

# Selective catalytic reduction of NO by propane in excess oxygen over IrCu-ZSM-5 catalyst

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## Abstract

The selective reduction of NO by propane over bimetallic IrCu-ZSM-5 was investigated in this study. IrCu-ZSM-5, together with Cu-ZSM-5 and Ir-ZSM-5, was characterized by FTIR of pyridine adsorption, UV–vis spectroscopy and H<sub>2</sub>-TPR. The results indicated that the nature of Cu species changed with iridium as a modifier. The reaction mechanism over IrCu-ZSM-5 was investigated using in situ DRIFT spectra and nitrate species were observed as the main reaction intermediate for NO reduction by propane. The addition of trace iridium into Cu-ZSM-5 favored the formation of nitrate species, and thus better catalytic activity could be obtained on IrCu-ZSM-5. © 2006 Elsevier B.V. All rights reserved.

**Keywords:** IrCu-ZSM-5; SCR; Nitric oxide; Propane; DRIFTS; Nitrate

## 1. Introduction

Nitric oxides, derived from transportation and power plants, are major air pollutants that greatly contribute to the formation of photochemical smog and acid rain [1]. The selective catalytic reduction of NO by hydrocarbons in excess oxygen (HC-SCR) is a potential method to remove NO from transportation sources [2,3]. Since the pioneering work of Iwamoto et al. [4] and Held et al. [5], extensive studies have been carried out on HC-SCR using zeolites and cation-exchanged zeolites catalysts [6–10], most probably due to their high catalytic activities as well as high selectivity to desired product N<sub>2</sub>. Cu-ZSM-5 is the earliest catalyst studied for HC-SCR reactions and it is regarded as a model catalyst for the HC-SCR reaction [11,12]. Although its hydrothermal stability is considered to be not sufficient under realistic

reaction conditions, it is still accepted that its catalytic performance is excellent and application seems possible, in particular, in the NO<sub>x</sub> reduction in diesel engines where the exhaust temperature is lower compared to gasoline engines.

In this study it is reported that the modification of a Cu-ZSM-5 catalyst by iridium (IrCu-ZSM-5) improves its performance in the SCR of NO by propane in excess of oxygen. The reaction conditions chosen have been concentrated on the investigation of the influence of iridium on the properties of a Cu-ZSM-5 catalyst to allow drawing more general conclusions on the function of the second metal. Therefore, effects of H<sub>2</sub>O, CO<sub>2</sub> and SO<sub>2</sub>, which would have made the feed composition more realistic, have not yet been regarded in this paper.

During the reaction on IrCu-ZSM-5 the appearance and disappearance of various surface species has been followed by in situ diffuse reflectance infrared spectroscopy (DRIFTS) to obtain additional information on the reaction mechanism.

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## 2. Experimental

### 2.1. Catalyst preparation

Table 1 displays the catalysts and preparation methods applied in the present study. H-ZSM-5 (Si/Al = 25) was supplied by the Catalyst Plant of Nankai University. The detailed preparation method and resulting metal contents can be found in the table. The obtained samples were dried at 80 °C over night and then calcined at 550 °C for 4 h in the air.

### 2.2. Catalyst characterization

The acidity of samples was determined by FTIR study of pyridine adsorption on a BrukerVector-22 spectroscopy. The sample (about 20 mg) was heated at 400 °C for 2 h and cooled to room temperature under vacuum. Pyridine was then introduced to the sample at saturated vapor pressure. Physisorbed pyridine was removed by heating the samples at 150 °C for 2 h before IR spectra were recorded.

The nature of metal species on ZSM-5 zeolite was determined by UV–vis spectroscopy. Diffuse reflectance spectra were recorded in the air against BaSO<sub>4</sub> in the region of 200–700 nm on a HP8453 UV–vis spectrophotometer.

Temperature-programmed reduction experiments were carried out in a microreactor using 5 vol.% H<sub>2</sub>/He as reductant heating at 10 °C min<sup>-1</sup> from 50 °C to 750 °C. Prior to the reduction procedure, the samples were calcined in He at 500 °C for 2 h. The consumption of the reducing agent was measured on-line by a gas chromatograph equipped with a TCD.

