

# Ir/ZSM-5/cordierite monolith for catalytic NO<sub>x</sub> reduction from automobile exhaust

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## Abstract

Ir/ZSM-5/cordierite was studied as promising catalyst for the reduction of nitrogen oxides from automobile exhaust under both stoichiometric combustion and lean conditions. ZSM-5 was in situ synthesized on the surface of honeycomb cordierite substrate and iridium was introduced to ZSM-5/cordierite by wet impregnation. Under stoichiometric combustion, Ir/ZSM-5/cordierite exhibited good catalytic activity approaching commercial three-way catalysts, and the three main pollutants nitrogen oxides, carbon monoxide and unburned hydrocarbons could be purified simultaneously. Under lean conditions, Ir/ZSM-5/cordierite also exhibited quite good deNO<sub>x</sub> activities though excess oxygen showed inhibition effect on NO<sub>x</sub> reduction.

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**Keywords:** Ir/ZSM-5/cordierite; Automobile exhaust; NO<sub>x</sub>

## 1. 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]. Based on noble metal Pt, Pd and Rh as main active ingredients, three way catalysts (TWC) can provide high level of emission control for nitrogen oxides, carbon monoxide and unburned hydrocarbons. Up to now, TWC have been proved to be efficient and reliable [2,3], and considered as optimal means to treat the exhaust under the condition of stoichiometric combustion. Current strategies attempting at minimizing of fuel consumption and CO<sub>2</sub> emission prompt the use of lean burn engine. However, TWC suffer from severe loss of activity for NO<sub>x</sub> reduction in the presence of excess oxygen, which is the prevalent condition for lean burn gasoline engines [4].

Many efforts have been carried out to develop alternative catalysts for NO<sub>x</sub> reduction in excess oxygen [6,7,5,8–10]. Ir-based catalysts have been reported be good catalysts for NO<sub>x</sub> reduction and received much attention from both experimental [11–15] and theoretical [16–18]. However, the loss of active component iridium is a serious problem to be solved, which prevents Ir-based catalysts from industry application. Correspondingly, no detailed engine test results on Ir-based catalysts are available up to now.

In this work, a promising monolithic catalyst Ir/ZSM-5/cordierite is prepared for the reduction of NO<sub>x</sub> from automobile exhaust under both stoichiometric combustion and lean conditions. The detailed engine test results will be reported and the reaction mechanism will also be discussed.

## 2. Experimental section

### 2.1. Catalysts preparation

#### 2.1.1. In situ synthesis of ZSM-5/cordierite

The detailed synthesis process of ZSM-5/cordierite has been described in our previous work [19]. In brief, sodium

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hydroxide, aluminum sulfate, silica sol and water were mixed with this proportion:  $1\text{Al}_2\text{O}_3$ :  $84\text{SiO}_2$ :  $10\text{Na}_2\text{O}$ :  $3500\text{H}_2\text{O}$ . After vigorous stirring for 2 h, the gained transparent gel and honeycomb cordierite (Corning incorporated,  $100\text{ cells/cm}^2$ , 0.2 mm average wall thickness) were put into a high-pressure autoclave together for static crystallization at  $180\text{ }^\circ\text{C}$  for 16 h. Subsequently, the as-prepared NaZSM-5/cordierite were taken out, ion-exchanged to H form by 0.5 M  $\text{NH}_4\text{Cl}$ , dried at  $100\text{ }^\circ\text{C}$  over night and then calcined at  $400\text{ }^\circ\text{C}$  for 6 h in air.

#### 2.1.2. Preparation of Ir/ZSM-5/cordierite by impregnation

Ir/ZSM-5/cordierite was prepared from HZSM-5/cordierite by wet impregnation. Different from conventional impregnation process, an ultra weak aqueous solution of  $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$  (2 mM) was used to improve the dispersion and stability of coated iridium this study. In a typical synthesis, 200 g HZSM-5/cordierite was placed into 200 mL 2 mM  $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$  aqueous solution. Under slowly stirring, the solution was evaporated in vacuum at the constant temperature of  $60\text{ }^\circ\text{C}$ . Then the obtained Ir/ZSM-5/cordierite sample was dried at  $100\text{ }^\circ\text{C}$  over night and calcined in flowing air at  $600\text{ }^\circ\text{C}$  for 4 h before use.

