Catalytic Removal of NO

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Catalytic removal of NO

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Abstract

The aim of this paper is to review the catalytic reactions for the removal of NO and, more particularly, to discuss the reduction of NO in the presence of NH_3, CO, H_2 or hydrocarbons as well as the decomposition of NO. The nature of the different active species, their formation due to dispersion and their interaction with different supports as well as the corresponding correlations with catalytic performance are also discussed. Another goal of this review is to explain the mechanism and kinetics of these reactions on different surfaces as well as the catalyst stability. © 1998 Elsevier Science B.V. All rights reserved.

Keywords: Removal of NO; Decomposition of NO; Mechanism and kinetics

1. Introduction

The reduction of nitrogen oxide emissions has become one of the greatest challenges in environment protection. This is why it is being intensely studied by numerous groups from academic as well as industrial research laboratories. The interest in the subject is reflected in the number of papers, including a large number of reviews and patents, published each year. There is hardly an issue of a journal related to catalysis that does not contain contributions dealing with the elimination of NO.

The nature of the catalyst is another element giving weight to the topic. Virtually all known categories of catalysts have been tested: metal and metal-supported catalysts, monocrystals and mixed phases, oxides and mixed oxides (with either acidic or basic properties), zeolites and heteropolyacids, alloys and amorphous alloys, membrane and monolithic catalysts, etc.

Due to the extraordinary diversity of catalysts, this topic is always discussed at various conferences on catalysis. Each year, at least two conferences are entirely devoted to environmental catalysis, not to mention an additional periodic conference on automotive pollution control.

The use of such a large number of catalysts to eliminate NO is logically associated with different ways of reaction. It is possible to divide these ways into four categories or methods:

1. the selective catalytic reduction of NO with ammonia, typical of chemical industrial plants and stationary power stations;
2. the catalytic reduction of NO in the presence of CO and/or hydrogen, typical of automotive pollution control;

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3. the selective catalytic reduction of NO in the presence of hydrocarbons and more particularly methane, a method which has not yet reached industrial use but can be applied both for automotive pollution control and in various industrial plants;
4. the direct decomposition of NO, which is a goal worth striving for since it eliminates the need for reductants, which in turn eventually eliminates the additional pollution associated with the other three methods.

All these methods have been extensively studied. The goal of this paper is to analyse the interaction of NO with different surfaces in the presence of various reductants or in the direct decomposition of NO. The paper intends to describe the effect of the different active species as well as the effect of their interaction and their dispersion with/on different supports on the catalytic performances of the catalysts. Explaining the mechanism and kinetics through which these reactions take place on different surfaces as well as the catalyst stability is another goal of this review.
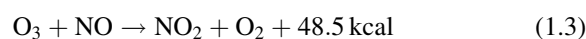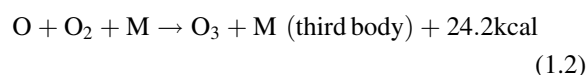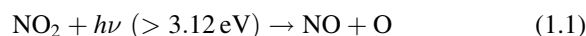
2. NO pollution

NO is a major atmospheric pollutant. It has the ability to generate secondary contaminants through its interaction with other primary pollutants (like carbonyl corresponding molecules, alcohol radicals, etc.) also resulting from the combustion of fossil fuels in stationary sources such as industrial boilers, power plants, waste incinerators, and gasifiers, engines, and gas turbines or from the decomposition of a large number of organic products by light or micro-organisms.

NO plays a major role in the photochemistry of the troposphere and the stratosphere. It reacts with photochemical pollutants such as ozone, formaldehyde, organic hydroperoxides and peroxyacyl nitrates that all are very reactive and have a very short lifetime. This is a very fast reaction which generates more nitrogen oxides and organic nitrates. The formed

NO_2 contributes substantially to so-called acid rains. Among the reactions involving ozone, the one with chlorofluorocarbons is very dangerous since it has a determining effect on the climate. The normal average content of ozone in the atmosphere is about 10^{-10} vol% and its interaction with NO also contributes to its diminution. The chemical depletion of ozone, in an important part due to nitrogen oxide species, is a prolonged phenomenon [2]. Carcinogenic products are also formed during these reactions.

