

# On the correlation between microstructural changes of Ag-H-ZSM-5 catalysts and their catalytic performances in the selective catalytic reduction of NO<sub>x</sub> by methane

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## Abstract

The silver catalyzed, selective catalytic reduction (SCR) of nitrogen oxides (NO<sub>x</sub>) by CH<sub>4</sub>, is shown to be a structure-sensitive reaction. Pretreatment has a great affect on the catalytic performances. Upon thermal treatment in inert gas stream, thermal induced changes in silver morphology lead to the formation of reduced silver species of clusters and particles. Catalysis over this catalyst indicates an initially higher activity but lower selectivity for the CH<sub>4</sub>-SCR of NO<sub>x</sub>. Reaction induced restructuring of silver results in the formation of ill-defined silver oxides. This, in turn, impacts the adsorption properties and diffusivity of oxygen over silver catalyst, results in the decrease in activity but increase in selectivity of Ag-H-ZSM-5 catalyst for the CH<sub>4</sub>-SCR of NO<sub>x</sub>.

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**Keywords:** Ag-H-ZSM-5 catalyst; Selective catalytic reduction; NO<sub>x</sub>

## 1. Introduction

The nature of cations in the zeolite lattices can have profound effects on the catalytic activity of the zeolite. Zeolites in which silver ions were incorporated have shown particular catalytic activities in the reactions, such as the photodimerization of alkanes [1], the photochemical cleavage of water to H<sub>2</sub> and O<sub>2</sub> [2], and the partial oxidation of ethylene to ethylene epoxide [3]. In this connection, silver in the zeolites has been extensively studied. Silver species such as isolated silver atoms, charged or neutral silver clusters, and metallic silver particles have been characterized by UV–vis [4–6], XRD [7] and ESR [4,8] measurements.

Recently, a considerable number of studies have explored the catalytic properties of silver catalysts for the selective catalytic reduction of NO<sub>x</sub> by hydrocarbons [9–17]. Different states of silver are supposed to behave differently in cataly-

sis. It is generally believed that highly dispersed silver ions strongly interacting with the supports are effective for the reaction [9–12]. While point of views on the catalytic roles of the aggregated silver entities in the SCR reaction are still conflicted [13,14]. Our recent studies show that the formation of nano-silver particles on the outer surface of the zeolite accelerates the SCR reaction apparently, they provide much stronger adsorption centers for NO<sub>x</sub>, on which adsorbed NO<sub>x</sub> can be effectively reduced by the activated methane [17,18].

Most of studies, as mentioned above, are focused on the steady state of the reaction. In fact, the mobility of silver in the zeolites has been noticed for a long time, while the possibility of forming highly dispersed silver clusters is the incentives for these work [4–7,19–21]. Less attention has been paid to the correlation between their catalytic performances in catalysis and the microstructural changes of silver catalysts. In the present study, an attempt is made to relate the mobility of silver with the catalytic performance in the CH<sub>4</sub>-SCR of NO<sub>x</sub>. Microstructural changes of Ag-H-ZSM-5 catalysts under thermal treatment in inert and oxidative atmospheres were

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characterized by XRD, TEM and UV–vis measurements, and their functions in catalysis were investigated in the reaction of CH<sub>4</sub>-SCR of NO<sub>x</sub>.

## 2. Experimental

### 2.1. Sample preparation

Silver catalysts were prepared by ion-exchange method using H-ZSM-5 (with Si/Al=25, provided by Nankai University) as the starting materials. Silver ion exchange was carried out at room temperature in the dark for 24 h using 100 ml of aqueous silver (I) nitrate solution (0.001 M) to exchange 1 g zeolite each time. Generally, the exchange was repeated three or four times to reach high Ag exchange level. After exchange, the sample was filtered, washed with deionized water, and then dried at 120 °C overnight in air. The final

sample was analyzed by inductively coupled plasma emission spectrometry (ICP) to determine Ag content. The catalyst was labeled as Ag-H-ZSM-5 and the weight concentration of silver in per gram of zeolite was 9 wt.%, Ag exchange level was 89% (where 100% Ag<sup>+</sup> exchange denotes one Ag<sup>+</sup> ion neutralizing one Al<sup>-</sup>, i.e. the atomic ratio Ag/Al = 1).

### 2.2. SCR tests

The catalytic activity was measured using a micro-catalytic reactor by feeding the gas mixture of 0.2% NO, 0.2% CH<sub>4</sub>, 10% O<sub>2</sub> in He balance at a rate of 50 ml/min to 0.2 g catalyst, corresponding to GHSV = 12 000 h<sup>-1</sup>. Effluent gases were analyzed by gas chromatograph with a TCD detector. A molecular sieve 5A column was used to separate O<sub>2</sub>, N<sub>2</sub>, CH<sub>4</sub> and NO. The amount of N<sub>2</sub> produced and CH<sub>4</sub> consumed were used to calculate the conversion of NO to N<sub>2</sub> and the conversion of CH<sub>4</sub> to CO<sub>2</sub>. The selectivity of CH<sub>4</sub>