### 2.3. Catalytic test

The SCR reaction of NO by propane at atmospheric pressure was carried out in a fixed-bed flow microreactor. The typical reactant gas mixture consists of NO (1000 ppm), C<sub>3</sub>H<sub>8</sub> (1000 ppm) and O<sub>2</sub> (5.0%), balanced with He to 100%. The total flow of the inlet gas was set at 60 mL min<sup>-1</sup> and 0.12 g catalyst were used to obtain a gas hourly space velocity (GHSV) of about 30 000 h<sup>-1</sup>. The catalyst sample was initially treated at 500 °C in He for 1 h before reactant gas mixture was introduced to the catalyst.

The products were analyzed on-line using a gas chromatograph (HP 6890 series) equipped with a TCD detector. A molecular sieve 5A column served for separation

of N<sub>2</sub>, O<sub>2</sub> and CO, and a porapak Q column for separation of CO<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, N<sub>2</sub>O, NO and H<sub>2</sub>O.

### 2.4. In situ DRIFTS study

In situ DRIFTS results were recorded on a NEXUS 670-FTIR (Thermo Nicolet), equipped with a liquid N<sub>2</sub> cooled high sensitivity MCT detector. The samples for this study were finely ground and placed in a ceramic crucible in an in situ chamber. Prior to each experiment, the samples were heated in He flow at 600 °C for 30 min, and then cooled to the desired temperature for taking a reference spectrum. All gas mixtures were fed at a flow rate of 100 mL/min. All spectra were measured with a resolution of 4 cm<sup>-1</sup> and with an accumulation of 100 scans.

## 3. Results and discussion

FTIR study of adsorbed pyridine allows a clear distinction between Brønsted and Lewis acid sites. As a good Lewis base, pyridine molecules interact with Brønsted acid sites forming pyridinium ions, characterized by bands in the FTIR spectra from 1512 to 1567 cm<sup>-1</sup> (centered at 1545 cm<sup>-1</sup>). Pyridine molecules can also adsorb on surface Lewis acid site through its lone pair electrons on nitrogen atom, characterized by bands in the FTIR spectra from 1423 to 1472 cm<sup>-1</sup> (centered at 1445 cm<sup>-1</sup>). The peak centered at 1489 cm<sup>-1</sup> can be ascribed to the overlapping of Brønsted acid and Lewis acid sites [13,14]. The FTIR spectra of pyridine adsorption on the H-ZSM-5 and modified HZSM-5 samples are shown in Fig. 1. As seen in the figure, both Brønsted and Lewis acid sites could be found over H-ZSM-5 and all the modified HZSM-5 samples. The addition of iridium in H-ZSM-5 showed dramatic negative effect on the Brønsted and Lewis acid sites. During impregnation and subsequent calcination process, HCl formed and caused the dealumination of the ZSM-5 zeolite. Hence, a severe loss in the Brønsted and Lewis acid sites could be observed. While for IrCu-ZSM-5, ion-exchange of copper was first performed and the copper, with a rather high ion-exchange degree, could then protect ZSM-5 framework against dealumination to a great extent in the following process.

The diffuse reflectance UV–vis spectra of Cu-ZSM-5, Ir-ZSM-5 and IrCu-ZSM-5 catalysts are displayed in Fig. 2. The bands for iridium species observed on Ir-ZSM-5 were very weak and obscure, probably because of the low iridium content. Cu-ZSM-5 showed bands at 232 nm and

Table 1  
Catalysts and preparation methods

Catalyst	Precursor	Preparation method	Solution (mM)	Metal content (wt%) <sup>a</sup>
Cu-ZSM-5	H-ZSM-5	Ion-exchange	20 Cu(NO <sub>3</sub> ) <sub>2</sub>	Cu 2.4%
Ir-ZSM-5	H-ZSM-5	Impregnation	50 H <sub>2</sub> IrCl <sub>6</sub>	Ir 0.2%
IrCu-ZSM-5	Cu-ZSM-5	Impregnation	50 H <sub>2</sub> IrCl <sub>6</sub>	Cu 2.3%; Ir 0.2%

<sup>a</sup> Analyzed by ICP (IRIS Advantage, TJA solution).

