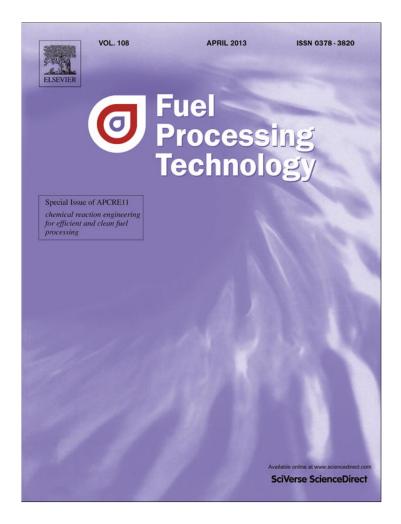
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Combination catalyst for the purification of automobile exhaust from lean-burn engine

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ABSTRACT

LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite were prepared and studied as possible catalysts for the selective reduction of nitrogen oxides in excess oxygen. LaCu-ZSM-5/cordierite exhibited good activity in C_3H_6 -SCR reaction and a maximal nitrogen oxide conversion of ca. 80% could be obtained at 623 K under reaction conditions employed. The existence of carbon monoxide in the reaction system showed positive effects on C_3H_6 -SCR over LaCu-ZSM-5/cordierite. Ir/ZSM-5/cordierite exhibited good activity in CO-SCR reaction and a maximal NO_x conversion of ca. 55% could be obtained at 523 K. The existence of C_3H_6 showed negative effects on CO-SCR over Ir/ZSM-5/cordierite at relatively low temperatures. Based on the catalytic results, combination catalyst LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite were developed for the reduction of nitrogen oxides from real lean-burn automobile exhaust by utilizing hydrocarbons and carbon monoxide as reducing agents. With contributions from both C_3H_6 -SCR and CO-SCR, the major pollutants in lean-burn automobile exhaust, e.g. nitrogen oxides, unburned hydrocarbons and carbon monoxide, could be purified simultaneously.

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1. Introduction

The gasoline engines for automobiles are typical internal combustion engines and various pollutants, e.g. nitrogen oxides, carbon monoxide and unburned hydrocarbons, are formed during the fuel combustion process. These pollutants can do great damage to the environment and should be purified before they are emitted to the atmosphere. One of the most difficult tasks is the removal of nitrogen oxides, which greatly contribute to the formation of photochemical smog and acid rain [1]. Three-way catalysts can effectively reduce nitrogen oxides to nitrogen under the condition of stoichiometric combustion and are therefore widely used in the purification of automobile exhaust [2]. However, current strategies attempting to minimize fuel consumption and carbon dioxide emission prompt the use of lean-burn engines instead of conventional gasoline engines. Three-way catalysts suffer from severe loss in activity for nitrogen oxide reduction in excess oxygen, which is the prevalent condition for lean-burn gasoline engines. Therefore, new techniques for nitrogen oxide removal in excess oxygen are highly desired.

Selective catalytic reduction (SCR) of nitrogen oxides is a potential approach for nitrogen oxide removal under lean-burn conditions. For practical purposes, it has been proposed to utilize reducing agents

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present in exhaust, i.e. unburned hydrocarbons and/or carbon monoxide, for nitrogen oxide reduction. Selective catalytic reduction of nitrogen oxides by hydrocarbons in excess oxygen (HC-SCR) has been extensively studied over various catalysts. Copper modified zeolites, e.g. Cu-ZSM-5, exhibit quite high deNOx activities in HC-SCR reaction and are probably the most promising catalysts for future application [3-9]. However, the temperature window of Cu-ZSM-5 with high deNOx activity in engine test is rather narrow. The introduction of La to Cu-ZSM-5 can effectively broaden the temperature window without any loss in deNOx activity [10]. Carbon monoxide is a very efficient reducing agent for nitrogen oxide reduction, however, the reaction between nitrogen oxides and carbon monoxide over most catalysts is strongly inhibited by the presence of excess oxygen. Exceptionally, iridiumbased catalysts have been reported to be active for the selective catalytic reduction of nitrogen oxides by carbon monoxide in excess oxygen (CO-SCR) and therefore receive great attention [11–15]. Despite an immense amount of research, the SCR technology suffers from insufficient efficiency for nitrogen oxide reduction and now is still some distance away from application. To improve SCR efficiency, a simple but very feasible means is utilizing both unburned hydrocarbons and carbon monoxide for nitrogen oxide reduction.