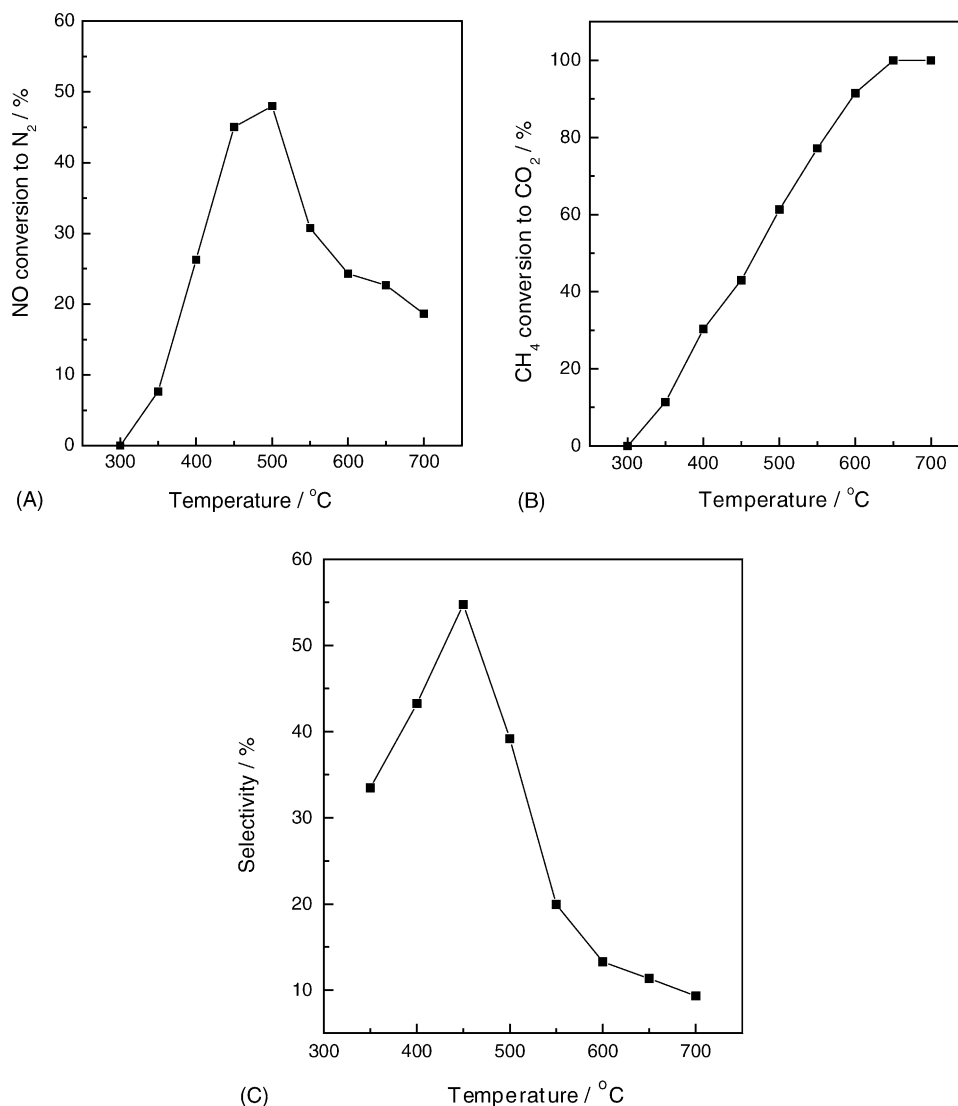


Fig. 1. Variation of NO conversion to N<sub>2</sub> (A), CH<sub>4</sub> conversion to CO<sub>2</sub> (B) and the selectivity (C) of Ag-H-ZSM-5 catalyst on reaction temperature.

was defined as the ratio of  $\text{N}_2$  produced to the amount of  $\text{CH}_4$  consumed.

### 2.3. Catalyst characterization

X-ray diffraction (XRD) was performed on a Rigaku powder diffract meter with  $\text{Cu K}\alpha$  radiation. The X-ray source was operated at 40 kV and 20 mA. The diffraction patterns were taken in the  $2\theta$  range of  $5\text{--}80^\circ$  at a scan speed of  $5^\circ/\text{min}$  and a step width of  $0.02^\circ$ .

UV–vis diffuse reflectance spectra were recorded in air on a V-550 UV–vis spectrophotometer. Reference spectra were collected with pressed polytetrafluoroethylene (PTFE) disks. The following parameters were used to collect data: 5.0 spectra band width, 0.5 nm data pitch, 800–190 nm measurement range, and 200 nm/min scanning speed.

Transmission electron microscopy (JEX-2000EX) operated at 100 kV was used to study the morphology of catalyst

samples. The sample was supported on a copper mesh to the TEM analysis.

## 3. Results

### 3.1. Activity measurements

In Fig. 1, the conversion of  $\text{NO}$  to  $\text{N}_2$  (A),  $\text{CH}_4$  to  $\text{CO}_2$  (B), and the selectivity (C) of Ag-H-ZSM-5 catalyst are shown as a function of reaction temperature. The  $\text{NO}$  conversion to  $\text{N}_2$  increased with reaction temperature before  $500^\circ\text{C}$ , up to that, the conversion decreased. However, the  $\text{CH}_4$  conversion increased monotonously with temperature, and the conversion reached 100% at  $650^\circ\text{C}$ . The selectivity gave a volcano-type curve, and decreased apparently at higher temperatures. This might be due to the direct combustion of  $\text{CH}_4$  with  $\text{O}_2$  was greatly accelerated by raising reaction temperature, which

