



# Fundamentals of Heterogeneous Catalysis: a Study of N<sub>2</sub>O Mitigation Reaction Over Modified Zeolite Catalysts

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## Abstract

This article provides the fundamental understanding of heterogeneous catalysis and the importance of nitrous oxide (N<sub>2</sub>O) conversion reactions. Solid catalysts play an important role in the reduction of several greenhouse gases. In developing countries, the topic of N<sub>2</sub>O mitigation reactions is relatively new and needs review particularly for early stage researchers. In this work, reaction catalysis, zeolite as a prominent catalyst support, and the importance of N<sub>2</sub>O dissociation reactions are briefly discussed. After an overview of global warming, the discussions continue to introduce the principles of reaction catalysis. Furthermore, N<sub>2</sub>O is a potent greenhouse gas, whereas its emissions into the environment can be reduced when reacted over active and selective solid catalysts. Presently, Fe-ZSM-5 is commercially used catalyst for N<sub>2</sub>O conversion reactions. Zeolites, for example, H-ZSM-5 (H<sub>n</sub>Al<sub>n</sub>Si<sub>96-n</sub>O<sub>192</sub>.16H<sub>2</sub>O) are aluminosilicate catalyst support with unique physicochemical properties. Catalytic activity of H-ZSM-5 may vary when loaded with metals or treated with acid/base solutions. The selectivity of reaction product changes when the same catalyst support is loaded with different metals.

**Keywords:** Nitrous oxide (N<sub>2</sub>O), Reaction catalysis, Zeolite supports.

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## Introduction

Chemical industrial emissions, fuel combustions, and spraying chemicals on agriculture fields are few main reasons behind the environmental degradation [1]. Few years back, world health organization (WHO) gathered data from different parts of the world and reported thousands of deaths because of air pollution [2]. Only 2 °C rise in earth surface temperature may result in the extinction of millions of living species, can initiate cyclones, activate volcanoes, and earthquakes [3]. For this reason, world leaders (Kyoto summit, 1997) agreed to enforce the emissions control regulations for six greenhouse gases, i.e. carbon dioxide (CO<sub>2</sub>), nitrous oxide (N<sub>2</sub>O), methane (CH<sub>4</sub>), sulfur hexafluoride (SF<sub>6</sub>), hydrofluorocarbons (HFCs), and perfluorocarbons (PFCs) [4].

N<sub>2</sub>O is a potent greenhouse gas, whereas its atmospheric concentration in pre-industrial age remained constant between the values of 270 - 288 ppbv [5]. However, now a days fertilizers, chemicals, fuel combustion (both stationary and mobile stations), and sewerage treatment reactions are releasing 7 million tons of N<sub>2</sub>O annually into the environment [6]. N<sub>2</sub>O in the troposphere is non-reactive molecule, however, its presence in the stratosphere layer (12 km - 50 km, from the earth surface) actively absorbs infrared radiation, and is more hazardous gas when compared to other greenhouse gases [7, 8]. N<sub>2</sub>O global warming potential (GWP) is 15 and 310 times of CH<sub>4</sub> and CO<sub>2</sub>, respectively [9]. Moreover, the photolysis of N<sub>2</sub>O leads to the production of stratospheric NO<sub>x</sub>, a molecule active in ozone (O<sub>3</sub>) depletion reactions [10-12]. The presence of O<sub>3</sub> layer is essential for

the absorption of lethal high frequency radiations [13]. The probable mechanism of  $N_2O/NO_x$  and  $O_3$  conversion reactions are still under experimental discussions [10, 12].

Nitric acid and adipic acid production plants are the main chemical industries responsible for the  $N_2O$  emissions [5,11,12]. Luckily, the mitigation of most of the greenhouse gases is possible when reacted over suitable solid catalyst. For example,  $N_2O$  can be converted in  $N_2$  and  $O_2$  under favorable reaction conditions. Till date, a number of solid catalysts were found active for  $N_2O$  conversion reactions. This review paper encompasses a brief overview of heterogeneous catalysis, zeolites materials, and  $N_2O$  conversion reactions.

### Introduction to Reaction Catalysis

In 1836, the term “catalysis” was used by a Swedish chemist, Jöns Jakob Berzelius (1779 – 1848). Whereas, Ostwald was the first scientist who used the word catalyst in 1885. According to Ostwald a catalyst is primarily used to increase the rate of a reaction [14]. However, dealing with reaction catalysis is not new, i.e. for the past 1000 years, different enzymes were commonly used in numerous fermentation reactions. All reactants have to overcome an energy barrier before conversion into product species. The catalyst lowers the energy barrier and provide a new route for the conversion reaction [14]. Ideally, reactants chemically interact with the catalyst and then convert into product species as presented in Fig. 1. Theoretically, the catalyst composition should remain the same, but in real reactions the molecular chemistry of catalyst changes because of reactants and catalyst interactions [14].