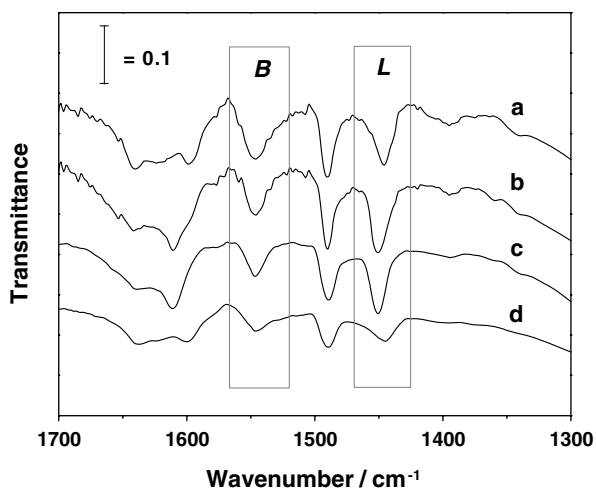


Fig. 1. FTIR spectra of the adsorption of pyridine on (a) H-ZSM-5, (b) Cu-ZSM-5, (c) IrCu-ZSM-5 and (d) Ir-ZSM-5.

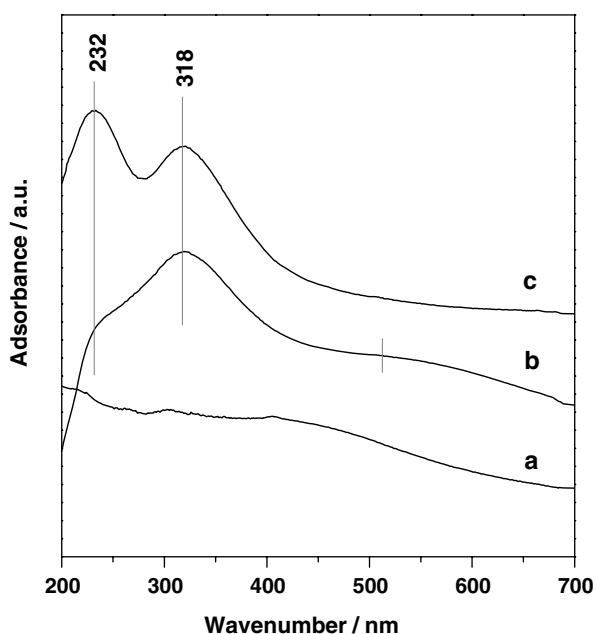


Fig. 2. Diffuse reflectance UV-vis spectra (a) Ir-ZSM-5, (b) Cu-ZSM-5 and (c) IrCu-ZSM-5.

318 nm, assignable to the charge transfer  $O \rightarrow Cu$  transitions of isolated Cu(II) ions in coordination with lattice oxygen [15] and Cu(II)– $O^-$  electronic transition species [16], respectively. Besides, weak bands in the region of 450–550 nm could be observed, corresponding to  $-O^{2-}-Cu^{2+}-O^{2-}-Cu^{2+}$  like chains in zeolite channel [17]. Similar to Cu-ZSM-5 sample, bands at 232 nm and 318 nm could also be observed on IrCu-ZSM-5 sample; only that the band at 232 nm was much stronger on IrCu-ZSM-5 than that on Cu-ZSM-5. Bands in the region of 450–550 nm, which could be observed on Cu-ZSM-5, disappeared on IrCu-ZSM-5. It is very clear that the addition of iridium on Cu-ZSM-5 sample could lead to change in the nature of Cu species on ZSM-5 zeolite.