Hydrocarbons in polluted air do not react among themselves under the action of sun radiations, not even to a very small extent, but show a high reactivity towards intermediate species such as peroxides RO_2 [1]. Such species react with the primary pollutants, NO, NO_2, O_3 and HC, according to a partially known mechanism. The photochemical complex HC–NO_x–O_x is formed during the HC interactions in the photolytic cycle of NO; the mixture of products generated is called "photochemical smog" and contains O_3, CO, peroxyacetyl nitrates, alkyl nitrates, ketones, etc.

The photochemical cycle of nitrogen oxides initiates under sunlight (3000–4600 Å). NO_2 is initially decomposed as follows [3]:

$$NO_2 + h\nu \ (> 3.12\,eV) \rightarrow NO + O \tag{1.1}$$

$$O + O_2 + M \rightarrow O_3 + M \ (third\,body) + 24.2kcal \tag{1.2}$$

$$O_3 + NO \rightarrow NO_2 + O_2 + 48.5\,kcal \tag{1.3}$$

until a dynamic equilibrium is reached:

$$NO_2 + O_2 \xrightarrow{h\nu} NO + O_3 \tag{1.4}$$

The overall dependence of photochemical air pollution on various factors may be written as [2]:

$$photochemical\ air\ pollution = \frac{(NO_x - conc)(organic\ conc)(sunlight\ intensity)(temperature)}{(wind\ spread)(inversion\ height)}.$$

In the presence of oxygen, NO is oxidized very quickly to NO_2 which, as mentioned before, is partly responsible for the acid rains and the urban smog. They have very negative effects in agriculture, but may also predispose to respiratory diseases by weakening the ability of the bronchopulmonary structures to function properly [4].

Table 1
Values of the equilibrium constant, K_p, and the dissociation degree, α, corresponding to the thermal decomposition of NO_2 into NO and O_2 and N_2 and O_2, respectively

T (K)	$NO_2 \rightarrow NO + 1/2\, O_2$		$NO_2 \rightarrow 1/2\, N_2 + O_2$	
	K_p	α	K_p	α
298	7.23×10^{-7}	1.69×10^{-3}	9.14×10^{8}	6.3×10^{-8}
400	2.53×10^{-4}	3.15×10^{-2}	3.32×10^{7}	1.7×10^{-8}
500	8.00×10^{-3}	1.70×10^{-1}	4.65×10^{6}	1.2×10^{-7}
600	8.09×10^{-2}	4.87×10^{-1}	1.26×10^{6}	4.6×10^{-7}
700	4.22×10^{-1}	8.77×10^{-1}	4.90×10^{5}	1.2×10^{-6}
800	1.47	9.55×10^{-1}	2.50×10^{5}	2.3×10^{-6}

Table 2
Evolution of the thermodynamic parameters: entropy (S^0), enthalpy (ΔH_f^0), Gibbs free energy of NO (ΔG_f^0), and Gibbs free energy of the NO decomposition

T (K)	NO		NO reaction	
	S^0 (cal mol K)	ΔH_f^0 (kcal mol^{-1})	ΔG_f^0 (kcal mol^{-1})	$(\Delta G_f^0)_r$ (kcal mol^{-1})
298	50.35	21.60	20.72	-2×20.72
300	50.40	21.60	20.71	-2×20.71
400	52.45	21.61	20.41	-2×20.41
500	54.06	21.62	20.11	-2×20.11
600	55.41	21.62	19.81	-2×19.81
700	56.57	21.62	19.51	-2×19.51
800	57.61	21.63	19.21	-2×19.21
900	58.54	21.63	18.91	-2×18.91
1000	59.39	21.64	18.60	-2×18.60

2.1. Thermodynamic stability of nitrogen oxide

The interconversion of nitrogen oxides is relatively easy. The values of K_p for $p = 1$ atm corresponding to the thermal decomposition of NO_2 to NO and NO_2 to N_2 and O_2, respectively, are presented in Table 1.

According to these data, NO_2 is practically 100% decomposed in NO and O_2 above 800 K. It appears that there is no direct thermal decomposition of NO_2 to N_2 and O_2 because of the difference in K_p values.