In the present work, LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite combination catalyst are developed for the purification of exhaust from real lean-burn engine. The carbon monoxide and unburned hydrocarbons available in the exhaust are effectively utilized as reducing agents for nitrogen oxides, and therefore, high purification efficiencies for

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| Table 1 |
|---|
| Preparation processes and physical-chemical properties of monolithic catalysts. |

| Sample | Precursor | Preparation method | Metal loading ^a | Surface area |
|---------------------------|-------------------------|-----------------------|-------------------------------|----------------------|
| Cu-ZSM-5/ cordierite | ZSM-5/ cordierite | lon-exchange | Cu 0.8% | 55 m ² /g |
| LaCu-ZSM-5/ cordierite | Cu-ZSM-5/ cordierite | lon-exchange | Cu 0.8% La 0.3% | 52 m ² /g |
| Ir/ZSM-5/ cordierite | ZSM-5/ cordierite | Impregnation | Ir 0.2% | 58 m ² /g |

^a Determined by ICP.

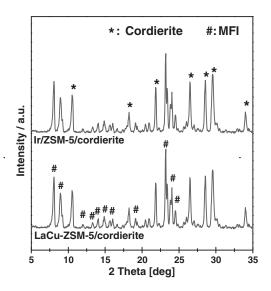


Fig. 1. XRD patterns of LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite.

nitrogen oxides, carbon monoxide and unburned hydrocarbons are obtained simultaneously.

2. Experimental

2.1. Catalyst preparation

ZSM-5/cordierite was prepared by in situ hydrothermal method, as described in our previous work [16]. In a typical process, silica sol, sodium hydroxide, aluminum sulfate, and water were mixed with the

molar ratio of 1 Al_2O_3 : 84 SiO₂: 10 Na_2O : 3500 H_2O . After 2 h of vigorous stirring, the gained colorless clear liquid and cordierite (Corning Incorporated, 60 cells/cm², 0.3 mm average wall thickness) were put into an autoclave together for static crystallization at 453 K for 12 h. The obtained ZSM-5/cordierite was taken out, washed by deionized water, and exchanged to NH_4 -ZSM-5/cordierite with 0.1 M NH_4NO_3 aqueous solution.

LaCu-ZSM-5/cordierite was prepared from NH₄-ZSM-5/cordierite through the solution ion exchange method and Ir/ZSM-5/cordierite was prepared by wet impregnation by using H_2IrCl_6 as precursor. The detailed conditions and the resulting metal loadings are summarized in Table 1. The final samples were thoroughly washed with deionized water and then calcined in the air at 773 K for 6 h.

2.2. Catalyst characterization

Powder X-ray diffraction (XRD) patterns of samples were measured on a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using Cu K α radiation (λ = 0.15418 nm). The monoliths were milled into powders before XRD analysis.

The loading of active metal components in the samples was measured by ICP (IRIS Advantage, TJA solution). Prior to surface area analysis, the monoliths were milled into powders and dissolved in the mixture of $HF-HCI-HNO_3$ solution.

The surface areas and pore diameters were determined by low temperature nitrogen adsorption–desorption on Micromeritics ASAP 2010 M facility. Prior to surface area analysis, the monoliths were milled into small pieces and outgassed at 573 K for 12 h.

2.3. Catalytic test

The selective catalytic reduction of NO at atmospheric pressure was carried out in a fixed-bed flow microreactor. The typical reactant gas composition was NO (500 ppm), C_3H_6 (0–500 ppm), CO (0–1000 ppm), O_2 (5%), H_2O (2%) and the balance He. The total flow of the inlet gas was set at 250 mL/min. A catalyst sample weight of 1 g was employed, corresponding to the gas hourly space velocity (GHSV) of 15,000/h. Prior to catalytic testing, the samples were calcined in 5%O₂/He (250 mL/min) at 773 K for 1 h. The products were analyzed on-line using a gas chromatograph (Agilent 6820) equipped with a TCD detector. A molecular sieve 5A column served for separation of N₂, O₂, and CO, and a Porapak Q column for separation of CO₂, C₃H₆, N₂O, NO, and H₂O. The NO and NO₂ in the products were also analyzed by a chemiluminescence NO_x analyzer (Ecotech EC 9841).

