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Selective Catalytic Reduction of Nitrogen Oxides from Exhaust of Lean Burn Engine over In-Situ Synthesized Cu–ZSM-5/Cordierite

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ZSM-5 zeolite was in-situ synthesized successfully on the surface of honeycomb cordierite substrate, certified by XRD and SEM techniques. Good thermal and hydrothermal stability of ZSM-5/cordierite could be obtained because of the in-situ synthesis method. Copper ion-exchanged ZSM-5/cordierite was studied as catalyst for selective catalytic reduction of nitrogen oxides. For practical reasons, the catalytic testing experiments were preformed on a real lean burn engine. Unburned hydrocarbons and carbon monoxide in the exhaust were directly used as reductants for NO_x reduction. Cu–ZSM-5/cordierite exhibited high catalytic activity, and at 673 K the maximal NO_x conversion to N₂ could reach 50% at gas hourly space velocity (GHSV) of about 25 000 h⁻¹. Hydrocarbons and carbon monoxide in the exhaust could also be purified at the same time. As expected, Cu–ZSM-5/cordierite catalyst exhibited good duration and antipoison properties. When traces of lanthanum were introduced to Cu–ZSM-5/cordierite catalyst as a modifier, the activated temperature of the catalyst could be decreased and the temperature window with high NO_x conversions broadened. Cu–ZSM-5/cordierite and LaCu–ZSM-5/cordierite were thought as promising automobile exhaust catalysts under lean conditions. Copper is the main active component in the Cu–ZSM-5/cordierite catalyst and Cu(I), which was found in the catalyst during the proceeding of reaction by XPS, is thought to be essential. On the basis of this, deNO_x process over Cu–ZSM-5/cordierite is also discussed.

Introduction

The automobile exhaust contains various pollutants: nitrogen oxides, carbon monoxide, unburned hydrocarbons, and so on. One of the most urgent problems is the removal of nitrogen oxides, which greatly contribute to the formation of photochemical smog and acid rain (1). Under condition of stoichiometric combustion, TWC, which is the best and widely used means to treat the automobile exhaust, has proved to be efficient and reliable (2, 3). Current strategies

attempting to minimize fuel consumption and CO₂ emission prompt the use of lean burn engine. However, TWC suffers from severe loss of activity for NO_x reduction in the presence of excess oxygen, which is the prevalent condition for lean burn gasoline engines. Thus, selective catalytic reduction (SCR) of NO_x by hydrocarbons in the presence of oxygen becomes a potential method to remove NO_x from exhaust and receives much attention (4–9). A breakthrough of the SCR technology is hindered by the insufficient low activity, narrow temperature window, and insufficient durability of the catalysts (10). Moreover, for practical purpose, catalytic powders have to be fixed on the shaped substrate. Honeycomb cordierite (2MgO·2Al₂O₃·5SiO₂) is the substrate in common use and the usual coating techniques are dip-coating, slip-coating, and spin-coating (11). However, it is well-known that crystalline zeolite materials are difficult to washcoat and that excessive use of binders often influences the activity of the catalyst and even results in a “second pollution” because of its friability. To solve the problems, it has already been proposed to prepare the catalytic zeolites component from crystallites grown on substrate surfaces. The main advantage of in-situ synthesis is that the substrate is used as a base for nucleation and that under specific conditions a chemical bonding between crystals and substrate layer is formed and no binder or glue is needed (12). Thus, the preparation course is greatly simplified and under the condition of high space velocities, the loss of catalyst can be prevented effectively. In the previous work, TS-1 zeolite had been successfully in-situ synthesized on the cordierite substrate (13) and Cu-TS-1/cordierite had been used as automobile exhaust catalysts with good performance (14).

In this paper, we will describe in-situ synthesized monolithic catalysts, Cu–ZSM-5/cordierite and LaCu–ZSM-5/cordierite, which exhibit good deNO_x activity in treating the exhaust of real gasoline engine under lean conditions. Some factors that influence deNO_x activity of catalyst for engine test, as well as the deNO_x process, will be discussed.

Experimental Section

Preparation of Catalysts. *In-Situ Synthesis of ZSM-5/Cordierite.* Silica sol was used as silicon resource and aluminum sulfate as aluminum resource. No template was needed throughout the synthesis process. Silica sol, sodium hydroxide, aluminum sulfate, and water were mixed with this proportion: 1Al₂O₃:84SiO₂:10Na₂O:3500H₂O. After 2 hours' strenuous stirring, the gained transparent liquid and honeycomb cordierite cylinder (Φ24 × 50 mm, 60 cells cm⁻², 0.3-mm average wall thickness) were put into the high-pressure poly(tetrafluoroethylene) (PTFE) lined autoclave for static crystallization at 453 K (pressure: about 11 bar from water vapor) for 16 h together. Then, the samples were taken out, washed by distilled water, and dried at 373 K overnight.