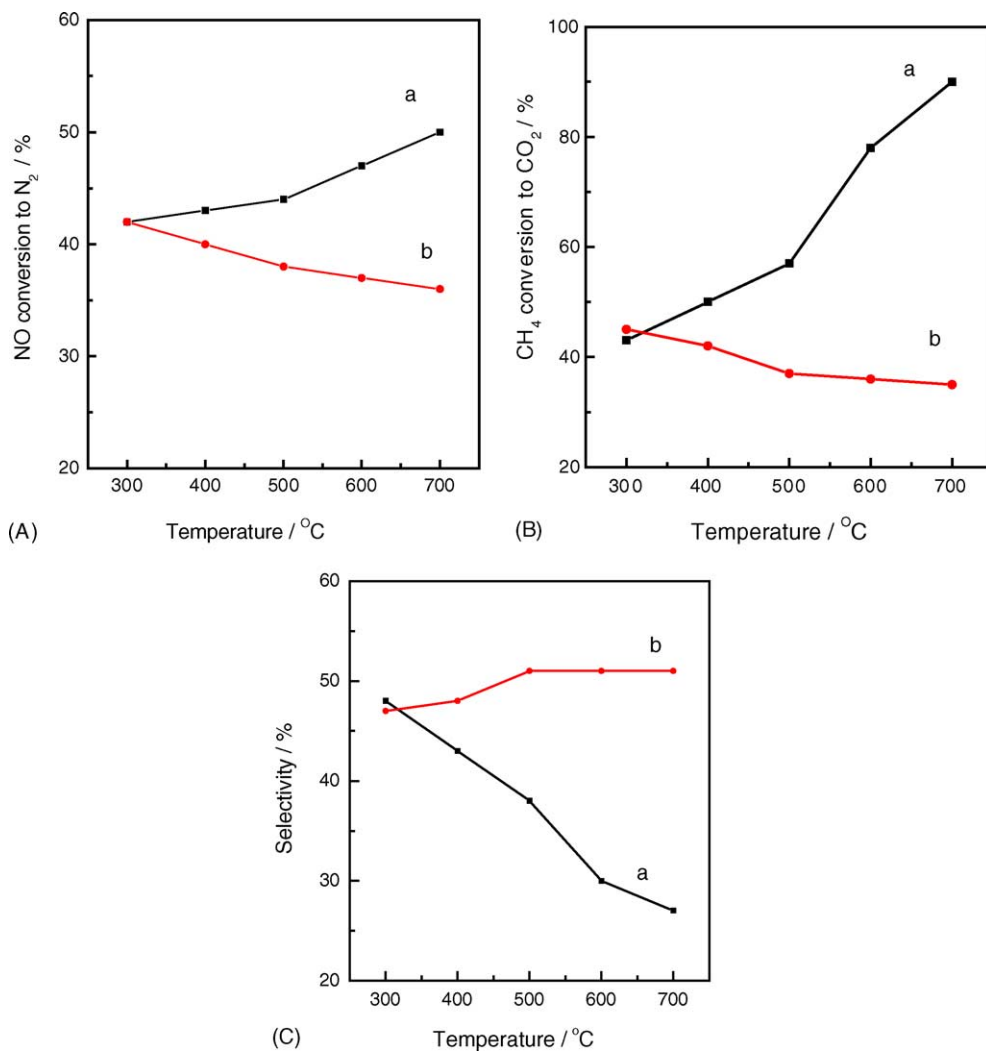


Fig. 2. Dependence of  $\text{NO}$  conversion to  $\text{N}_2$  (A),  $\text{CH}_4$  conversion to  $\text{CO}_2$  (B) and the selectivity (C) of Ag-H-ZSM-5 catalyst on pretreatment temperature in the atmospheres of He (a) and 30%  $\text{O}_2/\text{He}$  (b), respectively.