#### 2.2. Catalysts characterization

The crystallinity of the synthesized Ir/ZSM-5/cordierite was given by XRD data collected with a Rigaku D/max 2500 diffractometer, equipped with a graphite monochromator and using  $\text{Cu K}\alpha$  radiation.

SEM from a HITACHI S-3500N scanning electron microscope detected the surface feature of Ir/ZSM-5/cordierite monolith. TEM images were acquired on a JEOL 2010 transmission electron microscope at an accelerate voltage of 200 kV. The particles obtained after the irradiation and workup were dropped onto the surface of carbon membrane and dried at ambient conditions.

Surface areas and pore diameters were determined by nitrogen adsorption on the ASAP 2010 M facility (Micromeritics).

ZSM-5 loading in ZSM-5/cordierite was determined by calculating the weight increase of cordierite after hydrothermal synthesis. The iridium loading in Ir/ZSM-5/cordierite was determined by ICP (IRIS Advantage, TJA solution).

#### 2.3. Catalytic testing

Catalytic evaluation experiments were carried out on a 4-valve S.I. (spark ignited) gasoline engine, in which, the controllable quasi-homogenous mixture inside the cylinder made by controllable injection realized fast quasi-homogenous mixture combustion. The catalyst was fixed inside the vent-pipe of the engine, heated by electrical heater. The products after catalytic reaction were on-line analyzed with an exhaust analyser (MW56-AVL DIGAS 4000 LIGHT). The entire equipment of the catalytic assessment experiments is graphed elsewhere [20].

#### 2.4. In situ DRIFTS Study

In situ DRIFT spectra were recorded on a NEXUS 670-FTIR (Thermo Nicolet), equipped with a liquid  $\text{N}_2$  cooled high sensitivity MCT detector. The Ir/ZSM-5/cordierite sample (0.5 g) was finely ground and placed in the reaction chamber. Prior to each experiment, the sample was heated in He flow at  $600\text{ }^\circ\text{C}$  for 1 h, and then cooled to the desired temperature for taking a reference spectrum. All gas mixtures were fed at a flow rate of 50 ml/min. All spectra were measured with a resolution of  $4\text{ cm}^{-1}$  and with an accumulation of 100 scans.

### 3. Results and discussion

#### 3.1. Characterization of catalysts

The synthesized Ir/ZSM-5/cordierite sample is characterized by XRD and SEM techniques (Fig. 1). In the XRD patterns, the typical peaks of both ZSM-5 and cordierite substrate have been lined out. It is well demonstrated that ZSM-5 zeolite have been in situ synthesized on the cordierite substrate. From the SEM image, it is found that sandwich ZSM-5 zeolite crystals (about  $5\text{ }\mu\text{m}$ ) grow on cordierite substrate in high quality and completely cover the irregular surface of cordierite substrate. Some other textural properties of Ir/ZSM-5/cordierite catalyst were displayed in Table 1.

The typical TEM image of as-synthesized Ir/ZSM-5/cordierite is shown in Fig. 2. From the figure, it is seen that well-crystallized ZSM-5 zeolites with clear lattice structure connected tightly with cordierite substrate. No iridium species could be observed in the TEM images, probably due to the low iridium loading and high dispersion.

In monolithic Ir/ZSM-5/cordierite, ZSM-5 zeolite is not only the coatings on substrate but also the direct support of iridium: ZSM-5 zeolite coatings act as a bridge connecting cordierite substrate and active component iridium. On one side, by in situ synthesis, crystallization of ZSM-5 zeolite occurs not only on the external surface of cordierite substrate but also on the internal surface of cordierite [21]. Good stability and accessibility of ZSM-5 zeolite on cordierite substrate can be achieved [21,22]. On the other side, ZSM-5 coatings are good support for iridium species. The use of ultra weak  $\text{H}_2\text{IrCl}_6 \cdot 6\text{H}_2\text{O}$  solution for wet impregnation allows a homogenous deposition of anionic  $\text{IrCl}_6^{2-}$  and thus an improved dispersion of Ir species. After calcinations in the air, HCl is released and  $\text{IrO}_x$  clusters are formed. Generally, iridium tends to form volatile oxides, and the use of Ir-containing catalyst always suffers from severe loss of activity, or even cause a second pollution to the environment at relative high temperatures [23,24]. Here, the iridium in Ir/ZSM-5/cordierite might be stabilized and loss of active component iridium in the catalyst could be avoided to a great extend. In fact, no iridium loss is observed after 30 hours' catalytic reaction ( $400\text{ }^\circ\text{C}$ , GHSV =  $30,000\text{ h}^{-1}$ ) and the iridium loading in catalyst

