 21 Nm; rotate speed = 1800 r/min.

between 20.0 and 23.5. The catalyst was fixed inside the vent-pipe of the engine, heated by electrical heater. The temperature was measured by NiCr–NiAl thermojunction and controlled by relay and temperature controller. The products after catalytic reaction were on-line analyzed by five-component exhaust analyzer (MW56-AVL DIGAS 4000 LIGHT). The equipment is shown in Fig. 1.

3. Results and discussion

3.1. Characterization of catalysts

Both TS-1 and cordierite substrate have their own typical peaks. From the comparison of XRD patterns of in situ synthesized TS-1/cordierite, TS-1 powder and blank cordierite patterns of in situ synthesized TS-1/cordierite, TS-1 powder and blank cordierite in Fig. 2, we can see typical peaks at 7.84, 8.76, 23.12, 23.88, 24.32° (d = 11.27, 10.09, 3.84, 3.72, 3.66 Å) in XRD pattern of TS-1/cordierite corresponding to the characteristic MFI structure peaks of TS-1 zeolite. All this suggests TS-1 zeolite crystallized and grown on the cordierite substrate commendably.
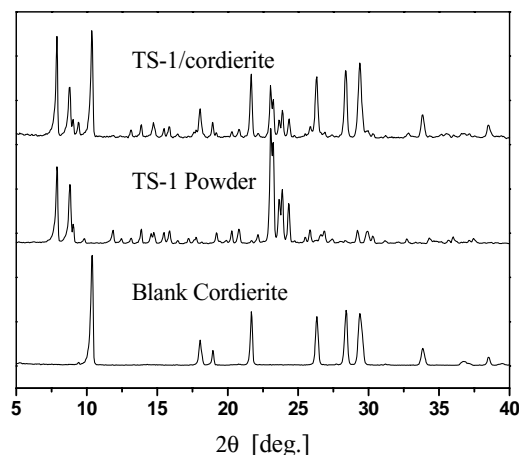

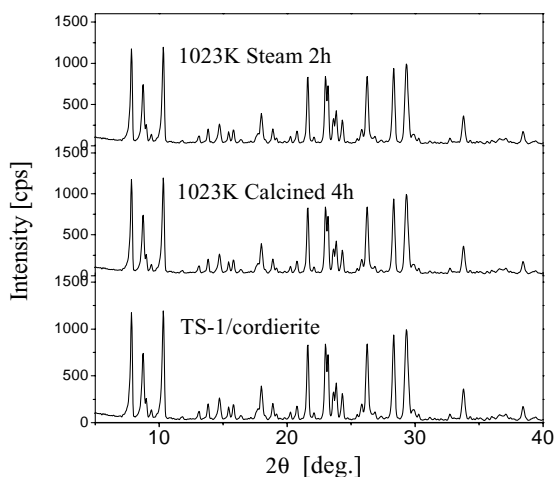Fig. 2. XRD patterns of blank cordierite, TS-1 powder and TS-1/cordierite.

Fig. 3. XRD patterns of TS-1/cordierite before and after thermal and hydrothermal treatment.

In the real mobile exhaust environment, which contains about 10% water vapor, the catalysts have to endure the temperature from the normal to above 1000 K. Therefore, their thermal stability and hydrothermal stability are very important. The TS-1/cordierite before and after calcination at 1023 K and the high temperature vapor treatment was characterized and the results are shown in Fig. 3. The compared results show that there is no obvious difference between their crystallinity. These exemplify the good thermal and hydrothermal stability of TS-1/cordierite.

Utilizing SEM we can observe the surface of sample intuitively. In Fig. 4, we can see cubical TS-1 zeolite crystalloid whose size is about 5 μm grown on the surface of cordierite substrate compactly and homogeneously. TS-1 crystalloid covers the irregular surface of cordierite entirely.