The catalytic test was also carried out on a 4-valve spark ignited gasoline engine. The fast quasi-homogeneous mixture lean combustion

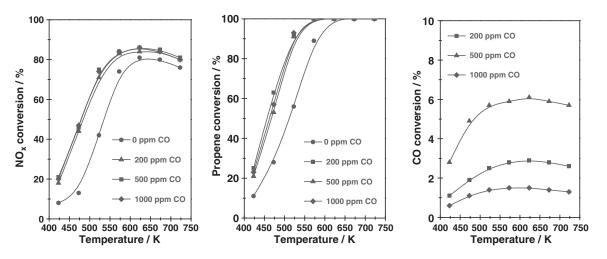


Fig. 2. Effects of CO on C₃H₆-SCR over LaCu-ZSM-5/cordierite. Reaction conditions: 500 ppm NO, 500 ppm C₃H₆, 0–1000 ppm CO, 2% H₂O, 5% O₂, He balance, GHSV = 15,000/h.

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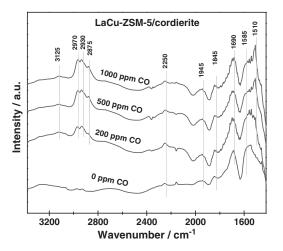


Fig. 3. In situ FTIR spectra of adsorbed species formed on LaCu-ZSM-5/cordierite at 523 K. Reaction conditions: 500 ppm NO, 500 ppm C_3H_6 , 0–1000 ppm CO, 2% H₂O, 5% O₂, He balance, GHSV = 15,000/h.

inside the cylinder was realized by controllable injection. The catalyst monolith of 200 g was fixed inside the vent pipe of the engine, corresponding to a GHSV of 15,000/h. The products before and after catalytic reaction were analyzed on-line by an exhaust analyzer (MW56-AVL DIGAS 4000 LIGHT). The scheme for real engine test can be found elsewhere [10].

2.4. In situ FTIR study

In situ FTIR spectra were recorded on a Bruker Tensor 27 spectrometer, equipped with a liquid N_2 cooled high sensitivity MCT detector. The samples for this study (100 mg) were finely ground and placed in the in situ chamber (Harrick). Prior to each experiment, the samples were heated in 5%O₂/He at 773 K for 1 h, and then cooled to the desired temperature for taking a reference spectrum. The gas mixtures were then fed to the in situ chamber and the spectra were recorded with a resolution of 4 cm⁻¹ and with an accumulation of 128 scans.

3. Results and discussion

3.1. Characterization results

The preparation process and physical-chemical properties of monolithic catalysts are summarized in Table 1. The surface area of

cordierite substrate is less than 1 m²/g, while high surface areas of more than 50 m²/g can be obtained in as-prepared monolithic catalysts.

The XRD patterns of LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite catalysts employed in this study are shown in Fig. 1. Diffraction peaks corresponding to the characteristic MFI structure of zeolites coating $(2\theta = 7.9, 8.8, 11.9, 13.9, 14.9, 23.0, 23.9, and 24.4^{\circ}, marked with #)$ and diffraction peaks corresponding to the structure of ceramic substrate $(2\theta = 10.4, 18.0, 21.6, 26.4, 28.4, 29.4 and 33.9^{\circ}, marked with *)$ can be observed, indicating the formation of ZSM-5/cordierite composite in samples. Besides, no obvious diffraction peaks corresponding to metal modifier are observed, probably due to low loading and high dispersion of metal modifier.

3.2. Effects of CO on C₃H₆-SCR over LaCu-ZSM-5/cordierite

The effects of CO on C₃H₆-SCR over LaCu-ZSM-5/cordierite are shown in Fig. 2. The only product from nitrogen oxide reduction is N₂, and the formation of N₂O is not detected during the whole process. Without carbon monoxide in the reaction system, LaCu-ZSM-5/ cordierite exhibits good deNOx performances in C₃H₆-SCR and the maximal nitrogen oxide conversion of ca. 80%, with C₃H₆ conversion of 100%, can be achieved at 623 K under reaction conditions employed. The introduction of 200 ppm carbon monoxide to the reaction system distinctly improves the deNO_x performance of LaCu-ZSM-5/cordierite and the maximal nitrogen oxide conversion increases from ca. 80% to ca. 85% at 623 K. The promotion effect of carbon monoxide is more pronounced at lower reaction temperatures. Typically, the nitrogen oxides conversion increases from ca. 40% to ca. 70% at 523 K. Meanwhile, the C_3H_6 conversion is also promoted by the existence of carbon monoxide in the reaction system. Surprisingly, the promotion effect of carbon monoxide is not dependent on carbon monoxide concentration, and nitrogen oxide conversion almost keeps unchanged with increasing carbon monoxide concentration from 200 to 1000 ppm. The very low carbon monoxide conversion indicates that the main function of carbon monoxide is promoting C₃H₆-SCR over LaCu-ZSM-5/cordierite instead of reducing nitrogen oxides.