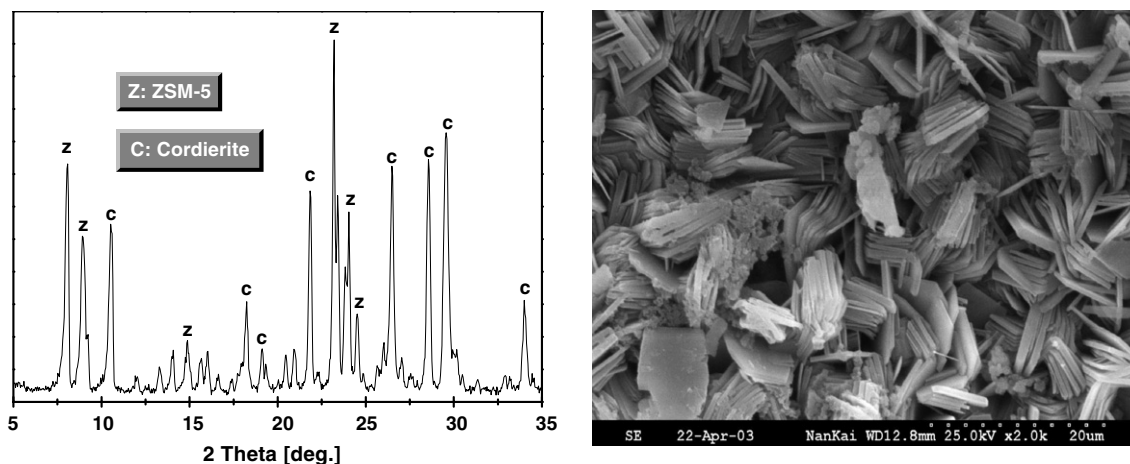


Fig. 1. XRD patterns (left) and SEM image (right) of Ir/ZSM-5/cordierite.

Table 1  
Textural properties of Ir/ZSM-5/cordierite catalysts

Catalyst	BET surface area (m <sup>2</sup> /g)	ZSM-5 loading (wt%) <sup>a</sup>	Si/Al ratio <sup>b</sup>	Ir loading (wt%) <sup>c</sup>
Ir/ZSM-5/cordierite	56	16.3	15.2	0.02

<sup>a</sup> In ZSM-5/cordierite.

<sup>b</sup> Of ZSM-5 coatings, cordierite substrate excluded.

<sup>c</sup> In Ir/ZSM-5/cordierite monolith.

Table 2  
Testing of iridium loss for Ir-based catalysts

Sample	Iridium loading (wt%) <sup>a</sup>		Ir loss (%)
	After calcination <sup>b</sup>	After aging <sup>c</sup>	
Ir/ZSM-5	0.1601	0.1564	2.31
Ir/Al <sub>2</sub> O <sub>3</sub>	0.1417	0.0795	43.90

<sup>a</sup> Determined by ICP, average of multiple metering.

<sup>b</sup> 550 °C, 6 h, in the air.

<sup>c</sup> 500 °C, 240 h, in the air.

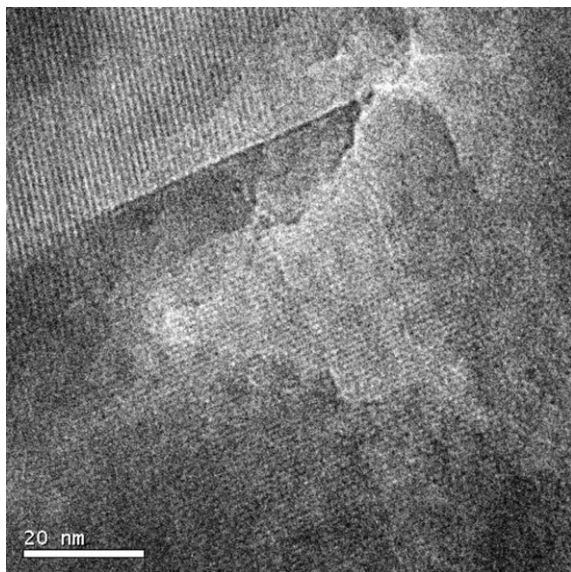


Fig. 2. TEM image of Ir/ZSM-5/cordierite monolith after calcinations.

