Ag-ZSM-5 Catalyst for the Catalytic Decomposition of NO

Jia Wei TENG[1], Tian Xi CAI[1], Xin He BAO[2, *]

[1]School of Chemical Engineering, Dalian University of Technology, Dalian 116012
[2]State key Laboratory of Catalysis, Dalian Institute of Chemical Physics, Dalian 116023

Abstract: The catalytic decomposition of NO over Ag-ZSM-5 catalyst prepared by ion-exchange was investigated. The exchanged silver in the zeolite was reduced and it collected in the course of the reaction to form silver particles of about 20 nm. The catalytic reaction induced a pronounced restructuring of the Ag particles through preferential formation of the (111) facets. These facets were shown to bind a tightly bound oxygen species (O_γ) . The O_γ species occupies the active sites for NO adsorption resulting in catalyst deactivation. It could be removed by appropriate reducing agents, such as CO, to recover the active sites at elevated temperatures.

Keywords: Ag-ZSM-5 catalyst; NO; decomposition.

Nitrogen oxides (mainly NO) are major air pollutants that cause photochemical smog and acid rain. Therefore, there is a worldwide effort to discover improved solutions for the effective removal of NO_x emissions[1]. Until now, no suitable catalyst that can effectively convert NO into N_2 and O_2 although the chemical reaction is thermodynamically favorable at low temperatures. Previous studies have shown that the highly active catalysts, for example, noble metals and metal oxides, usually exhibit a strong affinity for atomic oxygen, and can hold the adsorbed atomic oxygen to higher temperatures. The tightly bound oxygen species on the surface occupies the active sites for NO adsorption and impedes the adsorption and decomposition of NO on the catalyst surface, resulting in catalyst deactivation. It is widely known that silver shows a weak affinity towards oxygen, and atomic oxygen species adsorbed on silver can, except for a few percentages of adsorbed surface oxygen atoms diffuse into the bulk phase of silver, recombine at the surface and desorb into the gas phase at about 600 K. The unique redox character of silver hints at the ability of Ag-containing catalysts for catalyzing NO decomposition. The objective of the work described here is to study the activity of Ag-ZSM-5 for the decomposition of NO and the structural variations of Ag particles in the course of catalytic reaction.

Experimental

Na-ZSM-5 supplied by Degussa (Si/Al=20.1) was first converted into the NH_4-form, and then was exchanged with an aqueous silver nitrate solution at room temperature in the dark.

After the desired repetition of ion- exchange treatments, the obtained sample was washed and dried in air at 373 K.

NO decomposition was carried out using about 0.25 g catalyst in a conventional fixed-bed flow reactor . A gas mixture including NO (2.0vol%) and He (balance) was fed at 10 $cm^3 \cdot min^{-1}$ flow rate. The product distribution was detected by QMS (OmniStar 200) and chromatography using a molecular sieve 5A column. The activity was evaluated in terms of conversion as: $N_2=2[N_2]_{out}/[NO]_{in}\times 100\%$

XRD spectra were obtained using a Rigaku D/max-γb X-ray diffractometer with carbon-filtered copper K_α radiation.

Results and discussion

Figure 1. Temperature dependence of the catalytic decomposition of NO over Ag-ZSM-5.

Test conditions:
2.0%NO in He, W/F=1.5g.s.cm^{-3}.
a) First run
b) Second run.

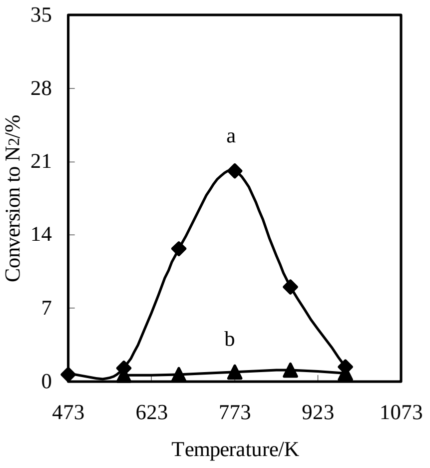
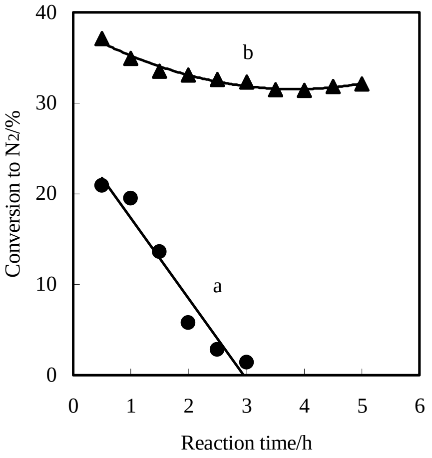


Figure 2. Time dependence of the catalytic decomposition of NO over Ag-ZSM-5 at 773K.
Test conditions:
a) 2.0%NO in He, W/F=1.5g·s·cm^{-3}
b) 1.0%NO + 1.0% CO in He,



