Catalysis Letters 6 (1990) 239–244

SELECTIVE REDUCTION OF NITROGEN OXIDES WITH HYDROCARBONS OVER SOLID ACID CATALYSTS IN OXYGEN-RICH ATMOSPHERES

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Received 5 May 1990; Accepted 7 August 1990

Nitrogen oxides selective reduction, hydrocarbon, propane, solid acid catalysts, alumina, silica-alumina, zirconia, titania

Highly selective reduction of nitrogen oxides to dinitrogen occurs to a high level in oxygen-rich atmospheres by using a small amount of propane as a reducing agent over alumina, silica-alumina, titania and zirconia catalyst. Judging from the data of activity and ammonia TPD measurement on a series of silica-alumina catalysts, acidity is suggested to be one of the main factors that determine catalytic activity.

1. Introduction

The adverse effect of increasing emission of nitrogen oxides (NOx) is well known. Selective catalytic reduction (SCR) process with ammonia [1] is now widely used to remove NOx from stationary sources such as industrial boilers and power stations. The principal advantage of this process is its ability to reduce NOx in the presence of oxygen [2]. However, the use of ammonia which is difficult to handle makes this process unsuitable for oxygen-rich NOx emissions such as small-scale diesel engine exhausts.

Several investigations have been made to develop selective agents other than ammonia. For example CO and H_2 have been known to be effective under very limited conditions [3–5]. With respect to hydrocarbons, Volkswagen [6] and Toyota [7] have patents of catalytic systems able to remove NOx in auto exhausts with oxidizing atmospheres. They claim use of transition metal-containing zeolite catalysts or supported copper catalysts. However, the evaluation of hydrocarbons as the selective reducing agents is not clear because they are generally considered to be non-selective.

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During investigations of NOx reduction with hydrocarbons over various catalysts, we have recently found that the reduction occurs highly selectively even in the presence of about 10% of oxygen by using decationated H-form zeolite catalysts and small amounts of hydrocarbons as reducing agents [8]. Since it was speculated that acidity of the zeolites is responsible for the selective reduction, other catalytic systems have successively been investigated.

The present study reports an excellent activity of some metal oxide catalysts such as alumina for the selective reduction of NOx with hydrocarbons in oxidizing atmospheres. The relationship between the activity and acidity of the catalysts is also discussed.

2. Experimental

Alumina (Al_2O_3) and silica-alumina (SiO_2-Al_2O_3, alumina content: 15%, 61%) were obtained from Catalysts & Chemicals Ind. Co. The surface area was 285, 215 and 352 m^2 g^{-1}, respectively. Silica gel (SiO_2, surface area: 335 m^2 g^{-1}) was supplied from Fuji-Davison Chemical Co. Titania (TiO_2, anatase, surface area: 45 m^2 g^{-1}) was prepared by hydrolysis of titanium tetraisopropoxide, followed by drying and calcination in air at 803 K for 3 h. Zirconia (ZrO_2, amorphous, surface ares: 114 m^2 g^{-1}) was synthesized by decomposition of zirconium hydroxide in air at 773 K for 3 h.

The reactions were carried out with a fixed-bed flow reactor by passing a mixed gas of 1079 ppm NO, 9.9% O_2 and 323 ppm propane in helium at a rate of 62 cm^3 min^{-1} over 1 g catalyst unless otherwise specified. The reactor effluent was analyzed by gas chromatography with a molecular Sieve 5A column and a Porapak Q column. The catalytic activity was expressed in terms of percentage conversion of NO to N_2. The formation of CO and CO_2 through the oxidation of propane was also checked.

Temperature-programmed desorption measurements of ammonia were performed by using a conventional TPD apparatus with a thermal conductivity detector. A sample was dried in flowing helium at 973 K for 1 h, exposed to 29% NH_3/He at 373 K for 10 min and then purged with helium at 373 K for 30 min. TPD was done from 373 K to 973 K with a heating rate of 10 K min^{-1} and with helium as carrier gas.