can be kept at the initial level (0.02%, wt). Further experiments for testing iridium loss of different Ir-based catalysts are carried out. As seen in Table 2, iridium loss after long time aging on Ir/Al<sub>2</sub>O<sub>3</sub> was 43.90%, while iridium loss was only 2.31% on Ir/ZSM-5 with the similar initial iridium loading. Obviously, much better stability of iridium species on ZSM-5 support could be achieved.

### 3.2. Catalytic tests

The catalytic test of Ir/ZSM-5/cordierite is carried on a real gasoline engine, in which, hydrocarbons and CO in exhaust are used directly as reductant for NO<sub>x</sub> reduction. The burning gasoline is commercially available from Shell gas station. The exhaust contained about 10% steam and 100 ppm SO<sub>2</sub> from combustion of the commercial gasoline. Fig. 3 displays the status of the engine exhaust treated by Ir/ZSM-5/cordierite at the stoichiometric combustion condition (A/F = 14.7). Ir/ZSM-5/cordierite was activated at a temperature around 190 °C when NO<sub>x</sub> conversion (to N<sub>2</sub>) was about 50%. At 260 °C, the activity (for NO<sub>x</sub> reduction) of Ir/ZSM-5/cordierite reached its maximal value and the maximal NO<sub>x</sub> conversion was about 94%. Afterwards, the activity (for NO<sub>x</sub> reduction) of Ir/ZSM-5/cordierite began to decrease. While, a positive effect of reaction temperatures on the conversion of both hydrocarbons and CO was observed: the maximal conversion of hydrocarbons (100%) and CO (98.4%) could be obtained since 280 °C and 240 °C, respectively. It was observed that most pollutants NO<sub>x</sub>, HC and CO could be converted to harmless N<sub>2</sub>, H<sub>2</sub>O and CO<sub>2</sub> (conversions > 90%) at rather low temperatures between 250 °C and 260 °C. Under common working condition of the engine, the purification results were satisfying and approaching to the commercial TWC. The high catalytic activity of commercial TWC was achieved under the co-function of active components Rh,

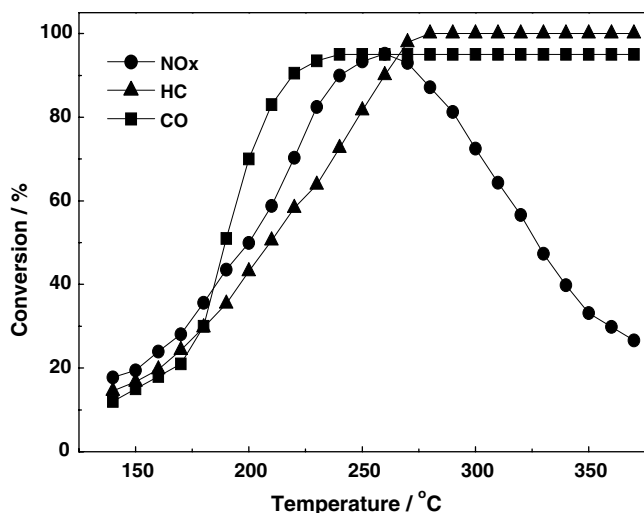


Fig. 3. Conversions of three main pollutants in exhaust varied with temperatures catalyzed by Ir/ZSM-5/cordierite. Working status of engine: A/F = 14.7; Load = 0.3 Mpa; GHSV = 30,000 h<sup>-1</sup>; Exhaust before catalytic reaction: NOx = 2310 ppm, HC = 197 ppm, CO = 0.45%.

Pt, Pd and some additives [3], while the catalytic activity of Ir/ZSM-5/cordierite could be achieved with single active component iridium at a very low content of about 0.02%. Considering the simple preparation method and much lower price compared to TWC, Ir/ZSM-5/cordierite or modified Ir/ZSM-5/cordierites were expected to be good alternative for commercial TWC in treating automobile exhaust under stoichiometric combustion condition in the future.