As shown in **Figure 1**, the decomposition of NO starts at 573 K over Ag-ZSM-5 catalyst, and the maximum activity with about 20% NO conversion to N_2 is at about 773K. This is markedly lower than that reported for the same reaction over catalysts with precious metals as an active component. It was reported that in the reaction of NO decomposition, NO adsorbs dissociatively producing atomic nitrogen and oxygen on the surface at elevated temperatures. The atomic nitrogen formed recombines and desorbs as di-nitrogen in a wide window of temperatures, while the atomic oxygen is bound tightly to the active sites and leaves the surface only at high temperatures. The adsorbed oxygen competes with NO for adsorption sites, resulting in catalyst deactivation. Most studies on the interaction of oxygen with silver showed that metallic silver has a weak affinity towards oxygen, and the surface oxygen species (O_α) formed by exposing silver to oxygen at low temperatures can desorb from the surface at about 600 K[2]. This will vacate the surface for a subsequent adsorption. Accordingly, silver-containing catalysts should show significant catalytic activity for the decomposition of NO at this characteristic temperature (about 600K). This explains the low starting temperature of the reaction on Ag-ZSM-5, as shown in **Figure 1**. However, the catalytic decomposition of NO over this catalyst gave an unexpectedly low activity. The apparent conversion of NO was only about 2% at 573 K. A systematic study on the interaction of silver with NO/O_2 on the Ag (110) single crystal surface by Bao *et al* [3] showed that the adsorption of oxygen on the silver surface in the presence of NO is quite different from that in only an oxygen atmosphere. Even at low exposure temperatures, the resultant oxygen species showed high thermal stability, and did not desorb from the surface until the sample temperature reached 775 K. This is about 200 K higher than that needed for the desorption of the oxygen species formed in an atmosphere containing only oxygen. The coincidence of the temperature of oxygen desorption and maximum activity suggests that the reaction activity of NO decomposition over Ag-ZSM-5 catalyst is correlated closely with the desorption of oxygen species from the silver surface.

As presented in curve (a) of **Figure 1**, after a maximum at 773 K, the conversion of NO drops distinctly with increase in the reaction temperature. Moreover, the activity cannot be simply recovered by lowering the reaction temperature from 973 K again to 773 K **Figure 1 (**b). This reaction feature indicates that catalyst deactivation at high temperatures is not due to any changes in reaction mechanism, and it may be attributed to some irreversible structural variations of the active sites of the catalyst during the reaction.

Table 1. Content of Ag and Al in Ag-ZSM-5 from ICP measurement

Catalyst	Content (wt%)		Conditions
	Ag	Al	
Ag-ZSM-5	3.94	2.15	Before reaction
Ag-ZSM-5	4.07	1.95	After reaction

The corresponding ICP measurements are listed in **Table 1**. The results revealed that the amount of silver in the used catalyst did not change markedly compared with that in the fresh Ag-ZSM-5, indicating that silver suffered no obvious loss during the reaction. Corresponding XRD data summarized in **Table 2** showed that no XRD patterns assigned to crystalline silver were obtained from the fresh Ag-ZSM-5, indicating that the silver in the zeolite incorporated by ion-exchange was highly dispersed. After reaction, the silver was reduced and collected to form larger particles in the catalyst, as evidenced by the emergence of the characteristic patterns of crystalline silver in the XRD results. The dimension of the silver particles, calculated using the Scherrer equation from the broadening of the corresponding x-ray diffraction lines, increased in the initial stages of the reaction and then kept apparently constant when the reaction temperature was raised from 673K to 973K, as presented in **Table 2**. Therefore, the actual decrease in the conversion of NO to N_2 at high temperatures (**Figure 1**) would not be caused by a variation of the dimension of the silver particles, that is, in the decrease of the active area of silver.

In the studies on the interaction of O_2 with silver single crystals [4, 5], it was found that the treatment of silver in an oxygen atmosphere at high temperatures might lead to a pronounced restructuring of silver surface. The interaction of oxygen with the restructured silver surface gives rise to an activated formation of a novel oxygen atom, named O_γ on the silver surface. This tightly held species is thermally very stable, and desorbs at temperatures between 750 K and 950 K, depending on the temperature used for the oxygen treatments. In the present experiment, the existence of oxygen atoms (produced in the decomposition of NO) would also lead to restructuring of the aggregated silver particles, as evidenced by XRD measurements. The interaction of oxygen with the restructured silver surface may lead to the formation of a tightly held species-O_γ, which does not leave the surface at the temperature used for NO decomposition. The competition of O_γ with NO for adsorption sites impedes the adsorption and decomposition of NO on the silver surface, resulting in the decrease in the catalytic activity at high temperatures.

Table 2. Silver particle sizes obtained from x-ray diffraction

D (nm)	Reaction conditions				
	Fresh	673K	773K	873K	973K
D_{111}	undetected	22.2	21.3	25.2	20.5
D_{220}	undetected	41.3	38.7	31.0	34.4

The data in curve (a) in **Figure 2** reveals a marked instability in the activity of NO decomposition over Ag-ZSM-5 at 773 K. Conversion of NO to N_2 decreased from 20% to low levels within about 3 hours. However, the addition of 1% CO into the feed gas induced a stable activity (profile b). This is due to the actual reaction of the coexisting CO with the tightly bound oxygen species, recovering the active sites for the decomposition of NO. To summarize the experimental results, metallic silver is not a suitable catalyst for the decomposition of NO at low temperature (<775 K). However, if the reconstruction of the surface of the silver particle which form the favorable structures for holding tightly bound oxygen species can be effectively avoided or such oxygen species can be removed immediately by appropriate reducing agents, the Ag-containing materials would be a good catalyst for the direct decomposition of NO at low temperature.

References

1. J. N. Armor. *Catal. Today*, **1995**, *26*, 99.
2. C. Rehren, M. Muhler, X. Bao *et al* . *J Phys Chem*, **1991**, *174*, 11.
3. X. H. Bao, U. Wild, M. Muhler *et al* . *CUI HUA XUE BAO*, **1998**, *19*, 18.
4. X. Bao, J. V. Barth, G. Lehmpfuhl *et al* . *Surf Sci*, **1993**, *284*, 14.
5. X. Bao, M. Muhler, Th. Schedel-Niedrig *et al* . *Phys Rev B*, **1996**, *54*, 2249.

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