Ion-Exchange. Cu–ZSM-5/cordierite and LaCu–ZSM-5/cordierite were prepared by solution ion-exchange method at room temperature and were stirred slowly. The detailed ion-exchange conditions are shown in Table 1.

The ion-exchanged catalysts were washed five times by ultrasonic generator, 10 min each time, to remove the metal ions appendiculating on the surface of catalysts.

Catalysts Characterization. The synthesized ZSM-5/cordierite and copper ion-exchanged ZSM-5/cordierite were incised into small thin pieces (8 mm × 8 mm) for catalysts characterization. The crystallinity of the synthesized ZSM-5/cordierite was given by XRD data collected with a Rigaku D/max2500 diffractometer, equipped with a graphite monochromator and using Cu Kα radiation.

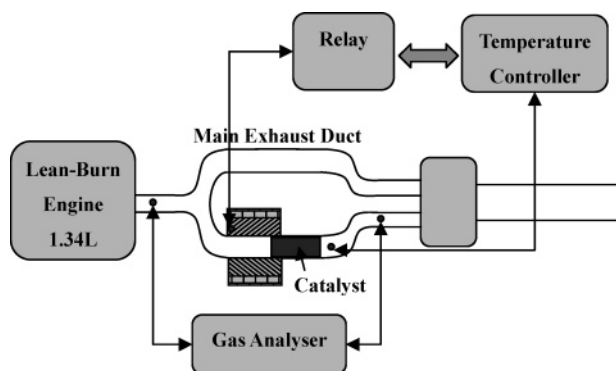
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TABLE 1. Preparation Process of Cu–ZSM-5/Cordierite and LaCu–ZSM-5/Cordierite

precursor	ion resources	pH	time	products
ZSM-5/cordierite	0.05 M Cu(AC) ₂	5.5~6	20 h × 4	Cu–ZSM-5/cordierite
ZSM-5/cordierite	0.05 M La(NO ₃) ₃	6~6.5	15 h × 4	La–ZSM-5/cordierite
LaZSM-5/cordierite	0.05 M Cu(AC) ₂	5.5~6	15 h × 4	LaCu–ZSM-5/cordierite


FIGURE 1. Equipment for catalytic testing experiments on real lean burn engine. Working status of the engine: load = 21 Nm; rotate speed = 1800 r/min.

SEM from a HITACHI X-650 scanning electron microscope detected the surface feature and degree of accumulated homogeneity. Surface areas and pore diameters were determined by nitrogen adsorption on the ASAP 2010M facility (Micromeritics).

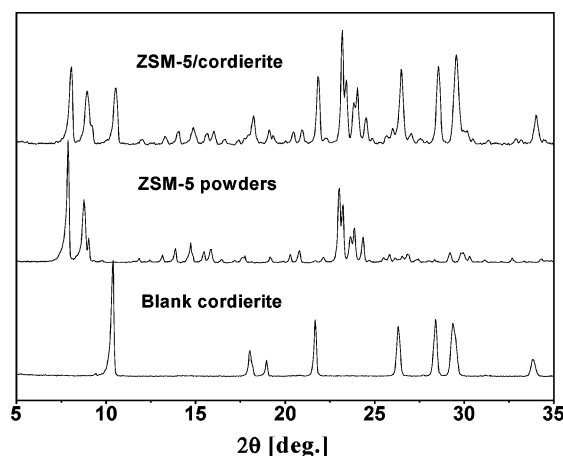
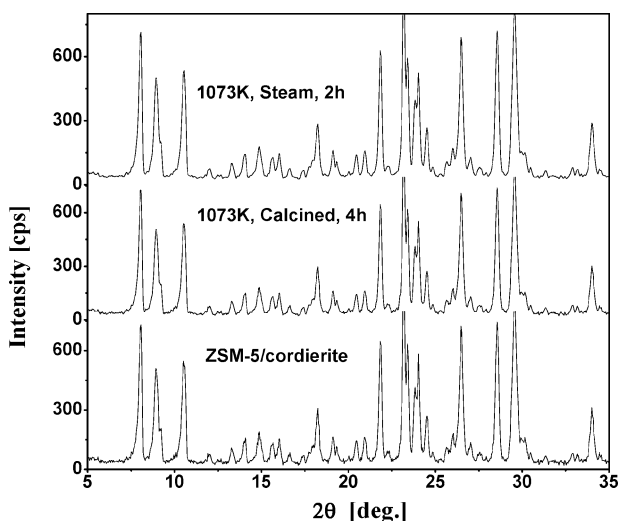
The concentration of copper and lanthanum in the synthesized catalysts was mensurated by ICP (IRIS Advantage, TJA solution). Chemical valence states of copper in the catalysts before and in reaction were measured by XPS with a PHI-5300 instrument with Mg K α X-ray excitation source. Accurate ± 0.1 eV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