Fig. 4 shows the catalytic efficiency of Ir/ZSM-5/cordierite as a function of GHSV at the constant reaction temperature of 290 °C. With GHSV increasing from 10,000 h<sup>-1</sup> to 50,000 h<sup>-1</sup>, HC conversion was maintained at 100% while

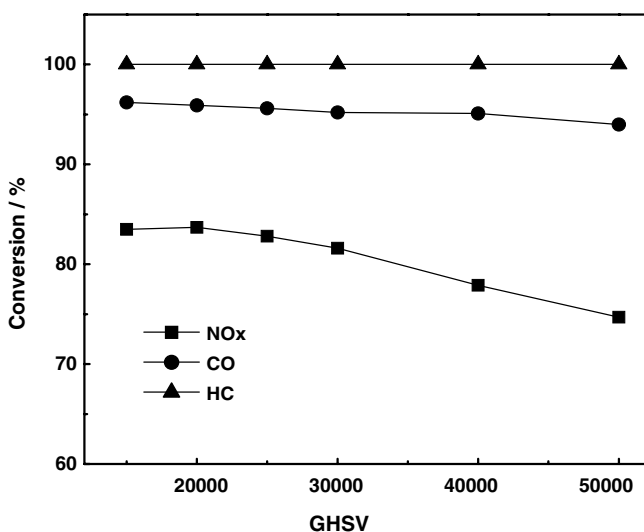


Fig. 4. Catalytic efficiency of Ir/ZSM-5/cordierite as a function of GHSV at the reaction temperature of 290 °C. Working status of engine: A/F = 14.7; Exhaust before catalytic reaction: NOx = 2310 ppm, HC = 197 ppm, CO = 0.45%.

CO conversion and NOx conversion slightly declined from 96% to 93% and from 83% to 73%, respectively. The catalytic efficiency of Ir/ZSM-5/cordierite is insensitive to the change in GHSV, which makes it potential catalyst for practical application of automotive exhaust.

Lean burn technique can not only greatly reduce specific oil consumption but also lead to much lower pollutants emission [25]. The curve of oil consumption varied with air fuel ratio of our testing engine is displayed in Fig. 5 and the pollutants concentration in exhaust at several different air fuel ratios are available in Table 3. It is concluded that the optimal air fuel ratio is 17.5–19 considering both economical and environmental factors. In this work, Ir/ZSM-5/cordierite is tested as automobile exhaust catalysts under different lean conditions. As seen in Fig. 6, similar volcano-type curves of NOx conversion varied with reaction temperatures can be observed for different air fuel ratios. Ir/ZSM-5/cordierite was activated at the temperature of 190 °C and the maximal NOx conversion was obtained at the temperature of about 260 °C for all air fuel ratios studied. The difference only lied in the maximal NOx converted, which decreased with the increase of air fuel ratio. Since the oxygen concentration in exhaust increases

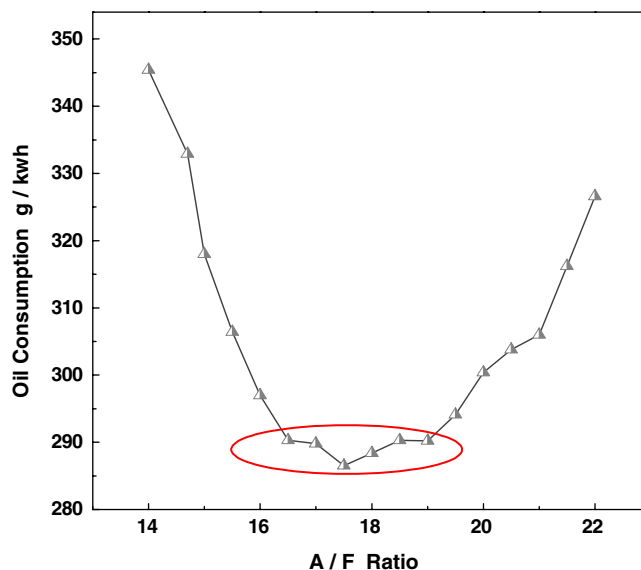


Fig. 5. Specific oil consumption of testing engine varied with air fuel ratio. Working status of engine: Load = 0.3 Mpa, GHSV = 30,000 h<sup>-1</sup>.