In Fig. 5, we compare the surfaces of catalysts Cu–TS-1/cordierite prepared from different methods. In the right photo we can observe impregnated Cu species form
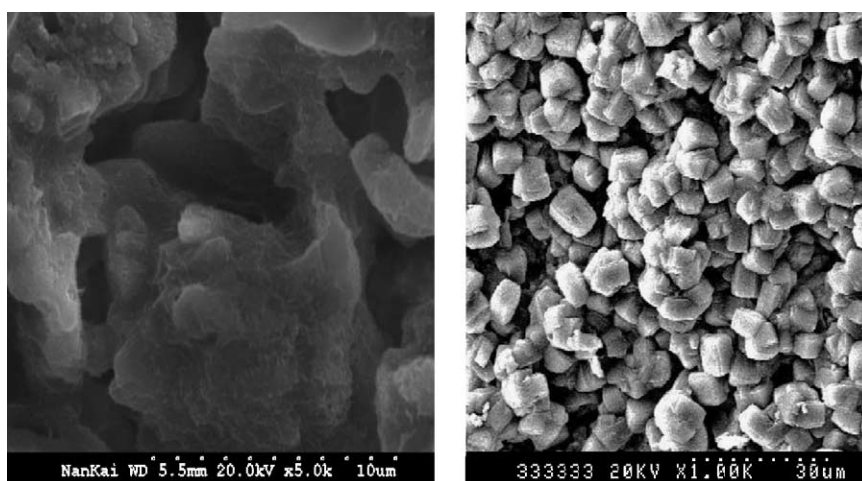

Fig. 4. SEM photo of the surface blank cordierite (left) and TS-1/cordierite (right).
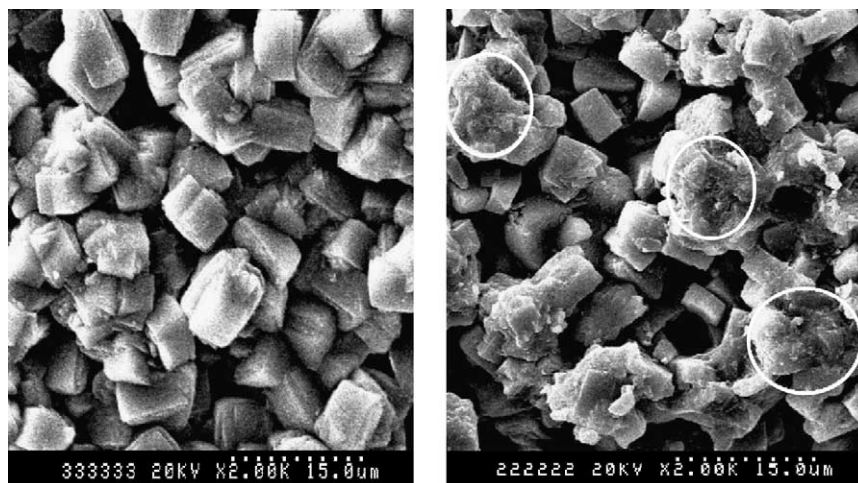

Fig. 5. SEM photo of the surface of Cu–TS-1/cordierite from different preparation methods: solution ion-exchange (left) and impregnation (right).

Table 2
Main composition of exhaust gas

Components	Concentration (vol.%)
N_2	71.0
CO_2	12.0
H_2O	10.0–11.0
O_2	5.0–6.0
CO	0.10–0.30
NO_x	0.03–0.10
HC	0.008–0.03

block of aggregation (examplified within white ring) and cover part of the catalyst's surface while it cannot be seen on the surface of catalyst prepared from solution ion-exchange method. The aggregation of Cu species on the surface of catalyst can affect the anti-poison property, which will be further discussed in the following text.

3.2. Catalytic results

In the research of de-NO_x catalysts, single substance, such as methane and propane, is usually chosen as reducing material with inertia components. For practical purpose, in our experiments, hydrocarbons and CO in car exhaust were used directly as reducing materials for NO_x reduction. The burning gasoline was commercial used 95# bought from Shell (China). Main components of lean burn engine exhaust and their concentrations are shown in Table 2. Besides the components, there is a little SO_2 and particulates containing lead, whose concentrations are related to the gasoline composition and engine models.

Fig. 6 displays the status of the lean burn engine exhaust treated by Cu–TS-1/cordierite prepared from ion-exchange method and the cooper loading is 0.018% (wt.%).