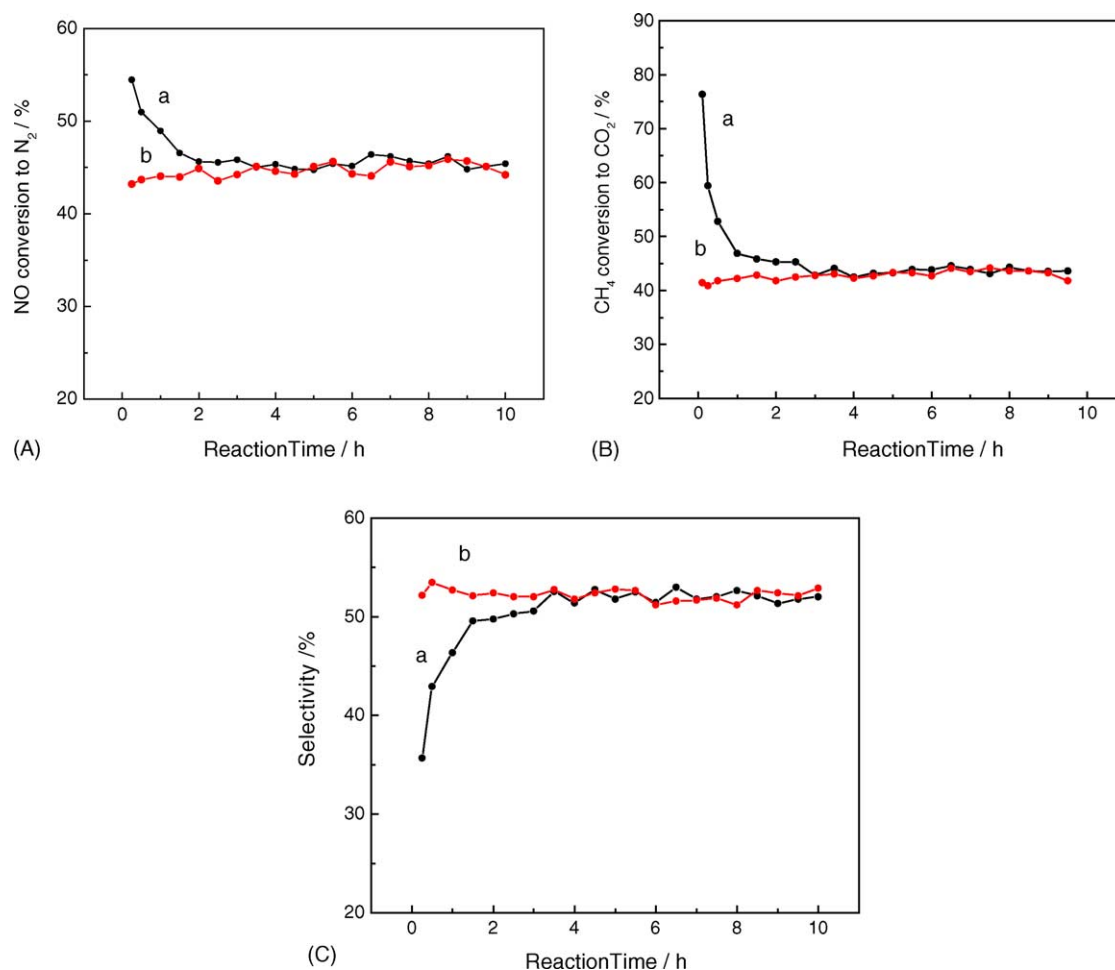


Fig. 3. Variation of NO conversion to N<sub>2</sub> (A), CH<sub>4</sub> conversion to CO<sub>2</sub> (B) and the selectivity (C) of Ag-H-ZSM-5 catalyst on reaction time upon thermal treatment in He (a) and 30% O<sub>2</sub>/He (b) gas streams.

resulted in the decrease of selectivity for the CH<sub>4</sub>-SCR of NO<sub>x</sub>.

Pretreatment in inert and oxidative gas streams have different influence on the catalytic activity and selectivity of Ag-H-ZSM-5 catalysts for CH<sub>4</sub>-SCR of NO<sub>x</sub>. Fig. 2 shows the NO conversion to N<sub>2</sub> (A), CH<sub>4</sub> conversion to CO<sub>2</sub> (B) and the selectivity (C) of Ag-H-ZSM-5 catalysts at 500 °C as related to pretreatment temperatures in He (a) and 30% O<sub>2</sub>/He (b) gas streams. The data were collected when the feed gases were introduced just 15 min. With raising the pretreatment temperatures from 300 to 700 °C in He gas stream, the catalytic activity was increased apparently. Since CH<sub>4</sub> conversion was simultaneously enhanced from 42% to 90%, the selectivity of Ag-H-ZSM-5 catalyst for the CH<sub>4</sub>-SCR of NO<sub>x</sub> was decreased with the increase of pretreatment temperature. However, upon thermal treatment in 30% O<sub>2</sub>/He gas streams, the NO and CH<sub>4</sub> conversions decreased with the pretreatment temperature. Due to the debasement of CH<sub>4</sub> conversion was more significant than that of NO conversion, the selectivity of Ag-H-ZSM-5 catalyst was enhanced.

Fig. 3 compares the variation of NO conversion to N<sub>2</sub> (A), CH<sub>4</sub> conversion to CO<sub>2</sub> (B) and the selectivity (C) of Ag-H-

ZSM-5 catalyst at reaction temperature of 500 °C on reaction time. The catalysts were pretreated at 500 °C for 1 h before the reaction in pure He (a) and 30% O<sub>2</sub>/He (b) gas streams, respectively. Upon thermal treatment in inert gas stream, Ag-H-ZSM-5 catalyst showed the highest NO conversion to N<sub>2</sub> in the initial stage of the reaction, then gradually lost its activity from 54% to 45% in the following 2 h. While the selectivity was increased from 35% to 50% in this period. The activity and selectivity of Ag-H-ZSM-5 catalyst stabilized at ca. 45% and 50% within the following hours. However, upon thermal treatment in 30% O<sub>2</sub>/He gas streams, the activity and selectivity of Ag-H-ZSM-5 catalyst did not change with reaction time. Moreover, similar catalytic activity and selectivity were observed in the steady stage of the reaction, no matter the catalyst was pretreated in inert or oxidative atmospheres. The results suggest that different microstructural changes of silver might occur upon thermal treatment in inert gas stream and oxidative atmospheres, which leads to the different catalytic performances of Ag-H-ZSM-5 catalysts in the initial stage of reaction. The structures formed under oxidative atmospheres are stable in the CH<sub>4</sub>-SCR of NO<sub>x</sub> reaction.