To achieve a better understanding of the promotion effect of carbon monoxide on C_3H_6 -SCR over LaCu-ZSM-5/cordierite, the adsorbed species formed under reaction conditions are investigated by in situ FTIR spectra, as shown in Fig. 3. Without carbon monoxide in the reaction system, a series of bands at 2250, 1945, 1845, 1690 and 1585 cm⁻¹ are observed under C_3H_6 -SCR reaction condition at 523 K. The band at 1585 cm⁻¹ is assigned to chelating bidentate nitrates [17,18] and the band at 1690 cm⁻¹ is assigned to bridged carbonates [19]. The band at 2250 cm⁻¹ is assigned to isocyanate, probably bound to Al cation sites [20]. The bands at 1845 and 1945 cm⁻¹ are assigned to

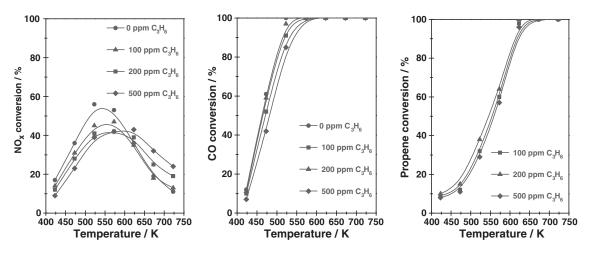


Fig. 4. Effects of C₃H₆ on CO-SCR over Ir/ZSM-5/cordierite. Reaction conditions: 500 ppm NO, 0–500 ppm C₃H₆, 1000 ppm CO, 2% H₂O, 5% O₂, He balance, GHSV = 15,000/h.

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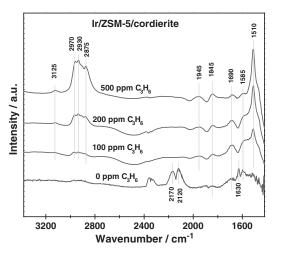


Fig. 5. In situ FTIR spectra of adsorbed species formed on Ir/ZSM-5/cordierite at 523 K. Reaction conditions: 500 ppm NO, 0–500 ppm C_3H_6 , 1000 ppm CO, 2% H_2O , 5% O_2 , He balance, GHSV = 15,000/h.

mononitrosyls on isolated and associated cationic sites, respectively [21,22]. These observations indicate that N_xO_y species are preferentially formed on LaCu-ZSM-5/cordierite under C_3H_6 -SCR reaction conditions. The surface N_xO_y species can react with gaseous C_3H_6 to produce N_2 , CO_2 and H_2O , probably via isocyanates as important reaction intermediates. When carbon monoxide is fed to the reaction system, strong bands at 2970, 2930 and 2875 cm⁻¹ assignable to $-CH_x$, together with very weak IR band at 3125 cm⁻¹ assignable to $-R = CH_2$ [23], appear. Moreover, IR band at 1510 cm⁻¹ assignable to carboxylate species [19] appear. The intensity of IR band due to isocyanates increases slightly. Obviously, the introduction of carbon monoxide can promote the adsorption and activation of C_3H_6 on LaCu-ZSM-5/cordierite. As a result, formation of reaction intermediate isocyanates is enhanced and the C_3H_6 -SCR reaction is promoted.

3.3. Effects of C₃H₆ on CO-SCR over Ir/ZSM-5/cordierite

The effects of C_3H_6 on CO-SCR over Ir/ZSM-5/cordierite are shown in Fig. 4. Without C_3H_6 in the reaction system, LaCu-ZSM-5/cordierite exhibits good deNO_x performances in CO-SCR. The nitrogen oxide conversion increases with increasing reaction temperature, reaches a maximum of ca. 55% at 523 K and then decreases with further increasing temperature. The introduction of C_3H_6 to the reaction system significantly changes the deNO_x beviour of Ir/ZSM-5/cordierite. Typically, the

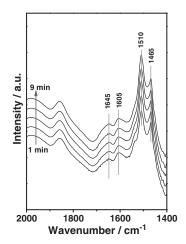


Fig. 6. FTIR spectra of adsorbed species formed on Ir/ZSM-5/cordierite upon C_3H_6 adsorption at 523 K. Reaction conditions: 500 ppm C_3H_6 , He balance, GHSV = 15,000/h.