Table 3  
Pollutants and oxygen concentrations in exhaust

A/F ratio	Concentrations in exhaust gas			
	NOx (ppm)	CO (%)	HC (ppm)	O <sub>2</sub> (%)
14.7	2310	0.45	197	1.2
15.5	1840	0.39	133	2.5
16.5	1350	0.24	110	3.6
17.5	1260	0.19	120	4.4
18.5	720	0.16	124	5.2
19.5	550	0.12	125	6.7

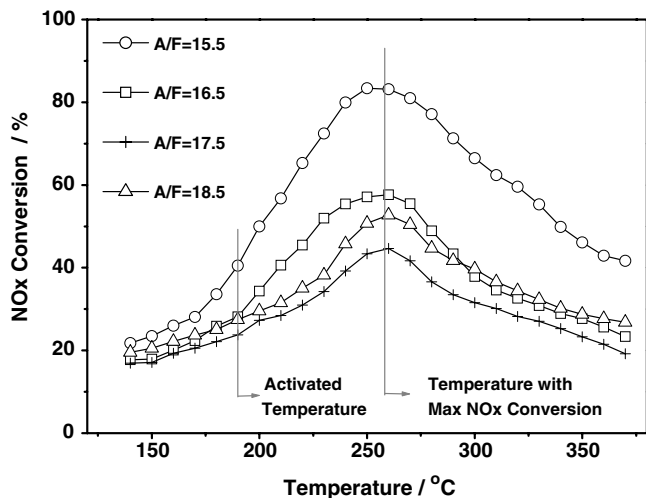
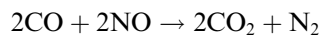


Fig. 6. NO<sub>x</sub> conversions varied with reaction temperatures catalyzed by Ir/ZSM-5/cordierite at different air fuel ratios. Working status of engine: Load = 0.3 MPa, GHSV = 30,000 h<sup>-1</sup>.

with air fuel ratio (Table 3), it is concluded that maximal NO<sub>x</sub> converted decreases with increasing oxygen concentration. In our reaction system, the hydrocarbons concentration is quite low and is far not enough to reduce the NO<sub>x</sub> in the exhaust. So, carbon monoxide acts as the main reductant for NO<sub>x</sub> reduction and the following two reactions are considered to operate in lean conditions:



Excess oxygen is known to show great inhibition effect for NO<sub>x</sub> reduction on commercial TWC [26]. A comparison between maximal NO<sub>x</sub> conversion over Ir/ZSM-5/cordierite and commercial TWC (TWX<sup>TM</sup>, Engelhard) at different air fuel ratios is shown in Fig. 7. It is seen that

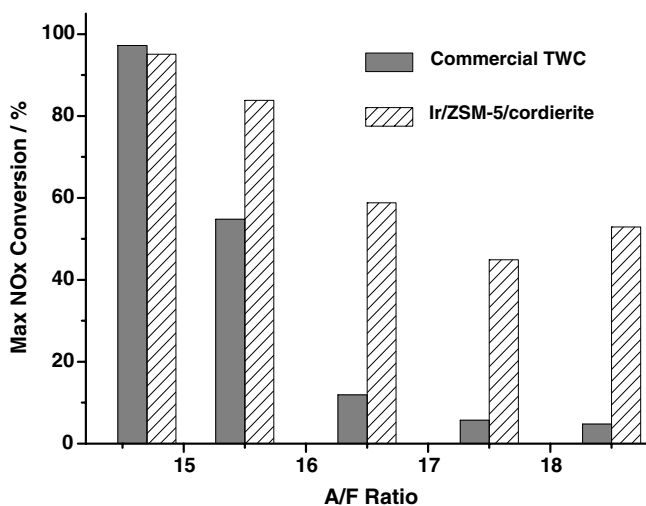


Fig. 7. Maximal NO<sub>x</sub> conversion varies with air fuel ratios over Ir/ZSM-5/cordierite and commercial TWC. Working status of engine: Load = 0.3 MPa, GHSV = 30,000 h<sup>-1</sup>.

though oxygen inhibition effect on NO<sub>x</sub> reduction can be observed over both catalysts, the inhibition extent on Ir/ZSM-5/cordierite is much milder than that on commercial TWC. The catalytic performance of Ir/ZSM-5/cordierite is also compared to Cu-ZSM-5/cordierite, which is known as one of the best automobile exhaust catalysts under lean conditions [20]. Ir/ZSM-5/cordierite shows much better performance than Cu-ZSM-5/cordierite from the results in Fig. 8. HC and CO conversions over Ir/ZSM-5/cordierite were much higher than those over Cu-ZSM-5/cordierite at most temperatures studied. Maximal NO<sub>x</sub> conversion over Ir/ZSM-5/cordierite was about 5% higher than that over Cu-ZSM-5/cordierite and more important, the temperature of maximal NO<sub>x</sub> conversion was 120 °C lower, which was good for the purification of automobile exhaust automobiles in cold startup stage.