Catalytic Testing. The catalytic assessment experiment was carried through on a four-valve S. I. engine. The controllable quasi-homogeneous mixture inside the cylinder made by the controllable injection on this engine realized the fast quasi-homogeneous mixture combustion. The air fuel ratio (A/F) was controlled between 18 and 21. The catalyst was fixed inside the vent-pipe of the engine, heated by an electrical heater. The temperature was measured by NiCr–NiAl thermojunction and controlled by relay and temperature controller. The products after catalytic reaction were online analyzed by a five-component exhaust analyzer (MW56-AVL DIGAS 4000 LIGHT). The deNO_x activity of the catalyst is expressed as the conversion of NO_x to N₂. The catalytic testing equipment is shown in Figure 1.

Results and Discussion

Characterization of Catalysts. The XRD method allows an easy and straightforward judgment about the crystallinity and structure of the zeolite. Both zeolites and cordierite substrate have their own typical diffraction pattern. From the comparison of in-situ synthesized ZSM-5/cordierite, ZSM-5 powder, and blank cordierite samples shown in Figure 2, we can see typical peaks at 7.88, 8.76, 23.04, 23.88, and 24.36° ($d = 10.98, 9.86, 3.83, 3.70$, and 3.63\AA) in XRD pattern of ZSM-5/cordierite corresponding to the characteristic MFI structure peaks of ZSM-5 zeolite. From the XRD results, it is deduced that zeolite crystallites with MFI structure have grown on the cordierite substrate.

In the real mobile exhaust environment, which contains about 10% water vapor, the catalysts have to endure the


FIGURE 2. XRD patterns of blank cordierite, ZSM-5 powder, and ZSM-5/cordierite.

FIGURE 3. XRD patterns of ZSM-5/cordierite after thermal and hydrothermal treatment.

temperature from the ambient to above 1000 K. Therefore, their thermal stability and hydrothermal stability are very important. The ZSM-5/cordierites before and after high-temperature calcination and high-temperature steam treatment at 1073 K under atmosphere pressure were characterized by XRD and the results are shown in Figure 3. No obvious change in crystallinity can be observed on ZSM-5/cordierite after treatment, indicating the good thermal and hydrothermal stability of in-situ synthesized ZSM-5/cordierite, compared to ZSM-5 powder, which undergoes about 10% decrease of crystallinity at the same treatment. Under our synthesis conditions, some aluminum atoms of the cordierite become the base for zeolite nucleation and may go into the framework of the zeolites. Strong interactions exist not only between the aluminum atoms and the zeolite but also between the aluminum atoms and the cordierite substrate. The aluminum atoms are then greatly stabilized. Thus, the dealumination process can be suppressed and the

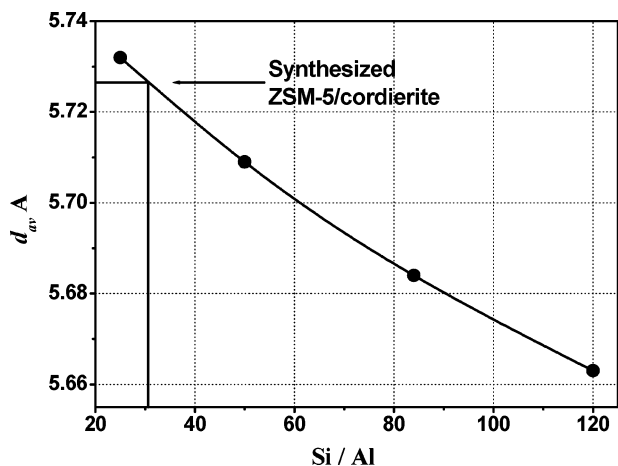


FIGURE 4. Relation between average lattice plane distance and the Si/Al ratio of ZSM-5.

good thermal and hydrothermal stability of the ZSM-5/cordierite can be obtained, which is essential for the engine test.

There are considerable quantities of silicon and aluminum in the components of cordierite substrate that can leach to the synthesis system, so the Si/Al ratio of synthesized ZSM-5 zeolite differs greatly with the Si/Al ratio in material mixture. Figure 4 reports the relation between Si/Al ratio and average lattice plane distance d_{av} employed to determine the Si/Al ratio. From its d_{av} (5.726 Å), the calibration curve yields a Si/Al ratio of 31, lower than that in material mixture.