The  $H_2$ -TPR profiles of Ir-ZSM-5, Cu-ZSM-5 and IrCu-ZSM-5 samples are shown in Fig. 3. For Ir-ZSM-5 sample, a very weak peak at about 164 °C was observed in the TPR profile, probably ascribed to the reduction of highly dispersed  $IrO_x$  species [18]. For Cu-ZSM-5 sample, two reduction peaks were observed at 237 °C and 485 °C corresponding to the reduction of intrazeolitic Cu (II) to Cu (I) and Cu (I) to metallic Cu, respectively [19,20]. While for IrCu-ZSM-5, two reduction peaks at 225 °C and 412 °C were observed, which should also be attributed to the reduction of intrazeolitic Cu (II) to Cu (I) and Cu (I) to metallic Cu, respectively. However, both the reduction peaks corresponding to Cu (II) to Cu (I) and Cu (I) to metallic Cu on IrCu-ZSM-5 were lower than those observed on Cu-ZSM-5. Obviously, the oxidative activity of Cu species was improved, which might come from the change in the nature of Cu species on ZSM-5 caused by modifier iridium as proved by UV-vis spectra.

Catalytic performances of Cu-ZSM-5, Ir-ZSM-5 and IrCu-ZSM-5 for NO selective reduction with  $C_3H_8$  are shown in Fig. 4. Remarkably, the only product from NO was nitrogen; neither  $N_2O$  nor  $NO_2$  was formed in the whole reaction process for all the three catalysts. There was a little CO (<100 ppm) produced over Ir-ZSM-5 below 400 °C because of the incomplete oxidation of propane, which was ignored in this study. NO conversions increased with the reaction temperatures over all three catalysts and the highest NO conversion was obtained on IrCu-ZSM-5 followed by Cu-ZSM-5 and Ir-ZSM-5. Comparing the catalytic performances of Cu-ZSM-5 and IrCu-ZSM-5, it could be seen that the addition of trace iridium into Cu-ZSM-5 greatly promoted the activity and improved the utilization of the propane: NO conversion to  $N_2$  over IrCu-ZSM-5 was enhanced in comparison to the Cu-ZSM-5 catalyst, but the propane conversion was identical.

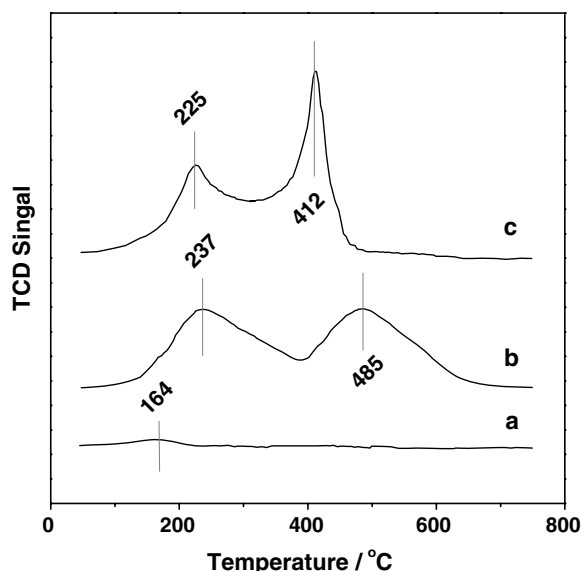


Fig. 3.  $H_2$ -TPR profiles of (a) Ir-ZSM-5, (b) Cu-ZSM-5 and (c) IrCu-ZSM-5.