Even though NO is an endothermic compound, no decomposition is observed at 825 K. The thermodynamic parameters (S^0, ΔH_f^0 and ΔG_f^0) corresponding to NO and the Gibbs free energy of the reaction are given in Table 2:

$$2NO \rightarrow N_2 + O_2 \tag{1.5}$$

for a relatively broad range of temperatures [5].

From a thermodynamic point of view, as can been seen from Table 2, the NO molecule is unstable even at 298 K and 1 atm. This is due to the electronic structure of the bond in NO. The reaction is spin-forbidden, and NO is kinetically stable. Thus, the high thermal stability of nitric oxide is due to its high energy of dissociation (153.3 kcal mol^{-1}) and to corresponding extremely low decomposition rates.

The reaction is not sensitive to pressure variations (the variation of the stoichiometric number is 0) but

reactions such as NO oxidation, its decomposition to N_2O and dimerization are. The evolution of the Gibbs free energy with temperature for the decomposition of NO to N_2O is presented in Table 3.

In the presence of a reductant, reactions lead to a strong decrease in the Gibbs free energy values. This explains that such reactions are used in practical applications. The Gibbs free energy values in the presence of the usual reductants in the catalytic reduction of NO are given in Table 4. The introduction of oxygen here leads to an additional reduction in the free energy. This point will not be discussed.

3. Selective catalytic reduction of nitric oxide with ammonia

General aspects. The catalytic reduction of nitrogen oxides in effluent residual gases from various industries, mainly nitric acid plants, can be carried out selectively using ammonia or urea. This is the so-called selective catalytic reduction (SCR) process. The reactions occur in a narrow temperature range; the main step is the reduction of NO or NO_2 to N_2. Generally, liquid ammonia is injected in the residual

Table 3
Evolution of the Gibbs free energy for the decomposition of NO to N_2O

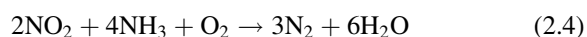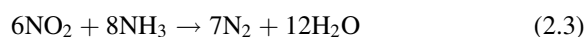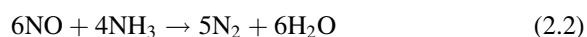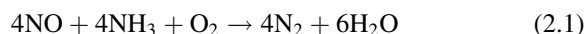| T (K)	298	300	400	500	600	700	800	900	1000
ΔG_f^0	33.34	33.24	28.46	23.66	18.88	14.10	−9.36	−4.62	+0.12

Table 4
Values of the Gibbs free energy for the reduction of NO in the presence of various reductants

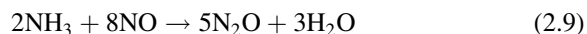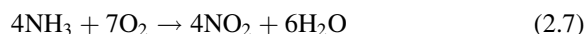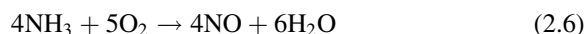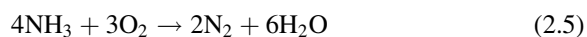| T (K)	$\Delta G_{r,r}^0$ (kcal mol^{-1})								
	$+H_2$	$+CO$	$+NH_3$	$+CH_4$	$+C_2H_4$	$+C_2H_6$	$+C_3H_6$	$+C_3H_8$	$+C_4H_{10}$
298	−150.92	−164.34	−87.36	−134.26	−146.21	−144.38	−144.04	−140.59	−136.83
300	−150.66	−164.24	−87.34	−134.22	−146.11	−144.21	−144.01	−140.57	−136.79
400	−147.86	−159.46	−87.62	−132.19	−145.28	−141.58	−143.52	−140.47	−135.11
500	−144.94	−154.62	−87.92	−130.13	−144.28	−139.37	−143.04	−140.39	−133.43
600	−141.94	−149.80	−88.24	−128.06	−143.67	−139.14	−142.57	−140.32	−131.75
700	−138.86	−144.96	−88.56	−125.99	−142.86	−138.81	−142.10	−140.24	−130.06
800	−135.72	−140.14	−88.86	−123.93	−142.04	−138.69	−141.61	−140.15	−128.42
900	−132.54	−135.34	−89.17	−121.89	−141.23	−138.46	−141.13	−140.07	−126.76
1000	−129.28	−130.52	−89.45	−119.85	−140.38	−138.19	−140.62	−139.94	−125.11

gas before the catalytic reaction takes place, using a sophisticated system of distribution.