3. Results and discussion

Table 1 summarizes the reaction results over metal oxide catalysts described above. When a catalyst was not used, reduction of NO to N_2 did not occur, although homogeneous gas phase oxidation of propane to CO_2 and CO was observed. The conversion of propane to CO_2 and CO was about 27% and 28% at

Table 1
Reduction of NO with propane over solid acid catalysts [a]

Catalyst	NO conv. to N_2/% at				
	573 K	673 K	773 K	873 K	973 K
blank	0	0	0	0	0
SiO_2	< 0.4	< 0.6	< 1.1	< 1.0	
SiO_2-Al_2O_3 (15%Al_2O_3)		1.2	4.1	7.1	
SiO_2-Al_2O_3 (61%Al_2O_3)		4.9	14	12	
Al_2O_3	0.5	13	32	17	
Al_2O_3			97 *		
TiO_2	0.8	4.8	8.9		
ZrO_2		23	20	9.1	

[a] Reaction conditions: NO = 1079 ppm, C_3H_8 = 323 ppm (* 1292 ppm), O_2 = 9.9%, gas flow rate = 62 $cm^3 min^{-1}$, catalyst weight = 1 g.

873 K, respectively. Silica gel did not give dinitrogen either. Since the extent of propane oxidation was almost the same as in the case of the noncatalytic reaction, it is concluded that silica gel does not work as a catalyst at all.

When silica-alumina and alumina were used, a formation of dinitrogen was clearly observed. This fact shows that the reductive decomposition of low concentration of NO to N_2 does take place with a small amount of propane even in the presence of about 10% oxygen. This high selectivity, which was also observed in the case of H-form zeolites [8], is very surprising since ammonia has been known as the only reductant of NOx that can work in oxidizing atmospheres.

Even more surprising is the fact that the reduction is catalyzed by such simple oxides containing no transition metal elements because redox reactions usually occur over transition metals having variable oxidation states. With respect to SCR with ammonia, however, H-mordenite was reported to be effective [9].

Fig. 1 indicates the variation of percentage conversion of NO to N_2 and the yield of CO and CO_2 with alumina content of silica-alumina catalyst at 773 K. The results on silica gel and pure alumina are also included in this figure. It can be seen that NO conversion to N_2 as well as CO_2 yield increases with alumina content. The most active catalyst was pure alumina, with which a removal of NO of 32% was attained. It should be noted from table 1 that the temperature at which maximum NO conversion is obtained tends to become lower as alumina content increases.

Fig. 2 shows the effect of reaction temperature on the selective reduction over alumina catalyst. At 873 K propane was completely oxidized to CO_2, and the conversion of NO to N_2 was 17%. As the temperature was decreased from 873 K, the yield of CO_2 decreased. However, NO conversion to N_2 reached a maximun at about 773 K. This fact suggests that the selective reduction is closely related to the extent of propane oxidation.

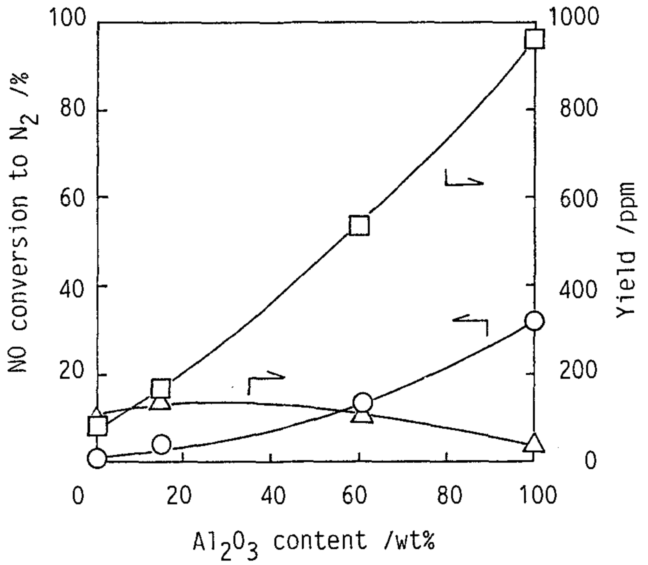

Fig. 1. Activity of silica-alumina catalysts. ○: conversion of NO to N_2, □: yield of CO_2, △: yield of CO.