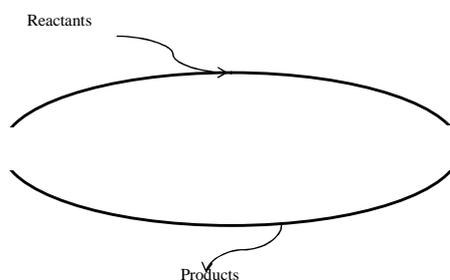
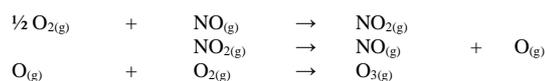


Figure 1. Catalytic cycle

Moreover, catalysts can be classified on the basis of phases (solid, liquid, or gas), chemical composition, and the state of reactants/products collection (homogeneous and heterogeneous). For example, as shown in the following homogeneous reactions, both catalysts and reactants are in the same phase, i.e. nitric oxide (NO) is a gas phase catalyst for the conversion of molecular oxygen into ozone ( $O_3$ ) gas.



Whereas in heterogeneous catalytic reactions, reactants and catalysts are in a different phase. For example, in the Fischer-Tropsch reaction, carbon monoxide reacts with hydrogen over cobalt (solid phase) catalyst and forms gasoline.



This solid phase catalyst is a combination of active sites and less active catalyst support [14]. Most of the industrial metal catalysts are actually loaded metal sites over less active metal oxide supports. Silica, alumina, activated carbon, and zeolites are few of the commonly used catalyst supports. These supports have high surface area ( $\sim 200 \text{ m}^2/\text{g}$ ) and maintains the surface area even at extreme high reaction temperatures ( $> 600 \text{ }^\circ\text{C}$ ). The reactant species hooks up to active metal sites and forms transition species and finally converts into reaction products. The stability (performance) of catalysts usually decreases with time (during the progress of reaction) and at higher temperatures [15].

Any modifications of catalyst surface alter the yield of reaction products. For example, acid or steam treatment of H-ZSM-5 causes dealumination, whereas alkaline treatment removes the silica content of the H-ZSM-5 framework, and both these supports when loaded with same metal have different selectivity for several hydrocarbon oxidation reactions [16]. For example, in  $CH_4$  and  $N_2O$  oxidation reaction, Bitter and co-workers treated H-ZSM-5 by stirring it in a solution of NaOH and observed an improvement in methanol selectivity in comparison to formaldehyde [16-18].

Pellet size and shape of catalysts used for any reaction is dependent on the scale of reactor. Few commonly used shapes and sizes are shown in Fig. 2. The powder form is generally used for small scale laboratory reactors (micro reactors). For medium and large scale reactors, which may hold several tons of catalyst, the powdered catalyst is compressed under pressure to form large pallets. In some cases the shape of catalyst is also important in order to minimize the pressure drop across the catalyst bed [16].

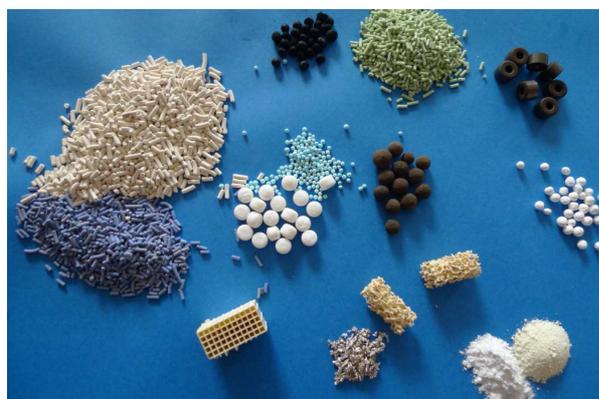


Figure 2. Different forms and shapes of metal supported catalysts

Last but not least, a good catalyst should have a high surface area for maximum reactants interactions, however, it is also true that in some cases the external surface area of catalyst is intentionally decreased in order to increase the selectivity towards desired reaction products. Catalyst can be prepared by different methods, such as ion exchange, impregnation, slurry precipitation, co-precipitation, fusion, physical mixing, and wash coating. For most reactions, the catalyst having the same composition when prepared by different methods have different activity and selectivity [15]. For example, Co-ZSM-5 prepared by ion exchange and impregnation methods have different activity for  $N_2O$  conversion reactions [19-21].