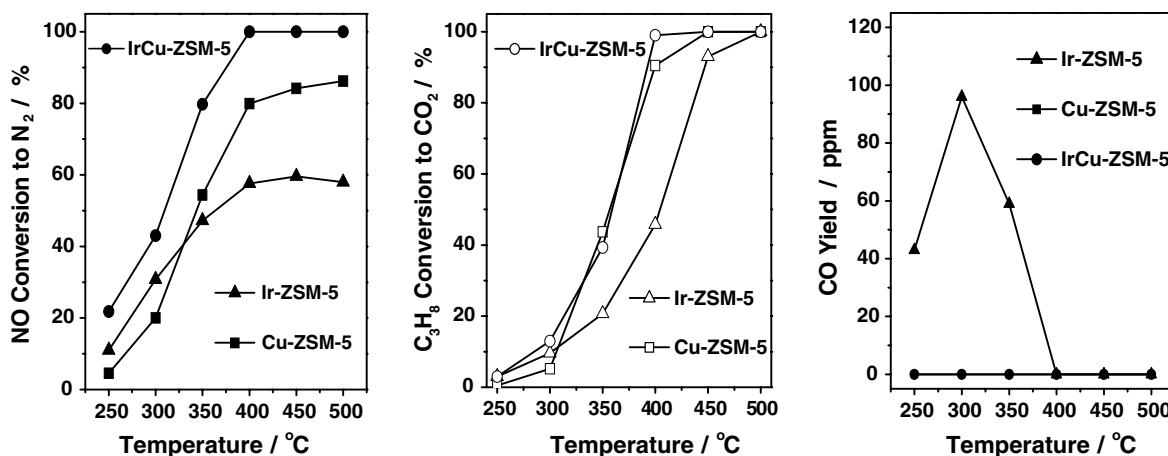


Fig. 4. Catalytic performances of Cu-ZSM-5, Ir-ZSM-5 and IrCu-ZSM-5 vs reaction temperatures. Reaction conditions: 1000 ppm NO, 1000 ppm C<sub>3</sub>H<sub>8</sub>, 5% O<sub>2</sub>, balance He; GHSV=30 000 h<sup>-1</sup>.

To have a better understanding of the deNO<sub>x</sub> mechanism, the NO–C<sub>3</sub>H<sub>8</sub>–O<sub>2</sub> reaction over Cu-ZSM-5, Ir-ZSM-5 and IrCu-ZSM-5 catalysts was investigated with in situ DRIFTS spectra. The reaction temperature selected for DRIFTS study was 400 °C, on which the great difference in catalytic activity over the three catalysts could be observed.

For Cu-ZSM-5, strong IR bands at 1625 cm<sup>-1</sup>, 1598 cm<sup>-1</sup> and 1568 cm<sup>-1</sup> could be detected in flowing NO/He as seen in Fig. 5. The bands at 1625 cm<sup>-1</sup> and 1598 cm<sup>-1</sup> were attributed to bridged nitrate species on the Cu<sup>2+</sup> ion [21,22]; while the band at 1568 cm<sup>-1</sup> was attributed to chelating nitrate species on Cu<sup>2+</sup> ion [23,24]. Some other weak IR bands could also be observed: a band at 2125 cm<sup>-1</sup> assignable to NO<sup>+</sup> species on Brønsted acid sites in ZSM-5 zeolite [25,26], a band at 1902 cm<sup>-1</sup> assignable to Cu–NO<sup>δ+</sup> species and a band at 1852 cm<sup>-1</sup> assignable to Cu–O–NO<sup>δ+</sup> species. Notably, IR band corresponding to Cu–O–NO<sup>δ+</sup> species were reported to

appear at 1890–1900 cm<sup>-1</sup> [27,28]. In this study, this band was broadened and shifted to lower wavenumber due to the high reaction temperature of 400 °C [29].

When excess oxygen was introduced into the NO/He reaction system, the intensity of IR bands corresponding to nitrate species (both bridged nitrate species and chelating nitrate species) showed a sharp increase. Besides, a mild increase in intensity of IR band corresponding to NO<sup>+</sup> species could be observed. When C<sub>3</sub>H<sub>8</sub> was added in, no C-containing species, such as carbonaceous deposits and acetate, could be observed and all N-containing species remained unchanged in NO/O<sub>2</sub>/C<sub>3</sub>H<sub>8</sub> reaction system.

For Ir-ZSM-5, weak IR bands at 2125 cm<sup>-1</sup>, 1905 cm<sup>-1</sup>, 1850 cm<sup>-1</sup>, 1625 cm<sup>-1</sup>, and 1598 cm<sup>-1</sup> could be detected in flowing NO/He as seen in Fig. 5. IR band at 2125 cm<sup>-1</sup> was attributed to NO<sup>+</sup> species adsorbed on Brønsted acid sites in ZSM-5 zeolite [25]. IR bands at 1905 cm<sup>-1</sup> and 1850 cm<sup>-1</sup> could be attributed to NO linearly adsorbed as NO<sup>δ+</sup> onto iridium crystallites and iridium atoms influ-