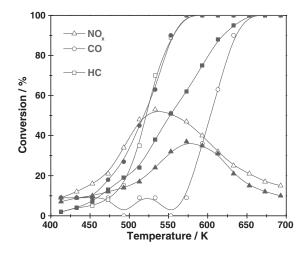


Fig. 7. Catalytic performance of single catalyst for the purification of exhaust from leanburn engine. Solid symbol: Ir/ZSM-5/cordierite. Open symbol: LaCu-ZSM-5/cordierite. Reaction conditions: 485 ppm NO, 139 ppm HC, 1100 ppm CO, 100 ppm SO₂, 10.5% H₂O, 6.8% O₂, GHSV = 15,000/h.

maximal nitrogen oxide conversion decreases and the temperature with maximal conversion shifts to higher range. These changes are more pronounced with higher concentrations of C_3H_6 in the reaction system. Meanwhile, the C_3H_6 in the reaction system is oxidized to CO_2 and H_2O . The C_3H_6 conversion increases with increasing reaction temperature and the complete conversion can be achieved at > 623 K. Considering that Irbased catalysts are active in HC-SCR reaction [24,25], the C_3H_6 in the reaction system may act as reducing agent for nitrogen oxides. Therefore, the deNO_x activity may be contributed by both CO-SCR and C_3H_6 -SCR. However, the presence of C_3H_6 show negative effects on CO-SCR over Ir/ZSM-5/cordierite at relative low temperature of below 600 K.

The species formed during CO-SCR over Ir/ZSM-5/cordierite with and without C_3H_6 in the reaction system are investigated by in situ FTIR spectra, as shown in Fig. 5. Without C_3H_6 in the reaction system, FTIR bands at 2170, 2120, 1690, 1630 and 1585 are observed at 523 K. Various N_xO_y species, including bridging bidentate nitrates (band at 1630 cm⁻¹), chelating bidentate nitrates (band at 1585 cm⁻¹), and nitrosonium ion NO⁺ (band at 2120 cm⁻¹) [26], are formed under CO-SCR reaction conditions. Besides, -NCO species on iridium sites (band at 2170 cm⁻¹) are observed as the reaction intermediates in

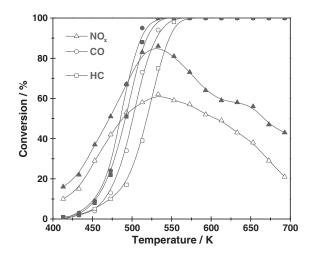


Fig. 8. Catalytic performance of combination catalyst for the purification of exhaust from lean-burn engine. Solid symbol: LaCu-ZSM-5/cordierite (first) and Ir/ZSM-5/cordierite (second) (1:1, volume based). Open symbol: Ir/ZSM-5/cordierite (first) and LaCu-ZSM-5/cordierite (second) (1:1, volume based). Reaction conditions: 485 ppm NO, 139 ppm HC, 1100 ppm CO, 100 ppm SO₂, 10.5% H₂O, 6.8% O₂, GHSV = 15,000/h.

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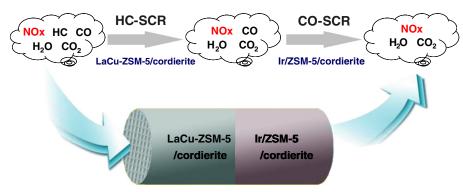


Fig. 9. Scheme of combination catalyst for the purification of exhaust from lean-burn engine.