### **Zeolite, a Catalyst Support**

Zeolites are microporous aluminosilicate sieves and because of structural aluminum its framework contains negative charge sites. The first natural zeolite (stilbite) was discovered in 1756 by a Swedish mineralogist named Axel Fredrick

Crönstedt (1722- 1765). The term Zeolite is derived from two Greek words, i.e. boiling stone [22]. Moreover, chabazites, mordenite, and clinoptildite are few common natural zeolites [23]. The melting of zeolites occurs at very high ( $>1000$  ° C) temperatures [22]. These minerals contains a network of cages and more importantly have the ability to trap ions, atoms, and molecules [23]. Usually water, alkali, and alkaline earth metals ions are part of zeolite framework, whereas, these bonded ions can be replaceable with other cations [22]. Zeolites have a number of commercial applications, for example, these are used as a catalyst, water softeners (removing magnesium and calcium ions), in concrete mixture, and for gas separations.

Natural zeolites contains several undesired chemical impurities and therefore usually not suitable for catalytic reactions [24]. Later on scientists synthetically prepared several zeolites with enhance catalytic properties having unique framework structures. For example, faujasites (zeolites X and Y) synthesized in 1962 is now commonly used for the catalytic cracking of heavy petroleum distillates [24]. There are several other industrial reactions, such as synthesis of ethylbenzene, and isomerization of xylene etc., where synthetic zeolites have improved the reaction selectivity [25].

The framework of zeolite is a three dimensional network of alumina ( $AlO_4$ ) and silica ( $SiO_4$ ). These adjacent tetrahedra are connected via common oxygen atoms forming macromolecular structures [24]. These materials are microporous with size range from 0.2 to 1 nm [24]. The net formulae of the tetrahedra is  $SiO_2$  and  $AlO_2^-$ , i.e. one negative charge resides in each tetrahedron containing aluminum [24]. These negative sites may compensate numerous equivalent cations. The topology of zeolite is described by a three letter code, for example ZSM-5, a specific MFI structure. The ratio of Si to Al determines the cation exchange capacity [24].

H-ZSM-5 (Zeolite Socony Mobil-5), a synthetic zeolite, have gained an extensive importance in heterogeneous catalysis [26, 27]. In 1972, Argauer and Landolt synthesized this

material, and Mobil Oil Company filed the patented in 1975 [27]. Alumina, silica, alkali metal oxide, water, and tetraalkylammonium compounds are hydrothermally treated under high pressure to form H-ZSM-5 zeolites [28]. These framework can compensate several cations at exchange sites [28]. H-ZSM-5 is highly microporous and contains perpendicular intersections with zig-zag patterns [29]. These channels are formed by a 10 membered oxygen rings as shown in Fig. 3 [29]. The unit cell structure is orthorhombic, while the crystallographic unit cell has 96 T sites (alumina or silica), 192 oxygen sites, and a fixed number of compensating cations (depends on Si/Al ratio) [30].

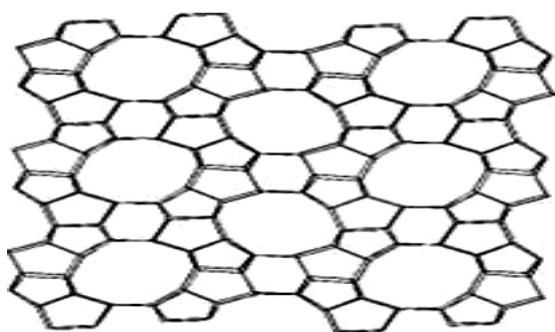


Figure 3. ZSM-5 lattice showing 10 membered oxygen ring [22]

Furthermore, transition metals cations can be loaded on H-ZSM-5 via different routes, such as volatile metal organic complex is decomposed over H-ZSM-5 surface [22], or metal cations are used as precursor salts (direct synthesis) [31], or by incipient or solution impregnation [32], and ion exchange method may also be used for cation loadings [33, 34]. Cobalt containing H-ZSM-5 support has shown excellent catalytic activity and selectivity for various reactions [21, 35]. Isolated cobalt ions are usually characterized as active sites [36], whereas during cobalt loading clusters may also be formed [37]. Different species of cobalt, i.e.  $\text{Co}^{2+}$ ,  $\text{Co}^{3+}$ , and  $\text{Co}^0$  have been reported as an active sites for the reactions [20].