The surface of blank cordierite and the surface of ZSM-5/cordierite can be compared in the SEM images. From the comparison of the two images in Figure 5, we can see sandwich ZSM-5 zeolite crystals of about 5 μm grown on the irregular surface of cordierite compactly and homogeneously. Figure 6 displays the SEM photo of the cross section of ZSM-5/cordierite. In the photo, we can clearly see a layer about 100- μm homogeneous ZSM-5 crystalloid growing on the wall of zeolite substrate. The zeolite and the substrate phases couple tightly and become a whole. In fact, ZSM-5 zeolite grew not only on the surface of cordierite substrate but also inside the irregular macroporous. After in-situ synthesis, the BET surface area of ZSM-5/cordierite can reach $110 \text{ m}^2\text{g}^{-1}$ with ZSM-5 loading about 10% (wt %). The increase of the BET surface areas is thought to be essential to the catalytic reaction. Moreover, good accessibility, which is a

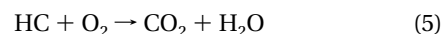
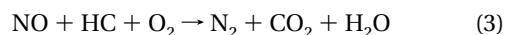
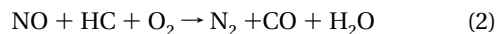
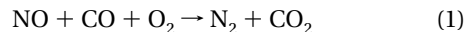
very important factor of catalysts in gas-phase reactions, can also be obtained using in-situ synthesis method (15).

Copper loading to the whole catalyst weight is 0.53% in Cu-ZSM-5/cordierite and 0.39% in LaCu-ZSM-5/cordierite. Lanthanum loading to the whole catalyst weight in LaCu-ZSM-5/cordierite is 0.16%. All these data are determined by ICP.

Catalytic Results. In the research of Cu-ZSM-5 catalysts, single reductant, 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.

Figure 7 displays the status of the lean burn engine exhaust treated by in-situ synthesized Cu-ZSM-5/cordierite. Cu-ZSM-5/cordierite was activated at the temperature around 580 K when NO_x conversion was 25%. At 680 K, deNO_x activity of the catalyst reached its maximal value and the maximal NO_x conversion was about 50%. Afterward, the activity of the catalyst began to decrease. With the increasing temperature, conversion of hydrocarbons increased gradually and hydrocarbons could be purified completely at 823 K. At 400 K, CO conversion was 10%, and the conversion decreased and kept at a very low level with increasing temperature till 650 K, when it started to increase rapidly.

Main reactions in SCR system on real engine are sketched as follows. (The stoichiometry of the reactions is hard to give out accurately because of the complexity of hydrocarbons.)



At 400 K, a comparatively low temperature, both reaction 1 and reaction 2 proceeded, that was to say, hydrocarbons and CO acted as reductants for reduction of NO together. With the increase of the temperature, reaction rates of

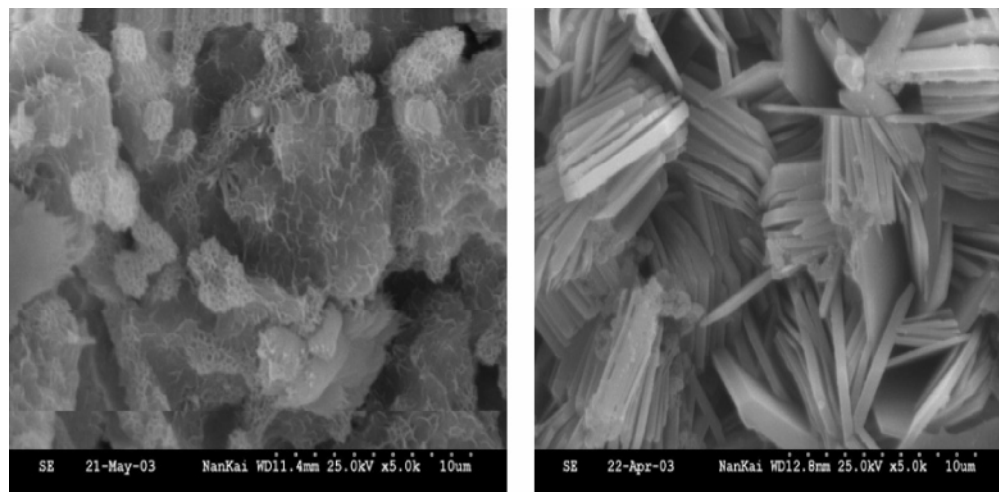


FIGURE 5. SEM images of surface of blank cordierite (left) and ZSM-5/cordierite (right).