The NO_x conversion is a criterion to value the catalyst's activity. Cu–TS-1/cordierite was activated at the temperature about 630 K when NO_x conversion was 29%. At 715 K,

Fig. 7. Conversions of NO_x in exhaust gas varied with temperature catalyzed by Cu–TS-1/cordierite and TS-1/cordierite. Working status of engine: A/F = 21; SV = 12,000 h^{-1}; Exhaust before catalytic reaction: NO_x = 550 ppm, HC = 126 ppm, CO = 0.24%.

activity of the catalyst reached its maximal value and the maximal NO_x conversion was 58%. Afterwards, the activity of the catalyst began to decrease. With the elevation of the temperature, the hydrocarbons conversion increased further and converted completely at 790 K. At 500 K, CO conversion was 21%, and the conversion decreased gradually with the rising temperature. The CO conversion reached its minimum value 7.9% at 675 K and kept at this value till 715 K when it started to increase rapidly.

To make sure what is the main active component in catalyst Cu–TS-1/cordierite, we compare the NO_x conversions catalyzed by TS-1/cordierite and Cu–TS-1/cordierite with different preparing methods at several different temperatures. In Fig. 7, we could see that TS-1/cordierite showed very low activity in the de-NO_x reaction while Cu–TS-1/cordierite prepared from impregnation method and ion-exchange method both showed parallel high activities. So we concluded that the high catalytic activity of Cu–TS-1/cordierite came from cooper species in the zeolite. Cooper loading in Cu–TS-1/cordierite prepared with impregnation method was 2.0% (wt.%). The cooper mainly aggregated together and attached on the surface of TS-1 zeolite (as seen in Fig. 5) by the function of hydroxyl on the surface of TS-1/cordierite. When calcined at 823 K, a very small part of this cooper on the surface moved into the duct of TS-1 zeolite while most of the cooper became CuO aggregating on the surface of TS-1/cordierite. Compare to the high cooper loading of catalyst prepared from impregnation method, cooper loading in the Cu–TS-1/cordierite with ion-change method was only 0.018% (wt.%). During the course of preparing, cooper attached on the surface was washed down by the ultrasonic and most of the cooper remained was in the duct of TS-1 zeolite. XRD patterns of cooper ion-exchanged TS-1/cordierite did not exhibit peak at 2.52 Å, typical of CuO crystallites [13], clearly certifying
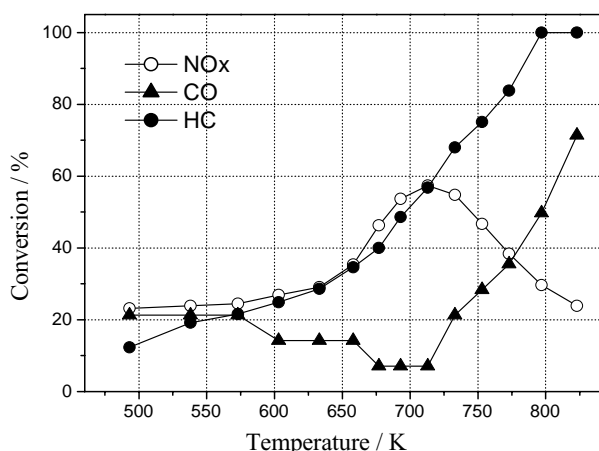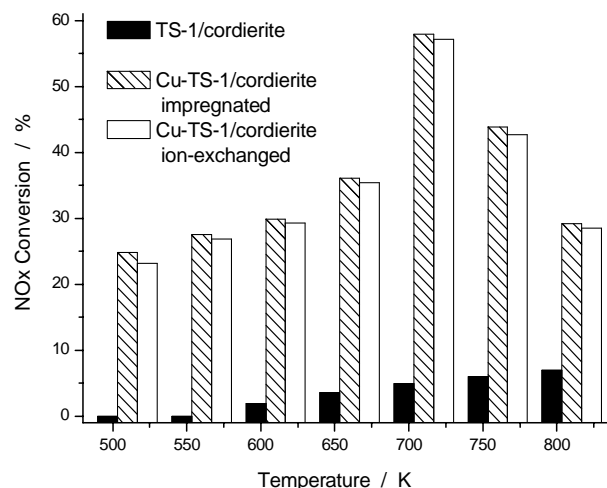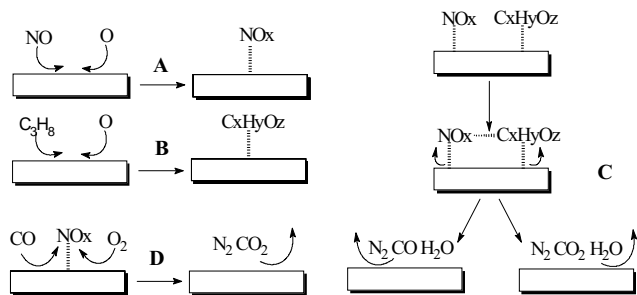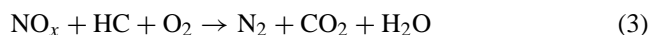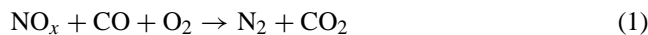