### 3.3. Reaction mechanism

To get a better understanding of NO reduction, the NO-CO-O<sub>2</sub> reaction on Ir/ZSM-5/cordierite monitored with in situ DRIFT spectra, as displayed in Fig. 9.

In flowing NO/He, strong IR band at 2133 cm<sup>-1</sup> is detected, which is assigned to the adsorbed NO<sup>+</sup> species on the Brønsted acid sites of ZSM-5 zeolite (-NO<sup>+</sup>) [27]. Some weak IR bands can also be observed: bands at 1900 cm<sup>-1</sup> and 1850 cm<sup>-1</sup> assigned to NO linearly adsorbed as NO<sup>δ+</sup> onto iridium crystallites and iridium atoms influenced strongly by the support respectively [28]; bands at 1604 cm<sup>-1</sup> and 1625 cm<sup>-1</sup> assigned to bridged nitrate species adsorbed on cation sites in ZSM-5 zeolite from -NO<sup>+</sup> and adsorbed O, similar to that formed on Cu site of Cu-ZSM-5 [29]. When CO is introduced, a strong IR band at 2169 cm<sup>-1</sup> can then be observed, which should be assigned to -NCO species adsorbed on iridium

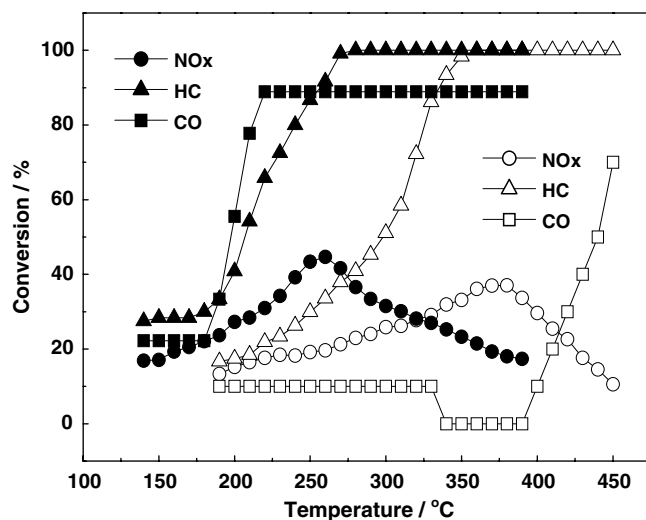


Fig. 8. Catalytic performance of Ir/ZSM-5/cordierite (filled symbols) and Cu-ZSM-5/cordierite (open symbols) (0.60% Cu loading, over exchanged) as automotive exhaust catalysts under lean condition. Working status of engine: A/F = 17.5; Load = 0.3 MPa; GHSV = 30,000 h<sup>-1</sup>.

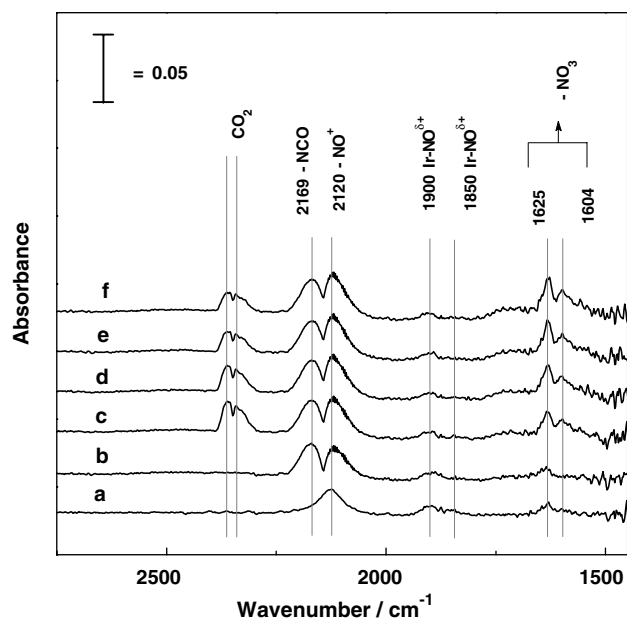
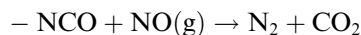
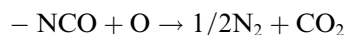
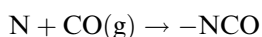
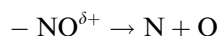
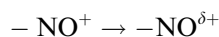
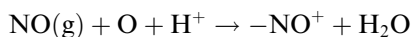