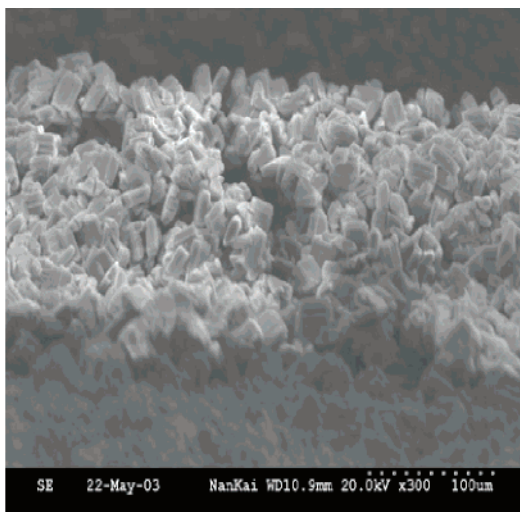
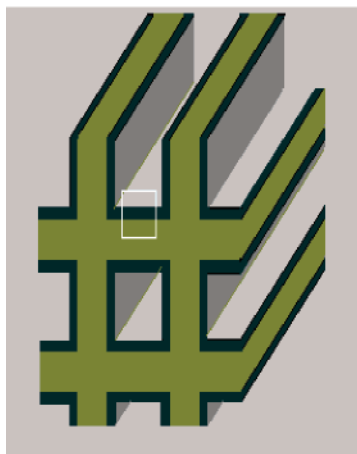


FIGURE 6. SEM image of the cross section of ZSM-5/cordierite.

TABLE 2. Main Composition of Exhaust Gas

components	concentration [vol %]
N ₂	71.0
CO ₂	12.0
H ₂ O	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

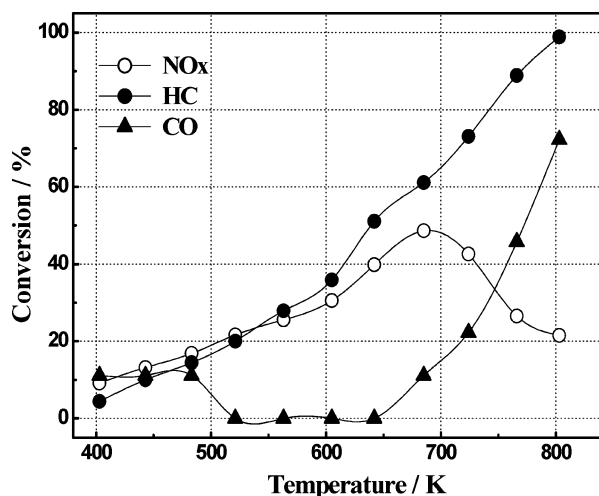


FIGURE 7. Conversions of three main components in exhaust gas vs reaction temperature catalyzed by Cu-ZSM-5/cordierite. Working status of engine: A/F = 21; GHSV = 25 000 h⁻¹; exhaust before catalytic reaction: NO_x = 550 ppm, HC = 134 ppm, CO = 0.11%

reaction 1 and reaction 2 both increased. However, 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 temperature reached around 650 K, reaction 2 began to be replaced by reaction 3. Because there was no CO produced in reaction 3, the CO consumption started to recover. When the temperature further increased, hydrocarbons and CO began to be oxidized by the oxygen in the reaction system. Reactions 4 and 5 proceeded and competed with reactions 1 and 3, resulting in the decrease of NO_x conversion since 680 K.

In our experiments, hydrocarbons and carbon monoxide in the exhaust acted as the reductants directly for NO_x

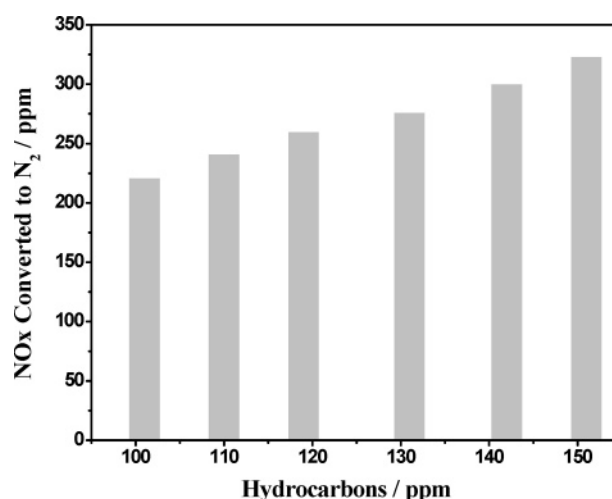


FIGURE 8. Influence of hydrocarbons concentration on the maximal value of NO_x converted to N₂. GHSV = 25 000 h⁻¹; NO_x = 500 ppm (±10 ppm).