Fig. 6. Conversions of three main components in exhaust gas varied with temperature catalyzed by Cu–TS-1/cordierite. Working status of engine: A/F = 21; SV = 12,000 h^{-1}; exhaust before catalytic reaction: NO_x = 550 ppm, HC = 126 ppm, CO = 0.24%.

Fig. 8. Proposed processes for de-NO$_x$ reactions over Cu–TS-1/cordierite on real lean burn engine.

Fig. 9. Cu2p$_{3/2}$ transition for Cu–TS-1/cordierite catalysts before (on the right top) and after reaction (in the centre).

it. Cu–TS-1/cordierite with two different preparing methods had obvious different cooper loadings, but the activities of them were similar (Fig. 7). From above, we could say that the catalytic activity of Cu–TS-1/cordierite mainly came from the cooper in the duct of TS-1 zeolite.

According to our experiment results, a possible de-NO$_x$ process is sketched as following. In the excess of oxygen, strongly bound NO$_x$ species are easily formed on the surface activating sites as seen in Fig. 8A. Simultaneously, oxygenated hydrocarbons C$_x$H$_y$O$_z$ species are formed in the same way from hydrocarbons and oxygen in the gas phase (Fig. 8B). The NO$_x$ (ads) and C$_x$H$_y$O$_z$ (ads) are the two important reaction intermediates. Under co-action, NO$_x$ (ads) and C$_x$H$_y$O$_z$ (ads) react with each other to give out N$_2$, H$_2$O and carbon oxides (carbon monoxide at lower temperature and carbon dioxide at higher temperature) (Fig. 8D). In our reaction system, there is much carbon monoxide which can not adsorb on active sites as strong as C$_x$H$_y$O$_z$ and the carbon monoxide in non-adsorption gas phase can react with NO$_x$ (ads) in the presence of oxygen as seen in Fig. 8C. Besides the de-NO$_x$ reactions, there are two side reactions in our reaction system: oxidation of hydrocarbons and oxidation of carbon monoxide. All the main reactions in our reaction system are sketched as following (the stoichiometry of the reactions is hard to be given out accurately because of the complexity of hydrocarbons' components):