Bosch and Janssen [6] (and references herein) reviewed the catalysts used in the selective reduction of NO with NH_3 and showed that the most investigated and effective systems are oxides prepared by thermal decomposition of an appropriate precursor or by impregnation of the supports. Other extensively investigated catalysts are supported noble metals and metal zeolites. Recently, Janssen and Meijer [7] showed that more than a thousand catalyst compositions have been tested for application in this reaction up to now. This is the most used technique to control the emission of NO_x.
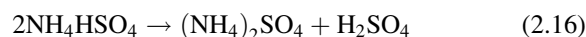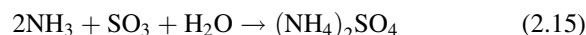
The main reactions that occur during SCR with ammonia are:

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (2.1)$$

$$6NO + 4NH_3 \rightarrow 5N_2 + 6H_2O \qquad (2.2)$$

$$6NO_2 + 8NH_3 \rightarrow 7N_2 + 12H_2O \qquad (2.3)$$

$$2NO_2 + 4NH_3 + O_2 \rightarrow 3N_2 + 6H_2O \qquad (2.4)$$

Unwanted secondary reactions can take place as a result of the catalyst nature, the oxygen content, the temperature or the presence of acid gases:

$$4NH_3 + 3O_2 \rightarrow 2N_2 + 6H_2O \qquad (2.5)$$

$$4NH_3 + 5O_2 \rightarrow 4NO + 6H_2O \qquad (2.6)$$

$$4NH_3 + 7O_2 \rightarrow 4NO_2 + 6H_2O \qquad (2.7)$$

$$4NH_3 + 2O_2 \rightarrow N_2O + 3H_2O \qquad (2.8)$$

$$2NH_3 + 8NO \rightarrow 5N_2O + 3H_2O \qquad (2.9)$$

$$6NH_3 + 8NO_2 + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (2.10)$$

$$4NH_3 + 4NO + 3O_2 \rightarrow 4N_2O + 6H_2O \qquad (2.11)$$

$$16NH_3 + 12NO_2 + 7O_2 \rightarrow 4N_2O + 24H_2O \qquad (2.12)$$
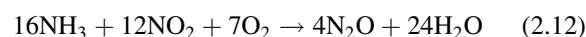
The presence of SO_2, CO_2 or HCl determines a consumption of NH_3 according to:

$$2SO_2 + O_2 \rightarrow 2SO_3 \qquad (2.13)$$

$$NH_3 + SO_3 + H_2O \rightarrow NH_4HSO_4 \qquad (2.14)$$

$$2NH_3 + SO_3 + H_2O \rightarrow (NH_4)_2SO_4 \qquad (2.15)$$

$$2NH_4HSO_4 \rightarrow (NH_4)_2SO_4 + H_2SO_4 \qquad (2.16)$$

$$NH_4HSO_4 + NH_3 \rightarrow (NH_4)_2SO_4 \qquad (2.17)$$

$$NH_3 + HCl \rightarrow NH_4Cl \qquad (2.18)$$

$$2NH_3 + CO_2 + O_2 \rightarrow (NH_4)_2CO_3 \qquad (2.19)$$

The resulting products have corrosive properties and can therefore destroy the equipment.

In the absence of catalysts, the reduction of NO_x occurs with satisfactory conversion rates at temperatures in the range 1075–1175 K while the oxidation of NH_3 to NO_x (reactions (2.6)–(2.7)) takes place at temperatures above 1200 K (1325–1475 K) and the reduction rate decreases abruptly. The reaction rate is very low at temperatures below 1075–1175 K. In the presence of catalysts, the temperature of the reaction depends on the catalyst nature and can be in the 355–425 K range for the more active systems.

In the process, it is vital to ensure a NH_3 to NO_x ratio close to that required by stoichiometry (according to reaction (2.1)) [8]. An oxygen excess reduces the catalyst selectivity to N_2 and favours the formation of N_2O (reactions (2.9)–(2.12)) or even the oxidation of ammonia to NO or NO_2. However, no matter what

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