reduction and it was believed that hydrocarbons played the leading role to reduce NO_x. We studied the influence of hydrocarbon concentration on the maximal value of converted NO_x catalyzed by the same Cu-ZSM-5/cordierite in Figure 8. The GHSV was fixed at 25 000 h⁻¹. NO_x concentration was controlled at about 500 ppm (±10 ppm) and different amounts of hydrocarbons (100–150 ppm) were gained by the control of burning inside the lean burn engine. From the results, we can see clearly that maximal value of converted NO_x increased with the increase of hydrocarbon concentration. This can be easily explained from the view of reaction balance. In a certain period of time, more hydrocarbons provided more chances to react with NO_x giving out N₂, H₂O, and carbon oxides.

Space velocity is an important factor that influences NO_x conversion. In our experiments, GHSV is adopted and the GHSV is concerned with Cu-ZSM-5/cordierite monolith (GHSV = volume flux of exhaust gas per hour/volume of monolithic catalyst). Noted that Cu-ZSM-5/cordierite contained about 90% (wt %) cordierite substrate, the GHSV concerned with pure Cu-ZSM-5 catalytic powders would be about 10 times higher. Figure 9 shows the effect of space velocity on NO_x conversion over Cu-ZSM-5/cordierite. The different space velocities were obtained by changing the volume of catalyst. It was obvious that space velocity had

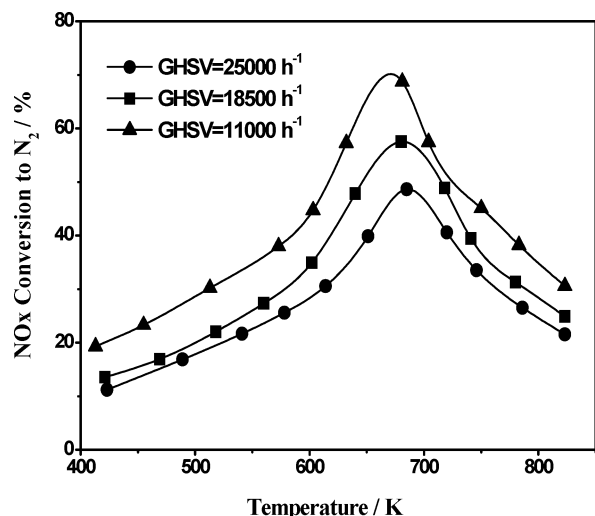


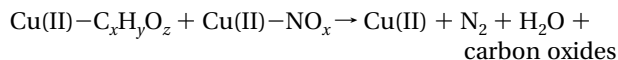
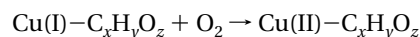
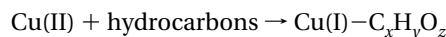
FIGURE 9. NO_x conversions vs reaction temperature over Cu–ZSM-5/cordierite under different space velocities. Working status of engine: A/F = 21; exhaust before catalytic reaction: NO_x = 520 ppm, HC = 121 ppm, CO = 0.14%.

great effect on NO_x conversion over all the temperature ranges studied and the NO_x conversion decreased with the increasing space velocity. For example, the maximal NO_x conversion could reach 70% at the GHSV of about 11 000 h⁻¹ under the common working conditions of the lean burn engine. This means that purification of main pollutants in exhaust like NO_x, hydrocarbons, and carbon monoxide is achieved to an appreciable extent under these “road” conditions. Cu–ZSM-5/cordierite is a promising SCR catalyst for practical treatment of lean burn exhaust.

According to our experimental results, a supposed deNO_x process is sketched as follows. In the excess of oxygen, strongly bound NO_x species are easily formed on the surface-activating sites. Simultaneously, oxygenated hydrocarbons C_xH_yO_z species are formed in the same way from hydrocarbons and oxygen in the gas phase (Figure 10 left). The NO_x (ads) and C_xH_yO_z (ads) are the two important reaction intermediates. Under coaction, NO_x (ads) and C_xH_yO_z (ads) react with each other to give out N₂, H₂O, and carbon oxides (carbon monoxide at lower temperature and carbon dioxide at higher temperature) (Figure 10 right). In our reaction system, there is much carbon monoxide which cannot adsorb on active sites as strong as C_xH_yO_z and the carbon monoxide in nonadsorption gas phase can react with NO_x (ads) in the presence of oxygen.