$$NO_x + CO + O_2 \rightarrow N_2 + CO_2 \tag{1}$$

$$NO_x + HC + O_2 \rightarrow N_2 + CO + H_2O \tag{2}$$

$$NO_x + HC + O_2 \rightarrow N_2 + CO_2 + H_2O \tag{3}$$

$$CO + O_2 \rightarrow CO_2 \tag{4}$$

$$HC + O_2 \rightarrow CO_2 + H_2O \tag{5}$$

At about 500 K, both reactions 1 and 2 proceeded. It is to say that hydrocarbons and CO acted as reductants for the reduction of NO$_x$ together and themselves were consumed. With the increase of the temperature, the reaction rates of reactions 1 and 2 both increased and the NO$_x$ conversion went up gradually. But, the reaction 1 went up more slowly than reaction 2 and the CO consumption was depressed because of the generation of CO in reaction 2. When the reaction temperature increased, reaction 2 began to be replaced
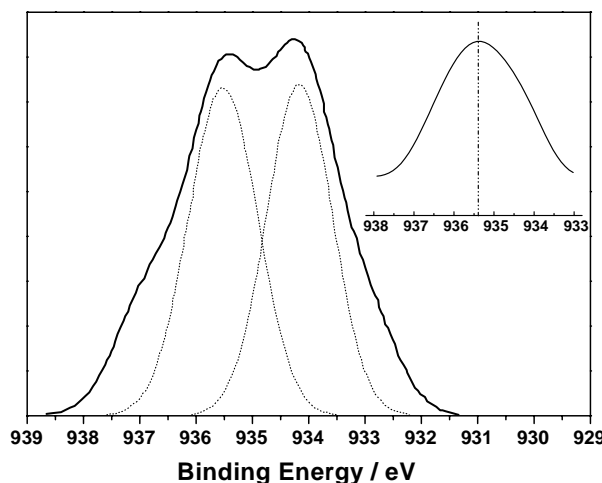
by reaction 3 gradually. Since there was no CO produced in reaction 3, the CO consumption started to be recovered. Our experiment was carried in the rich oxygen condition, so CO began to be oxidized by O$_2$, when the temperature exceeded 720 K. Reaction 4 started rapidly, resulting in a quickly decrease of CO. At the same time, hydrocarbons were also oxidized by O$_2$ (reaction 5) which resulted in a quickly decrease of hydrocarbons.

From the ion-exchange method of catalysts preparation, we suggest that the main active component cooper should exist in Cu(II) state before catalytic reaction and it had been proved easily by XPS. XPS spectra of sample before reaction shows a binding energy for Cu2p$_{3/2}$ of 935.4 eV assigned to intrazeolite Cu(II) species. The catalyst after reaction was analyzed by XPS immediately to inhibit further change at the surface and we found not only peak at 935.5 eV assigned to Cu(II) but also peak at 934.3 eV assigned to intrazeolite Cu(I) [14,15] (Fig. 9). It is deduced that some of intrazeolite Cu(II) was reduced to Cu(I) during the reactions by hydrocarbons adsorbed on copper species in the exhaust gas. However, because of the existence of oxygen, intrazeolite Cu(I) could be reoxidized to Cu(II) [16–18]. The conversion of Cu(II) to Cu(I) and Cu(I) to Cu(II) is shown below.

Cu(II) + Hydrocarbons → Cu(I)–C$_x$H$_y$

Cu(I)–C$_x$H$_y$ + Oxygen → Cu(II)–C$_x$H$_y$O$_z$ → Cu(II)
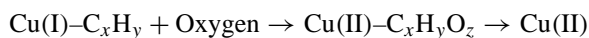
The above process circulated and at the same time, important reaction intermediate C$_x$H$_y$O$_z$ (ads) formated continuously, which reacted with NO$_x$ (ads) to give out N$_2$, H$_2$O and carbon oxides eventually.