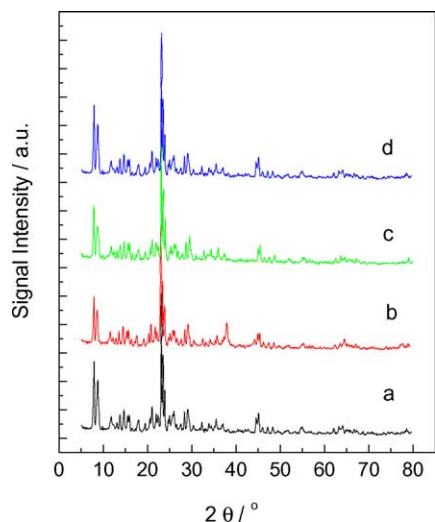


Fig. 4. XRD patterns of fresh Ag-H-ZSM-5 catalyst (a), the catalyst after the treatment in He stream (b) and the treatment in 30% O<sub>2</sub>/He (c) at 500 °C for 1 h, as well as the used catalyst in CH<sub>4</sub>-SCR reaction at 500 °C for 10 h (d).

### 3.2. Catalyst characterization

Fig. 4 shows the XRD patterns of the fresh Ag-H-ZSM-5 catalyst (a), the catalysts treated in pure He (b) and 30% O<sub>2</sub>/He (c) gas streams at 500 °C for 1 h, as well as the used catalyst in 0.2% NO/0.2 %CH<sub>4</sub>/10% O<sub>2</sub>/He at 500 °C for 10 h (d). For the fresh sample, only the diffractions of ZSM-5 zeolite are displayed, the diffraction peaks for silver oxide or metallic silver are not observed. After the thermal treatment in He stream, the diffraction peaks for metallic silver at  $2\theta$  of 38° and 44° appear, which indicate that reduced silver particles are formed on the zeolite surface upon the thermal treatment in inert gas stream. While upon the thermal treatment in oxidative atmospheres, no line due to silver oxide and metallic silver particles is observed, and only the diffractions of ZSM-5 zeolite are shown. As to the used sample, the XRD pattern is quite similar to that of the sample pretreated in oxidative atmosphere, only the diffractions of ZSM-5 zeolite are detected.

The morphology and particle size of silver for the thermal treated samples and the used catalyst were studied by TEM, and shown in Fig. 5. Nano-sized silver particles dispersed on the surface of zeolite crystals are observed over all of the samples, and the particle sizes range from several to ca. 30 nm as depicted by the figures. For the oxygen treated Ag-H-ZSM-5 sample, although no line due to crystallized silver oxide and metallic silver particles were observed by XRD measurement, nano-sized silver particles are presented on the surface of ZSM-5 zeolite, and the particle sizes are similar to those formed in inert gas stream as shown by the TEM photos. As to the used sample, silver particles are well dispersed on the zeolite surface, but the particle sizes are slightly larger than those of other samples.

The co-existence of different kinds of silver species, especially small silver species such as silver ions and silver clusters, can be discriminated by UV–vis spectroscopy. Fig. 6 shows the UV–vis spectra of the fresh Ag-H-ZSM-5 catalyst (a), the catalysts treated in pure He (b) and 30% O<sub>2</sub>/He (c) gas streams at 500 °C for 1 h, as well as the used catalyst in 0.2% NO/0.2% CH<sub>4</sub>/10% O<sub>2</sub>/He at 500 °C for 10 h (d). On the fresh sample, three strong overlapped bands centered at 196, 212 and 224 nm are discriminated. The three overlapped bands have been assigned to the  $4d^{10}-4d^95s^1$  electronic transition of isolated silver ions in the zeolites [9,22]. For the thermally treated sample in He stream, the three bands at 196, 212 and 224 nm for silver ions, though reduce absorbance, still remain on the sample. Except that, four new bands appear at 285, 322, 356 and 392 nm, respectively. The bands at 285 and 322 nm is ascribed to silver clusters located in zeolite channels, the size of these clusters is estimated to be smaller than several atoms [4,5,10]. The broad bands centered at 356 and 392 nm are the characteristic absorbance of metallic silver particles, which may be several nanometers or much larger [22–24]. The results indicate that some silver ions were reduced upon thermal treatment in inert gas stream. However, after thermal treatment in oxidative atmospheres, no absorption band due to the reduced silver particles of clusters and particles are observed. Instead of that, a broad band centered at 430 nm appears on the sample. The profile of the used sample is very similar to that of the sample treated in oxidative atmospheres, except that the band at 430 nm is much broader. As to the assignment of the band at 430 nm, Pestryakov et al. had ascribed this band to the absorption of metallic silver particles [25]. While Gellens et al. had assigned it to the charged silver species formed in oxidative atmospheres [26]. In this study, we found that a strong band at 430 nm was formed when AgNO<sub>3</sub> solution was deposited on the zeolite surface at pH > 9. Moreover, it should be pointed out that no XRD pattern relating either to metallic silver crystal or to silver oxides were found for the oxidized silver catalysts, although TEM image indicated nano-sized silver particles existed on the surface. Therefore, it can be concluded that the band at 430 nm is not due to the absorption of metallic silver but an amorphous character of ill-defined mixed oxides.