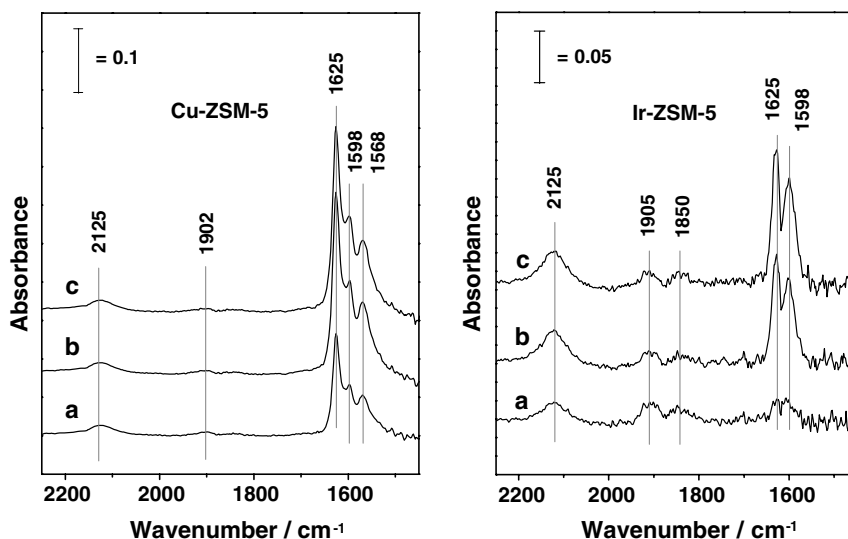


Fig. 5. DRIFTS study of adsorbed species on surface of Cu-ZSM-5 and Ir-ZSM-5 catalysts in a flow of (a) 1000 ppm NO, (b) 1000 ppm NO + 5% O<sub>2</sub>, (c) 1000 ppm NO + 1000 ppm C<sub>3</sub>H<sub>8</sub> + 5% O<sub>2</sub> with He balance at 400 °C.

enced strongly by the support (most probably through lattice-O) respectively [30,31]. There was no exact information about the IR bands at  $1604\text{ cm}^{-1}$  and  $1625\text{ cm}^{-1}$ . However, considering the wavenumbers of these two IR bands, we attributed them to nitrate species adsorbed on cationic positions in ZSM-5 zeolite similar to that formed on Cu sites of Cu-ZSM-5. When excess oxygen was added, the intensity of IR bands corresponding to nitrate species showed a sharp increase while the intensity of IR band corresponding to  $\text{NO}^+$  species showed a mild increase. Similar to the results on Cu-ZSM-5, no changes were observed for the species on Ir-ZSM-5 when  $\text{C}_3\text{H}_8$  was introduced into the reaction system.

For IrCu-ZSM-5 samples, some weak IR bands could be detected in flowing NO/He at  $400\text{ }^\circ\text{C}$  as seen in Fig. 6. Based on the DRIFTS results on Cu-ZSM-5 and Ir-ZSM-5, these bands were carefully attributed: band at  $2125\text{ cm}^{-1}$  attributed to  $\text{NO}^+$  species on Brønsted acid sites; bands at  $1902\text{ cm}^{-1}$  and  $1850\text{ cm}^{-1}$  attributed to  $-\text{NO}^{\delta+}$  and  $-\text{O}-\text{NO}^{\delta+}$  species adsorbed on cation sites in IrCu-ZSM-5 catalyst respectively; bands at  $1625\text{ cm}^{-1}$ ,  $1598\text{ cm}^{-1}$  attributed to bridged nitrate species while band at  $1568\text{ cm}^{-1}$  attributed to chelating bridged nitrate species on cation sites. Generally, Cu, Ir or both Cu and Ir could be the cation sites of IrCu-ZSM-5. It was difficult to tell exactly the adsorption sites for  $-\text{NO}^{\delta+}$ ,  $-\text{O}-\text{NO}^{\delta+}$  and nitrate species. However, Cu sites were regarded as preferred adsorption sites in IrCu-ZSM-5 considering the existence of chelating nitrate species similar to those on Cu sites in Cu-ZSM-5. When excess oxygen was introduced into NO/He system, a sharp increase in peak intensities of IR bands corresponding to nitrate species (both bridged and chelating) and a mild increase in peak intensity of IR band corresponding to  $\text{NO}^+$  species could be observed. When  $\text{C}_3\text{H}_8$  was further introduced, no obvious changes in IR bands could be detected.