Fig. 9. DRIFTS study of adsorbed species formed on Ir/ZSM-5/cordierite in a flow of (a) 1000 ppm NO, (b) 1000 ppm NO + 1000 ppm CO, (c) 1000 ppm NO + 1000 ppm CO + 1% O<sub>2</sub>, (d) 1000 ppm NO + 1000 ppm CO + 2.5% O<sub>2</sub>, (e) 1000 ppm NO + 1000 ppm CO + 5% O<sub>2</sub>, (f) 1000 ppm NO + 1000 ppm CO + 10% O<sub>2</sub> with He balance at 250 °C.

species [30,31]. Notable, no bonds corresponding to CO species adsorbed on iridium of Ir/ZSM-5/cordierite could be observed in flowing CO/NO/He, different from the results reported on Ir/Al<sub>2</sub>O<sub>3</sub> [28] or Ir/SiO<sub>2</sub> [31]. Based on the DRIFTS results, the main process for NO reduction on Ir/ZSM-5/cordierite catalyst was proposed as follows:



In the first step, gaseous NO together with O adsorbs as  $-\text{NO}^+$  species on Brønsted acid sites of ZSM-5 zeolite. Then,  $-\text{NO}^+$  species can be further oxidized by O to form bridged nitrato species  $-\text{NO}_3^-$ , or migrates to adjacent acceptor iridium sites strongly interacting with ZSM-5 support as  $-\text{NO}^{\delta+}$ . When migrated to iridium,  $-\text{NO}^{\delta+}$  will dissociate to N and O immediately [17]. The adsorbed N then reacts with gaseous CO to form isocyanate  $-\text{NCO}$  species. The  $-\text{NCO}$  species are regarded as high active reaction intermediate of NO–CO reaction and they can react with NO or O to produce N<sub>2</sub> and CO<sub>2</sub> [32,33].

When 1% oxygen is introduced into the NO–CO reaction system, the intensity of IR bonds at 1604 cm<sup>-1</sup> and 1625 cm<sup>-1</sup> (corresponding to bridged nitrato species) increase, while the intensity of IR bond at 2169 cm<sup>-1</sup>

(corresponding to species) remains unchanged. Besides, multiple IR bonds between 2300 cm<sup>-1</sup> and 2400 cm<sup>-1</sup> corresponding to adsorbed CO<sub>2</sub> species [34] appear. With oxygen concentration increase from 1% to 10%, the intensity of IR bonds corresponding to  $-\text{NO}_3^-$  species increases obviously while the intensity of IR bonds corresponding to  $-\text{NCO}$  species does not show obvious change. Increasing oxygen concentration results in greater negative effect on NO reduction, in consistent with the catalytic results (Fig. 6). However, it is also seen that oxygen will not suppress the formation of  $-\text{NCO}$  species, which are the main reaction intermediates for NO reduction. So, Ir/ZSM-5/cordierite exhibits considerable catalytic activity for NO reduction even under lean conditions.

#### 4. Conclusion

By in situ synthesis, ZSM-5 zeolites grew on the surface of honeycomb cordierite substrate and formed ZSM-5/cordierite. Trace iridium was introduced to ZSM-5/cordierite by wet impregnation and Ir/ZSM-5/cordierite became a stable monolith. Ir/ZSM-5/cordierite exhibited quite good catalytic performance for the reduction of nitrogen oxides from automobile exhaust under both stoichiometry combustion and lean conditions. The NO–CO–O<sub>2</sub> reaction on Ir/ZSM-5/cordierite catalyst was monitored using in situ DRIFT spectra and the isocyanate species were observed as the reaction intermediates for NO reduction.

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