### 3.3. Mobility of silver

The mobility of silver under thermal treatment in inert and oxidative atmospheres was further studied by UV–vis measurements. Fig. 7(A) shows the UV–vis spectra of Ag-H-ZSM-5 catalyst upon thermal treatment in He stream at various temperatures. Silver exchanged into H-form ZSM-5 zeolite exists only as silver ions. Below 120 °C, only the absorption bands for silver ions at 196, 212, and 224 nm are present. The absorbance bands for silver ions slightly decrease at 300 °C. The new bands at 285 and 322 nm for silver clusters and two weak and broad bands at 356 and 392 nm for metallic silver particles emerge. These facts suggest that some silver ions are reduced, and the reduced silver atoms ag-

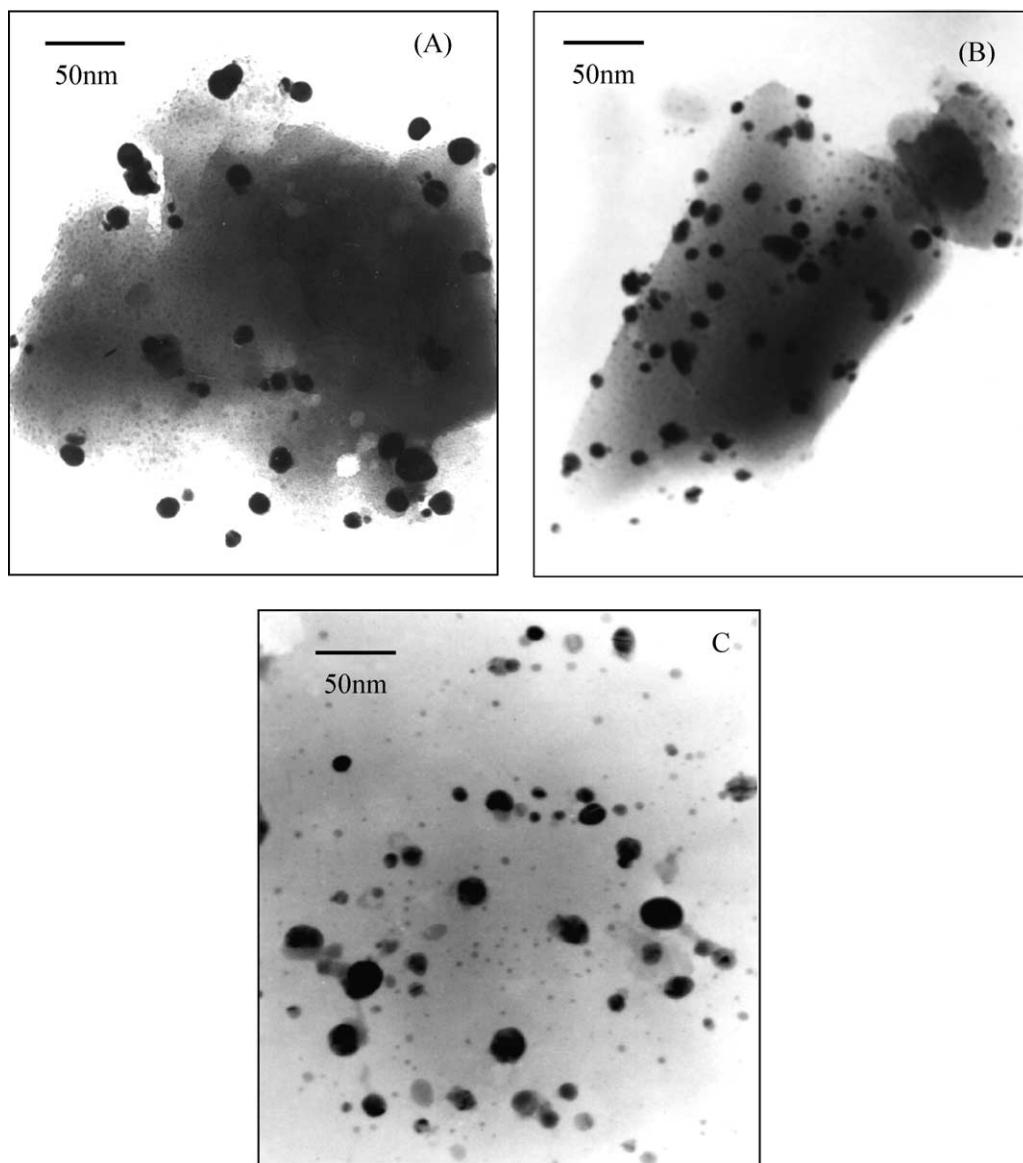


Fig. 5. TEM images in the Ag-H-ZSM-5 catalysts after pretreatment in He stream at 500 °C for 1 h (A), and the catalyst after pretreatment in 30% O<sub>2</sub>/He gas streams at 500 °C for 1 h (B), as well as the used catalyst in CH<sub>4</sub>-SCR reaction at 500 °C for 10 h (C).

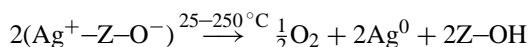
gregate together into silver clusters and further into metallic silver particles at this temperature. With the increase of pretreatment temperatures, the absorbance bands for silver ions and the absorbance for silver clusters gradually decrease, the bands at 356 and 392 nm for metallic silver particles grow and become much sharper. The highest absorbance bands at 356 and 392 nm, indicating a highest portion of metallic silver particles, is observed on the sample after the treatment at 700 °C. These changes in the UV–vis spectra clearly depict that silver ions are transformed into silver clusters, and finally into silver particles at elevated temperatures. The self-reduction, migration and aggregation of silver at elevated temperatures in the inert gas stream are afforded for the transformation.