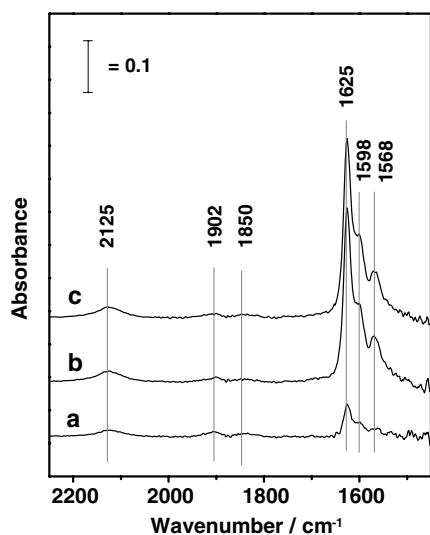


Fig. 6. DRIFTS study of adsorbed species on surface of IrCu-ZSM-5 catalyst in a flow of (a) 1000 ppm NO, (b) 1000 ppm NO + 5%  $\text{O}_2$ , (c) 1000 ppm NO + 1000 ppm  $\text{C}_3\text{H}_8$  + 5%  $\text{O}_2$  with He balance at  $400\text{ }^\circ\text{C}$ .

DRIFTS study of the species adsorbed on IrCu-ZSM-5 catalyst under reaction conditions ( $\text{NO} + \text{C}_3\text{H}_8 + \text{O}_2$ ) at different temperatures was also displayed. As seen in Fig. 7, there was no difference in the adsorbed species at the temperature from  $250\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$ ; only that the peak intensities of all IR bands corresponding to the species decreased with increasing temperatures.

Under  $\text{C}_3\text{H}_8$ -SCR conditions at  $400\text{ }^\circ\text{C}$ , the main adsorbed species on Cu-ZSM-5, Ir-ZSM-5 and IrCu-ZSM-5 were quite similar. Only adsorbed inorganic N-containing ( $-\text{NO}^+$ ,  $-\text{NO}^{\delta+}$ ,  $-\text{O}-\text{NO}^{\delta+}$  and  $-\text{NO}_3$ ) species were observed during the reaction and these inorganic N-containing species should be responsible for NO reduction. Adsorbed nitrate species should be the most active ones to be reduced by gaseous propane. The peak intensities of IR bands corresponding to adsorbed nitrate species could be observed as IrCu-ZSM-5 > Cu-ZSM-5 > Ir-ZSM-5 (Figs. 5 and 6), and so IrCu-ZSM-5 exhibited the highest  $\text{deNO}_x$  activity among the three. Adsorbed nitrate species were regarded as the main reaction intermediates for NO reduction. Therefore, bearing in mind that it is not yet clear in all cases if the adsorbed species observed by IR are intermediate or spectator species [3], the following proposal on the mechanism of  $\text{NO}_x$  reduction on IrCu-ZSM-5 is developed:

In the first reaction step, gaseous NO reacts with active oxygen and produces gaseous  $\text{NO}_2$ . Then nitrosonium ions ( $-\text{NO}^+$ ) are formed upon reaction between NO,  $\text{NO}_2$ , and the Brønsted acid sites as described in literature [32,33]. Newly formed  $-\text{NO}^+$  species can then migrate to neighboring acceptor at cation sites to produce  $-\text{NO}^{\delta+}$  or  $-\text{O}-\text{NO}^{\delta+}$  (interacting with lattice-O), probably by charge transfer. These  $\text{NO}^{\delta+}$  or  $-\text{O}-\text{NO}^{\delta+}$  species are not stable and will be oxidized to nitrate species by adsorbed oxygen atoms. The nitrates can then react with the reductant  $\text{C}_3\text{H}_8$  to give the final products  $\text{N}_2$ ,  $\text{CO}_2$  and  $\text{H}_2\text{O}$ .