From the method of catalysts preparation, we suggest that the copper should exist in Cu(II) state, and it has been proved easily in Figure 11. XPS spectra of sample before reaction shows a binding energy for Cu2p_{3/2} of 935.4 eV assigned to intrazeolitic Cu(II) species (16, 17). The catalyst

after reaction was analyzed by XPS immediately to inhibit further change at the surface, and we found not only a peak at 935.4 eV assigned to Cu (II) but also a peak at 934.3 eV assigned to intrazeolitic Cu(I) (17). It is deduced that some of the intrazeolitic Cu(II) was reduced to Cu(I) during the reaction by hydrocarbons (or carbon monoxide) in the exhaust gas. However, because of the existence of oxygen, intrazeolitic Cu(I) could be reoxidized to Cu(II) (18, 19). Then, there is a balance of Cu(II) and Cu(I) in the catalyst Cu–ZSM-5/cordierite. The interconversion of Cu(II) to Cu(I) and Cu(I) to Cu(II) is described below.



The above process circulated and at the same time, important reaction intermediate C_xH_yO_z (ads) formatted continuously, which reacted with NO_x (ads) to give out N₂, H₂O, and carbon oxides eventually.

Duration and antipoison properties are important criteria to catalysts. The Cu–ZSM-5 catalyst usually suffers from high deactivation in engine tests (20–22). Therefore, we compared the curves of NO_x conversion changing with temperatures after the reaction of 5, 10, 15, and 20 h at about 773 K under the same working conditions in Figure 11. The four curves (a–d) were quite similar. The NO_x conversion and the temperature at which maximal NO_x conversion was reached did not change obviously. Compared with Cu–ZSM-5, the in-situ synthesized Cu–ZSM-5/cordierite has good duration and antipoison capabilities. The differences between Cu–ZSM-5/cordierite and Cu–ZSM-5 catalysts may come from the substrate and the in-situ synthesizing method. Though in-situ synthesis, ZSM-5 zeolites interconnected with cordierite substrate or with each other regularly. Thus, when copper was introduced to the exchange sites of zeolite by solution ion-exchange method or inside zeolite pore after calcination, sintering might be prevented effectively and high dispersion could be obtained. XRD patterns of Cu–ZSM-5/cordierite after reaction did not exhibit peaks at 2.52 and 2.32 Å, typical of CuO crystallites (23, 24), clearly indicating a good dispersion of the active phase.

In the practical application, the exhaust temperature of the lean burn engine changes greatly, between 573 and 673 K most of the time. There is a great gap between catalyst activity and operating temperature window in which high NO_x conversion is located. To solve the problem, rare-earth-metal lanthanum was added in the Cu–ZSM-5/cordierite by ion-exchange method. Figure 13 displays the status of the lean burn engine exhaust treated by LaCu–ZSM-5/cordierite and Cu–ZSM-5/cordierite.

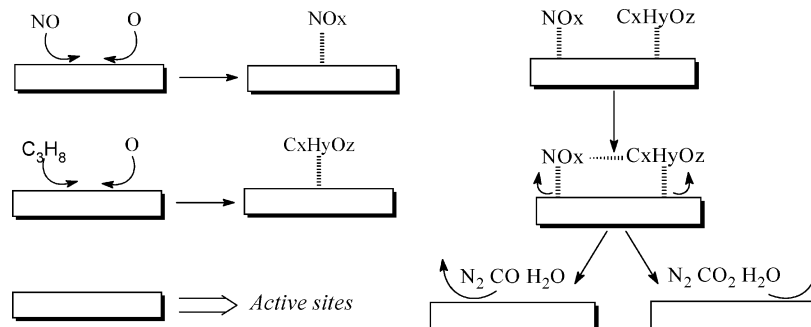


FIGURE 10. Proposed deNO_x mechanisms over Cu–ZSM-5/cordierite on real lean burn engine test.

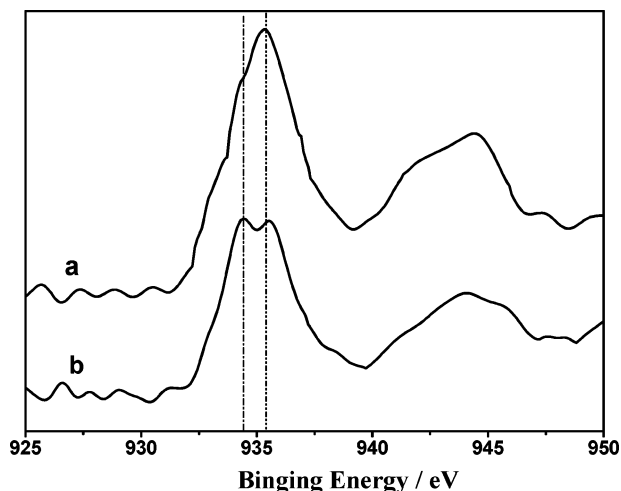


FIGURE 11. Cu2p_{3/2} transition for Cu-ZSM-5/cordierite catalysts before (a) and after reaction (b).