Fig. 7(B) shows the UV–vis spectra of Ag-H-ZSM-5 catalysts upon thermal treatment in 30% O<sub>2</sub>/He gas streams at

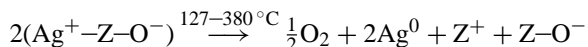
various temperatures. Different from those treated in flowing He, all the spectra are very similar. The absorption bands in the low wavelength region, which have been ascribed to the absorbance of silver ions, appear in all samples. The bands at 285 and 322 nm for silver clusters and the bands at 356 and 392 nm for metallic silver particles are not present in the whole temperatures. A broad band centered at 430 nm appears above 500 °C, and the absorbance increases with temperature. The band at 430 nm, as previously assigned, is due to the absorption of the ill-defined silver oxides. The results indicate that structure changes of silver catalysts occurring in oxidative atmosphere different from those in inert gas stream. It is also apparent that silver surface is extremely mobile under the applied conditions.

#### 4. Discussion

Silver ions in the zeolites can be automatically reduced to silver atoms during thermal dehydration [6]. The physico-chemical transformations involve (a) removal of molecular water from the zeolite; (b) partial reduction of silver ions with an evolution of oxygen and formation of lattice hydroxyl groups in a low temperature region according to



(c) further reduction of silver ions with additional evolution of oxygen and formation of Lewis acid centers in a high temperature region according to



These changes have been clearly observed in UV–vis spectra as shown in Fig. 7(A). However, because of the lower Tamann temperature (370 °C) of silver, the treatment at temperatures higher than 370 °C can cause bulk transformation of silver. Bulk transition may either be thermally induced or reaction induced [27,28]. Changes, which are thermally induced, occur with or without the presence of a reacting atmosphere. This process is driven in such a way as to result in a decrease of surface free energy. The high temperature treatment in inert gas stream (>370 °C) leads to the growing of the bands at 356 and 392 nm, which have been ascribed to the characteristic absorption of metallic silver particles. These results indicate that the bulk transformation of silver occurs above this temperature, reduced silver clusters aggregate into nano-silver particles to achieve a minimization of surface free energy.

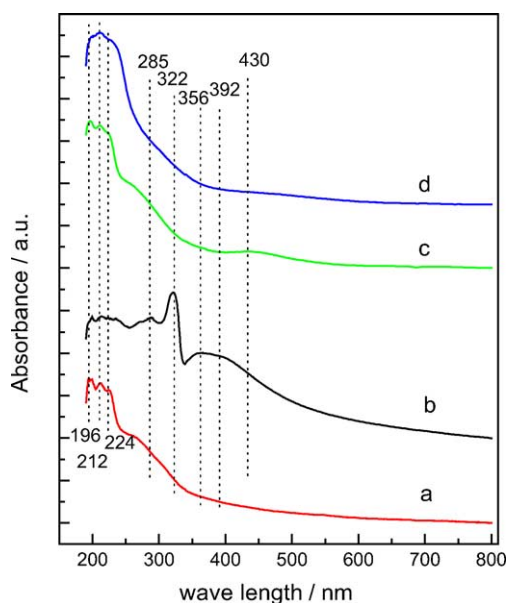
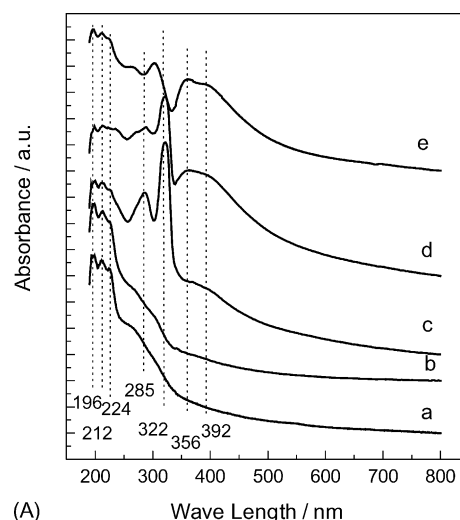


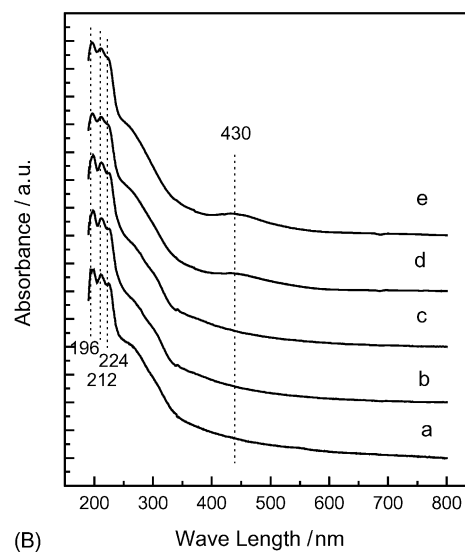
Fig. 6. UV–vis spectra of fresh Ag-H-ZSM-5 catalyst (a), the catalyst after pretreatment in He stream at 500 °C for 1 h (b), and the catalyst after pretreatment in 30% O<sub>2</sub>/He gas streams at 500 °C for 1 h (c), as well as the used catalyst in CH<sub>4</sub>-SCR reaction at 500 °C for 10 h (d).

Reaction induced microstructure changes occur in a reacting atmosphere and result in the formation of structures different from those in an inert gas or vacuum. Oxygen treatment of silver catalyst at elevated temperatures can cause thermally induced aggregation and reaction induced restructure of silver. The thermal reduction and aggregation of silver tends to the formation of silver clusters and nanometer silver particles. Oxygen oxidizes reduced silver species into silver ions and depresses the growing of silver particles. The formation of ill-defined silver oxidized particles can be a combined result of thermally induced aggregation and reaction induced restructure of silver.