Duration and anti-poison properties are important criteria to catalysts. The SCR de-NO$_x$ catalysts usually suffer from high deactivation in engine tests [19–21]. Therefore, we compared the max activities of Cu–TS-1/cordierite at 720 K prepared from ion-exchange and impregnation methods after a period of reaction under the same working conditions
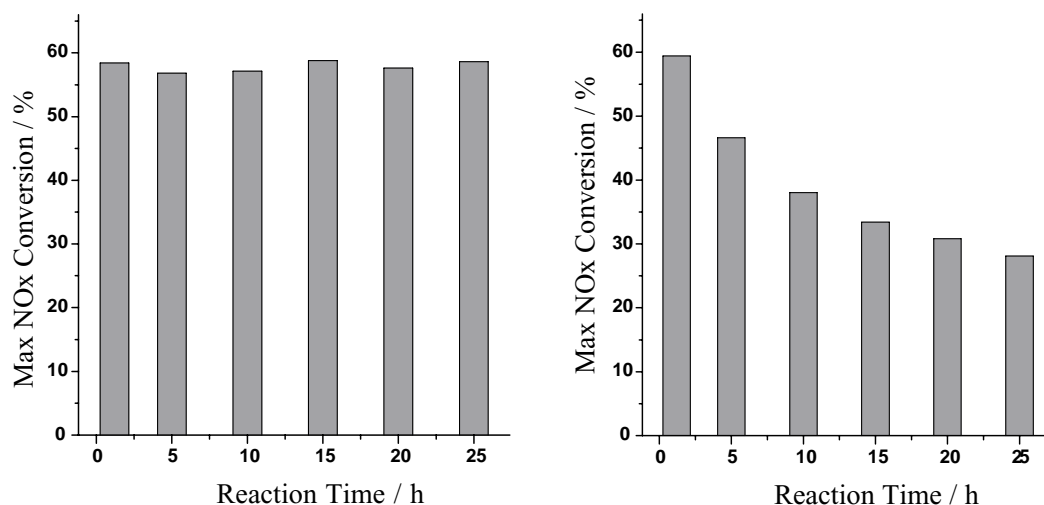
Fig. 10. Max NO_x conversion varied with reaction time catalyzed by different Cu–TS-1/cordierite: left: ion-exchanged; right: impregnated.
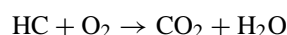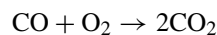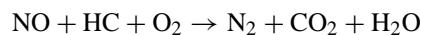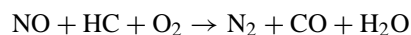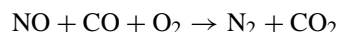
as primary experiments for the duration and anti-poison properties of the catalysts (working status of engine: A/F = 21; SV = 12,000 h^{-1}; Exhaust before catalytic reaction: NO_x = 540 ppm, HC = 120 ppm, CO = 0.20%). The results were shown in Fig. 10. From the left figure, we could see that max NO_x conversion did not change obviously. It was to say the ion-exchanged Cu–TS-1/cordierite had good duration and anti-poison properties. On the contrary, as shown in the right figure, the max activity of impregnated Cu–TS-1/cordierite decreased gradually. We thought sulfur deactivation in the presence of water vapor was the main reason of the decreased activity. The substance containing sulfur in the gasoline burned inside the engine and sulfur dioxide was exhausted. The exhausted sulfur dioxide was absorbed on the aggregated cooper on the surface of zeolite and then reacted with the cooper in the presence of water vapor and excessive O_2 to form $CuSO_4$ [22]. The formatted $CuSO_4$ covered the surface of catalysts and partly prevented the exhaust from meeting the cooper in the duct of zeolite, which was considered the main active components of the catalysts. Correspondingly, the activity of the catalyst decreased. As to cooper ion-exchanged TS-1/cordierite, because there was no aggregated cooper on the surface of catalyst, the sulfur dioxide absorbed on the surface of cooper which was in the duct of zeolite. The cooper is highly dispensed and the relative concentration of cooper was very low, so the adsorbed sulfur dioxide could not react with it and then disabsorb from the surface of cooper. Thus, the courses of absorb and disabsorb repeated and during the course, no active cooper was consumed. It was the reason why the cooper ion-exchanged TS-1/cordierite had good duration and anti-poison properties.

4. Conclusions

By in situ synthesis method, TS-1 zeolite crystallites grew on the cordierite substrate commendably and formed monolithic TS-1/cordierite, which had good thermal and hydrothermal stabilities.

Cu–TS-1/cordierite prepared with ion-exchange and impregnation methods from TS-1/cordierite were used in the purification of exhaust from lean burn engine. Main pollutants in the exhaust gas NO_x, hydrocarbons and CO can be treated at one time and good conversions were gained. Cooper ion-exchanged TS-1/cordierite had good duration and anti-poison properties while cooper impregnated TS-1/crodierite not. Cooper in the duct of TS-1 zeolite was the main active component of the catalyst and the existence of Cu(I) in the reaction was thought to be essential. Following main reactions during the treatment of exhaust from lean burn engine catalyzed by Cu–TS-1/cordierite were brought out:

$$NO + CO + O_2 \rightarrow N_2 + CO_2$$

$$NO + HC + O_2 \rightarrow N_2 + CO + H_2O$$

$$NO + HC + O_2 \rightarrow N_2 + CO_2 + H_2O$$

$$CO + O_2 \rightarrow 2CO_2$$

$$HC + O_2 \rightarrow CO_2 + H_2O$$

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