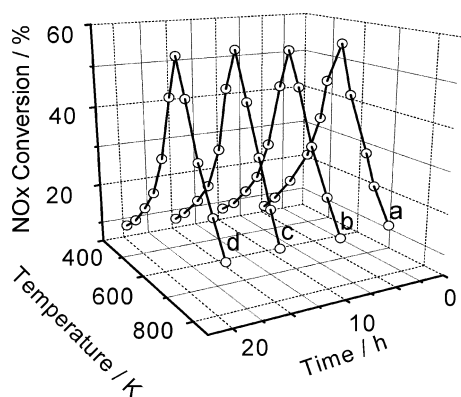


FIGURE 12. NO_x conversion vs reaction temperature over Cu-ZSM-5/cordierite after 5 h reaction (a), after 10 h reaction (b), after 15 h reaction (c), and catalyst after 20 h (d).

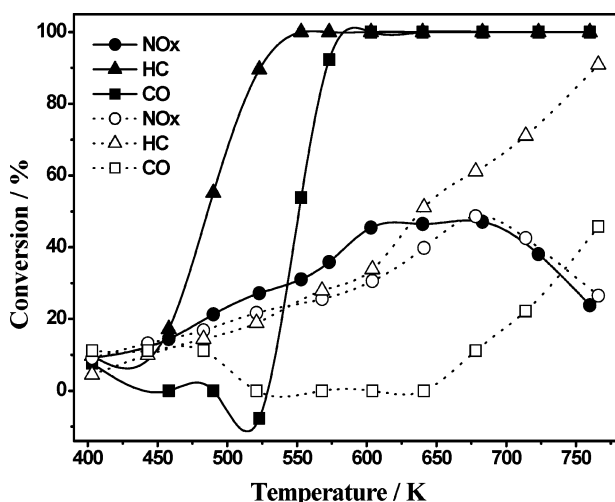


FIGURE 13. Conversions of three main components in exhaust gas vs reaction temperature catalyzed by Cu-ZSM-5/cordierite (solid lines) and LaCu-ZSM-5/cordierite (dash lines). Exhaust before catalytic reaction: NO_x = 506 ppm, HC = 114 ppm, CO = 0.13%; working status of engine: A/F = 21, GHSV = 25 000 h⁻¹.

From Figure 13, we could see that catalyst LaCu-ZSM-5/cordierite was activated at the temperature of about 525 K, 75 K lower than the activated temperature of Cu-ZSM-5/cordierite. At 605 K, catalyst activity reached its

maximal value and NO_x conversion reached 46.5%. NO_x conversion kept at about 46% from 605 to 680 K and then began to decrease. The temperature window with high NO_x conversion is close to the temperature of the exhaust from lean burn engine. Besides this, CO and hydrocarbons can be entirely converted to CO₂ and H₂O from the temperature of about 590 K. LaCu-ZSM-5/cordierite is considered to be more suitable to treat the exhaust from lean burn engine.

Lanthanum is known for its oxygen storage capacity. With modifier lanthanum, reaction of CO oxidation and hydrocarbon oxidation may be accelerated. At the same time, the undesired combustion of hydrocarbons can be suppressed (25). Thus, higher conversions of NO_x, CO, and hydrocarbons could be obtained over LaCu-ZSM-5/cordierite at low temperatures as described above. Also, modifier lanthanum may also inhibit the sintering of catalyst to a large extent (26). Further research on the effect of modifier lanthanum is being done.

By in-situ synthesis, ZSM-5 zeolite crystallites grew on the cordierite substrate commendably to form monolithic ZSM-5/cordierite, which had good thermal and hydrothermal stabilities. Copper ion-exchanged ZSM-5/cordierite was 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 high conversions were gained. Meanwhile, the catalysts showed good duration and anti-poison properties. In the reactions, existence of Cu(I), which was thought to be essential for the deNO_x process, was found in Cu-ZSM-5/cordierite catalyst by XPS. Addition of lanthanum as a modifier decreased the activated temperature of Cu-ZSM-5/cordierite and broadened the temperature window of high NO_x conversion successfully. LaCu-ZSM-5/cordierite was considered as a promising automobile exhaust catalyst in lean conditions.

Acknowledgments

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