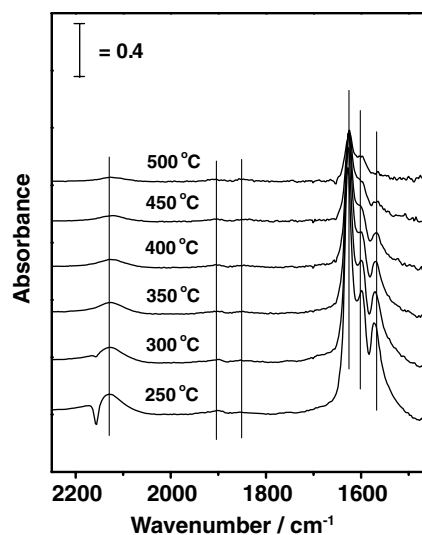


Fig. 7. DRIFTS study of adsorbed species on surface of IrCu-ZSM-5 catalyst in a flow reactant mixture (1000 ppm NO + 1000 ppm  $\text{C}_3\text{H}_8$  + 5%  $\text{O}_2$  with He balance) at the temperatures from  $250\text{ }^\circ\text{C}$  to  $500\text{ }^\circ\text{C}$ .

This proposal for the reaction mechanism of NO reduction on IrCu-ZSM-5 catalysts differs to a certain degree from the mechanism proposed for some other MFI catalysts containing Fe, Pd or Co [34]. It is, however, quite clear, that changes of the mechanism have to be expected if parameters of the reaction, e.g. the reductant or the catalytic active metal, are varied [3,34].

In his recent review article Burch has discussed the special properties of Ir-based catalysts in the NO<sub>x</sub> reduction reaction [3]. As he turned out, Ir can easily be oxidized when present in small particles. As a consequence, Ir-containing catalyst tend to oxidize NO to NO<sub>2</sub> rather than to reduce NO to N<sub>2</sub> or N<sub>2</sub>O. This is, indeed, shown for IrCu-ZSM-5.

In our opinion, the amount of Brønsted acid sites was a very important factor. In the first step for NO reduction, NO and NO<sub>2</sub> reacted with the Brønsted acid sites to form NO<sup>+</sup>. Obviously, the existence of Brønsted acid sites was necessary for the formation of –NO<sup>+</sup> and more Brønsted acid sites favored the formation of –NO<sup>+</sup>. However, in the following step, –NO<sup>+</sup> would migrate to the acceptor on cation sites of ZSM-5 to form –NO<sup>δ+</sup> or –O–NO<sup>δ+</sup>. Here, too many Brønsted acid sites were not good for the migration because they provided great interaction with –NO<sup>+</sup> species. Another important process for the formation of –NO<sub>3</sub> was the oxidation of –NO<sup>δ+</sup> or –O–NO<sup>δ+</sup> on the cation sites, which was determined by the properties of these sites. Obviously, higher oxidative activity was propitious to the formation of –NO<sub>3</sub> on cation sites.

In this study, the addition of trace iridium into Cu-ZSM-5 resulted in the change in the nature of copper species and improved the oxidative activity of copper species. The formation of nitrate species, the main reaction intermediates for C<sub>3</sub>H<sub>8</sub>-SCR, facilitated on IrCu-ZSM-5 than on Cu-ZSM-5. Thus, higher catalytic activity on IrCu-ZSM-5 could be obtained.

#### 4. Conclusion

Bimetallic IrCu-ZSM-5 was proved to be promising catalyst, better than Cu-ZSM-5 and Ir-ZSM-5, for the reduction of NO with propane in excess oxygen. The C<sub>3</sub>H<sub>8</sub>-SCR reaction mechanism over IrCu-ZSM-5, together with Cu-ZSM-5 and Ir-ZSM-5, was investigated and the formation of nitrate species was observed as main reaction intermediates for NO reduction with propane. The amount of Brønsted acid sites of catalyst and the oxidative activity of the cation sites were believed to have great effect on the formation of –NO<sub>3</sub> and then influenced the catalytic activity for NO reduction. The addition of trace iridium into Cu-ZSM-5 improved the oxidative activity of Cu sites and then promoted the deNO<sub>x</sub> activity of Cu-ZSM-5 in C<sub>3</sub>H<sub>8</sub>-SCR reaction.

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