### Nitrous Oxide Conversion Reactions

The emissions of  $\text{N}_2\text{O}$  into the atmosphere is comparatively low when compared with other greenhouse gases [6]. However,  $\text{N}_2\text{O}$  molecule

remains stable in stratosphere (2<sup>nd</sup> layer of the atmosphere) for approximately 150 years, and thus have a higher global warming potential with reference to  $\text{CO}_2$  and  $\text{CH}_4$  [38]. These nitrogen oxide molecules affectively absorbs infrared radiations and may reacts with ozone ( $\text{O}_3$ ) under favorable reaction conditions [7, 39, 40]. The concentration of  $\text{N}_2\text{O}$  remained constant for centuries (the value was approximately 270 ppbv), however, the current numbers are very high (presently around 310 ppbv) [40, 41].

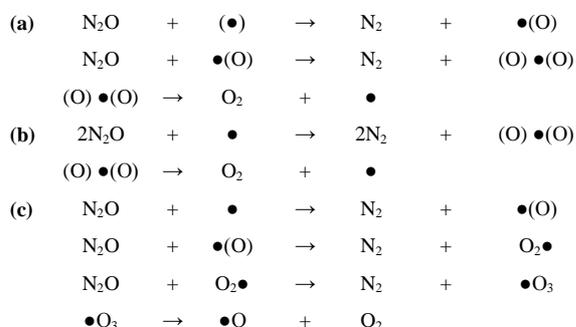
$\text{N}_2\text{O}$  production from point sources, for example, chemical plants (adipic and nitric acids production plants), fuel combustion, and sewage treatment plants are the main emission sources where catalytic emission control systems can be installed. The commencement of new emission reduction projects have already been started as reported in the recent United Nations meeting [42]. For comparison, the current size of emissions from different sources is given in Table 1 [42].

Table 1. Global nitrous oxide ( $\text{N}_2\text{O}$ ) emissions.

Source	$\text{N}_2\text{O}$ emissions (Mt $\text{N}_2\text{O}$ $\text{y}^{-1}$ )
<b>Natural</b>	<b>-13</b>
Soils	10
Oceans	2.9
Atmospheric chemistry	0.2
<b>Anthropogenic</b>	<b>-7</b>
Agriculture (including fertilizer)	3.5
Nitric acid production	0.4
Adipic acid production	< 0.1
Fossil fuel combustion (stationary)	0.2 – 0.5
Fossil fuel combustion (mobile)	0.4 – 0.9
Biomass combustion	1.0
Sewage treatment	1.5
Total of all sources	Approximately 20

Number of different catalysts, such as M-zeolites (M = Co, Fe, Cu etc.) [35], perovskite-like mixed oxides [43], and precious metal (Pd, Rh, etc.) supported catalysts were found active for the

N<sub>2</sub>O conversion reaction [44]. Few possible N<sub>2</sub>O (N<sub>2</sub>O → N<sub>2</sub> + 1/2O<sub>2</sub>) dissociation routes discussed in the literature [45-47].



Where the symbol  $\bullet$  is used to represent the active site of the catalyst.

Moreover, the selective catalytic reduction (SCR) with different hydrocarbons (CH<sub>4</sub>, C<sub>2</sub>H<sub>6</sub>, C<sub>2</sub>H<sub>4</sub>, C<sub>2</sub>H<sub>2</sub>, C<sub>3</sub>H<sub>8</sub>, and C<sub>3</sub>H<sub>4</sub>), CO, NO<sub>x</sub>, and NH<sub>3</sub> are currently applied for reducing N<sub>2</sub>O emissions [48]. The Uhde's EnviNO<sub>x</sub>® is commercially employed catalyst for N<sub>2</sub>O conversion reaction (Fe-ZSM-5). The literature also reports that the catalytic activity of Fe-ZSM-5 decreases in presence of H<sub>2</sub>O moisture [5, 49]. Few studied also suggests that Co-ZSM5 are more active than Fe-ZSM5 for N<sub>2</sub>O dissociation reaction [35]. The activity of reaction changes when same cobalt metal was loaded on different supports [50, 51].

## Conclusion

Viable strategies to reduce the emissions of greenhouse gases is highly active research area. The presence of N<sub>2</sub>O in higher altitudes of atmosphere is more hazardous when compared to other greenhouse gases. A number of catalysts have been studied to convert N<sub>2</sub>O molecules into cleaner gaseous products. Presently the knowledge of reaction catalysis is well documented, however, the current review only focuses on the relevant concepts of heterogeneous catalysis. For example, the progress of reaction under same reaction condition may change when the physicochemical properties of catalyst are varied. Zeolite minerals, particularly H-ZSM-5 has several practical application including as an active catalyst support for N<sub>2</sub>O reduction reactions.

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