Correlated the characterization results with the catalytic activity and selectivity of Ag-H-ZSM-5 catalyst for the CH<sub>4</sub>-SCR of NO<sub>x</sub>, it was shown that under thermal treatment in inert gas stream, silver ions self-reduced and aggregated into



(A)



(B)

Fig. 7. UV–vis spectra of Ag-H-ZSM-5 samples after pretreatment in He gas stream (A) and 30% O<sub>2</sub>/He gas streams (B) at different temperatures of (a) 120 °C, (b) 200 °C, (c) 300 °C, (d) 500 °C, and (e) 700 °C.

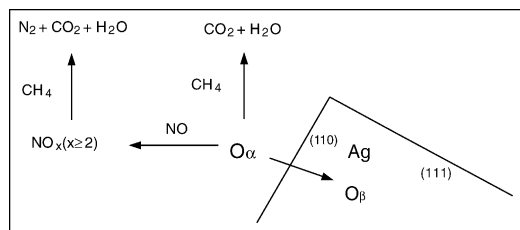


Fig. 8. Proposed mechanism for the participation of surface oxygen in the SCR of  $\text{NO}_x$  by  $\text{CH}_4$ .

silver clusters and nano-sized metallic silver particles. The catalysts showed initially higher activity but lower selectivity for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ . The reduced silver species were gradually oxidized into ill-defined oxides by the excess of  $\text{O}_2$  during the SCR reaction. Consequently, the catalyst lost part of its activity, but showed increasing selectivity for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ . The results indicate that Ag-H-ZSM-5 catalyst is a structure sensitive catalyst, the microstructure changes of that had great influence on the catalytic activity and selectivity for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ .

Various silver bound oxygen species formed during the reaction are discussed here in attempt to interpret the different catalytic behaviors of silver entities in the  $\text{CH}_4$ -SCR reaction as illustrated by Fig. 8. Under thermal treatment in inert gas stream, reduced silver clusters and metallic silver particles prevailed on the catalyst. When such surface was exposed to the reactant gases, oxygen would adsorb on it. These surface adsorbed oxygen species ( $\text{O}_\alpha$ ) might participate the SCR reaction in two ways. One is oxidation of NO to  $\text{NO}_x$  ( $x \geq 2$ ), which has been detected by FTIR measurements as active intermediates [10,16]. The other is catalyzing the direct combustion of methane. As has been extensively studied in the reaction of epoxidation of ethylene and oxidative coupling of methane, surface adsorbed oxygen species ( $\text{O}_\alpha$ ) on Ag catalyze the complete oxidation of hydrocarbons to  $\text{CO}_2$  and  $\text{H}_2\text{O}$  [26,29]. Thus at the beginning of the SCR reaction, due to the existence of large amount of active intermediates  $\text{NO}_x$  ( $x \geq 2$ ), silver catalysts showed higher activity for the selective catalytic reduction of  $\text{NO}_x$  by  $\text{CH}_4$ . Simultaneously, the direct combustion of  $\text{CH}_4$  with  $\text{O}_2$  was accelerated by the surface adsorbed oxygen, which decreased the selectivity of Ag-H-ZSM-5 for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ . With the proceeding of the SCR reaction, surface adsorbed oxygen may diffuse into the silver lattice to form bulk dissolved oxygen ( $\text{O}_\beta$ ) [30]. Due to the diffusion of surface adsorbed oxygen into the bulk, the amount of active intermediates  $\text{NO}_x$  ( $x \geq 2$ ) decreased. Simultaneously, the total oxidation of  $\text{CH}_4$  with surface adsorbed oxygen ( $\text{O}_\alpha$ ) was suppressed. These resulted in the decrease in activity but increase in selectivity of Ag-H-ZSM-5 catalyst for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ . When the adsorption and diffusion of oxygen on silver surface reached the dynamic equilibrium, the catalytic activity and selectivity of Ag-H-ZSM-5 catalyst did not change with reaction time.

## 5. Conclusions

Pretreatment in inert and oxidative gas streams had different influence on the catalytic activity and selectivity of Ag-H-ZSM-5 catalysts in the initial stage of  $\text{CH}_4$ -SCR of  $\text{NO}_x$  reaction. Upon thermal treatment in inert gas stream, silver catalysts had higher activity but poor selectivity for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ . While the catalysts showed higher selectivity but lower activity after the high-temperature pretreatment in oxidative gas streams. Catalyst characterization results indicated that the reduced silver species prevailed on the catalysts upon the thermal treatment in inert gas stream, while ill-defined silver oxides were formed in oxidative gas streams. Correlated catalytic performances with the characterization results, it was concluded that the NO conversion to  $\text{N}_2$  was increased on the reduced silver species, but the direct combustion of  $\text{CH}_4$  with  $\text{O}_2$  was accelerated simultaneously, which resulted in the lower selectivity of Ag-H-ZSM-5 catalyst for the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ . During the SCR reaction, the reduced silver species were gradually oxidized by the excess  $\text{O}_2$  in the feed gases. Thus the NO conversion to  $\text{N}_2$  decreased with the time on stream gradually, while the selectivity of Ag-H-ZSM-5 was increased. The migration of surface adsorbed oxygen species into the bulk was supposed to be responsible for the different catalytic behaviors of silver entities in the  $\text{CH}_4$ -SCR of  $\text{NO}_x$ .

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