CO-SCR [12]. With the introduction of C₃H₆, new FTIR bands corresponding to $-CH_x$ and $-R = CH_2$ species (bands at 3125, 2970, 2930 and 2875 cm^{-1}) as well as FTIR band corresponding to carboxylates (bands at 1510 cm^{-1}) appear. Their intensities increase with increasing C₃H₆ concentration. Meanwhile, the FTIR bands corresponding to nitrosonium ion and -NCO species disappear. These observations indicate that C₃H₆ in the CO-SCR reaction system may block the active Ir sites and the CO-NO reaction on Ir sites is therefore suppressed. For a direct view of the block of Ir sites by C₃H₆, FTIR spectra of C₃H₆ adsorption on Ir/ZSM-5/cordierite were recorded. As shown in Fig. 6, C_3H_6 is easily activated on iridium cationic sites (IR band at 1605 cm⁻¹ assignable to $-(CH_2 = CH_{\bullet})$ and IR band at 1465 cm⁻¹ assignable to $CH_2 = CH - CH_2$) and can be further oxidized to carboxylates (IR bands at 1510 cm^{-1}) [19,22]. Although the adsorbed C₃H₆ may react with surface N_xO_y species, e.g. bidentate nitrates, to contribute to the deNO_x activity via C₃H₆-SCR, the efficiency of C₃H₆-SCR is somewhat lower than CO-SCR over Ir/ ZSM-5/cordierite at <600 K.

3.4. Combination catalyst for the purification of automobile exhaust

For the purification of automobile exhaust, the ideal means is to utilize both unburned hydrocarbons and carbon monoxide in exhaust for nitrogen oxides reduction via combined HC-SCR and CO-SCR. Based on literature reports and our previous work, HC-SCR catalyst LaCu-ZSM-5/cordierite and CO-SCR catalyst Ir/ZSM-5/cordierite are selected as promising combination catalyst systems. Both LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite single catalysts show certain deNOx activity in engine test, as shown in Fig. 7. The combination of LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite results in significant promotion of deNOx activity. Moreover, the combination style shows great impacts on the catalytic performances. As shown in Fig. 8, LaCu-ZSM-5/cordierite (first) and Ir/ZSM-5/cordierite (second) show much better catalytic performances than Ir/ZSM-5/cordierite (first) and LaCu-ZSM-5/cordierite (second). Typically, the maximal nitrogen oxide conversion of ca. 85%, with carbon monoxide and hydrocarbon conversions approaching 100%, can be achieved at 523 K. These results are really amazing for real lean-burn engine test and the combination catalyst shows great potential for future application.

The scheme of combination catalyst for the purification of exhaust from lean-burn engine is illustrated in Fig. 9. In the first step, HC-SCR reaction occurs on LaCu-ZSM-5/cordierite and considerable amounts of nitrogen oxide are reduced by unburned hydrocarbons in the exhaust. Most hydrocarbons are consumed in HC-SCR and carbon monoxide shows promotion effect on HC-SCR with very little consumption (see Figs. 2 and 3). In the second step, the carbon monoxide in the exhaust acts as reducing agent for nitrogen oxides and CO-SCR reaction occurs on Ir/ZSM-5/cordierite. Since most hydrocarbons are consumed in the first step, the suppression of CO-SCR by hydrocarbons will not take place. With contributions from both HC-SCR and CO-SCR, very good $deNO_x$ performances can be achieved by the combination catalyst and the major pollutants in the exhaust, i.e. nitrogen oxides, hydrocarbons and carbon monoxide, can be purified simultaneously.

4. Conclusion

In this work, monolithic LaCu-ZSM-5/cordierite and Ir/ZSM-5/ cordierite are studied as eligible catalysts for C₃H₆-SCR and CO-SCR reactions, respectively. Special focus is laid on the effects of coexisting reducing agent on SCR reactions. LaCu-ZSM-5/cordierite exhibits good activity in C₃H₆-SCR and co-existing carbon monoxide shows positive effects on C_3H_6 -SCR by promoting the adsorption and activation of C₃H₆. Ir/ZSM-5/cordierite exhibits good activity in CO-SCR, while co-existing C₃H₆ shows negative effects on CO-SCR at relatively low temperatures by covering the active iridium sites. The concept of combination catalyst is therefore developed by utilizing both hydrocarbons and carbon monoxide as reducing agents for nitrogen oxide reduction. With contributions from both C₃H₆-SCR and CO-SCR, the major pollutants in lean-burn automobile exhaust, e.g. nitrogen oxides, unburned hydrocarbons and carbon monoxide, can be purified simultaneously by the combination catalyst LaCu-ZSM-5/cordierite and Ir/ZSM-5/cordierite. Surprisingly, the maximal nitrogen oxide conversion of ca. 85%, with carbon monoxide and hydrocarbon conversions approaching 100%, can be achieved at 523 K in a real lean-burn engine test.

Acknowledgments

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