Since propane concentration was expected to affect the NO reduction level, a reaction was conducted with 1292 ppm propane over alumina catalyst, the other reaction conditions being the same. The result is also shown in table 1. In this case, NO conversion to N_2 of about 97% was attained at 773 K. This result is

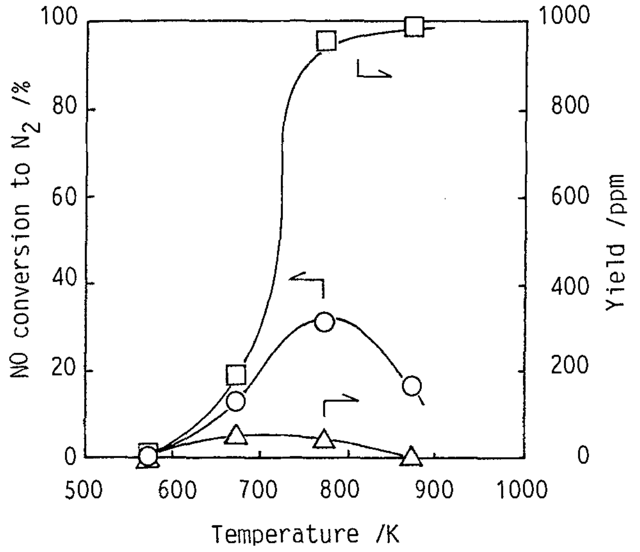

Fig. 2. Effect of reaction temperature on the selective reduction of NO over alumina catalyst. ○: conversion of NO to N_2, □: yield of CO_2, △: yield of CO.

Table 2
Amount of desorbed NH_3 in the TPD measurement on a series of silica-alumina catalysts

Catalyst	Amount of desorbed NH_3/mmol g^{-1}
SiO_2	0.02
SiO_2-Al_2O_3 (15%Al_2O_3)	0.85
SiO_2-Al_2O_3 (61%Al_2O_3)	1.21
Al_2O_3	3.03

quite amazing because it indicates that nearly complete removal of NO can be achieved by choosing appropriate conditions.

In table 1 are also presented the results on titania and zirconia catalysts. Both oxides showed catalytic activity for the selective reduction, although the activities were not so high as pure alumina. The catalytic activity was kept almost unchanged during the course of experiment in spite of possible catalyst sintering and phase transformation.

The effect of water vapor on this reaction is a matter of interest for practical applications since most combustion gases contain water. However, it seems improbable that the presence of water affects drastically the performance of the catalysts because some amounts of water should be formed as a result of reaction and nevertheless the catalytic activity was quite stable throughout the experimental period of a few days.

In order to get information on the active centers of the catalysts, ammonia TPD measurements were performed on the series of silica-alumina catalysts. The results are summarized in table 2, which shows that the total amount of desorbed ammonia is almost zero for silica and increases with alumina content. Therefore it is concluded that silica is not acidic and that total acid amount increases with alumina content. This tendency agrees quite well with the activity change for the selective reduction.

We suspect at present that acidity of the catalysts is one of the main factors that determine catalytic activity. However further studies will be necessary to clarify the true active centers of the catalysts and the reaction mechanism. Investigations on the detailed aspects of this selective reduction are now in progress.

References

[1] H. Bosch and F. Janssen, Catalysis Today 2 (1988) 369.
[2] M. Inomata, A. Miyamoto and Y. Murakami, J. Catal. 62 (1980) 140.
[3] M. Shelef and J.T. Kummer, Chem. Eng. Progress Symp. Ser. 67 (1971) 74.
[4] G.L. Bauerle, G.R. Service and K. Nobe, Ind. Eng. Chem. Prod. Res. Develop. 11 (1972) 54.

[5] J.H. Jones, J.T. Kummer, K. Otto, M. Shelef and E.E. Weaver, Environ. Sci. Technol. 5 (1971) 790.

[6] Ger. Offen. DE 3,642,018 (1987).

[7] Ger. Offen. DE 3,735,151 (1988).

[8] H. Hamada, Y. Kintaichi, M. Sasaki, T. Ito and M. Tabata, Appl. Catal. in press.

[9] L.A.H. Andersson, J.G.M. Brandin and C.U.I. Odenbrand, Catalysis Today 4 (1989) 173.