

Catalytic removal of nitrogen oxides: where are the opportunities?

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Abstract

There has been a great deal of recent activity in the catalytic removal of NO_x . This manuscript provides an analysis of the recent research methodology in this field, with a brief analysis of NO_x reduction with hydrocarbons (vs. other reductants), the decomposition on NO into N_2 and O_2 , and processes that do not produce NO_x . Limiting features of the current catalytic approaches to NO_x removal are discussed. The current effectiveness of recent catalytic NO_x removal is assessed. Further, suggestions are offered to help future investigators focus on key experimental parameters and on opportunities for additional research that offer major societal and economic impact.

Keywords: NO_x ; Reduction; Decomposition; Assessment; Opportunities

1. Introduction

There is a worldwide effort to discover improved solutions for the removal of NO_x emissions [1]. (Nitrogen oxides, NO_x , are major air pollutants that cause photochemical smog formation and acid rain.) The emission of various nitrogen oxides into our atmosphere occurs on a massive scale. Worldwide, over 30 million tons [2] of NO_x are vented to the earth's atmosphere each year. Catalytic reduction of NO_x offers one approach to this problem. Selective catalytic reduction (SCR) is the current, best available technology for reducing NO_x emissions at many power plants and during the production of chemicals [3,4]. However, there are several disturbing issues that may ultimately make this an unattractive technology in the future. New catalytic tech-

nology is already emerging which may ultimately offer more acceptable solutions. Iwamoto et al.'s breakthrough discovery [5] in the mid 1980's of a Cu-ZSM-5 catalyst for the direct decomposition of NO into N_2 and O_2 has generated a storm of interest now focused on characterizing and understanding the performance of Cu-ZSM-5.

The public is demanding greater control of the emissions of toxic NO_x into our atmosphere. This applies to emissions from both mobile and stationary engines. There is a strong desire to further regulate and reduce the levels of NO_x emitted from cars, trucks and buses which burn gasoline, methane or diesel fuels. In addition, any new technology that offers an acceptable solution to controlling NO_x emissions from methane fired stationary engines has the potential for generating over a billion dollars of business [6]. If one could provide acceptable solution for NO_x emissions in coal-fired power plants, this would provide addi-

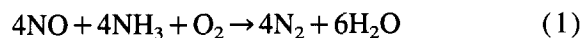
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tional multi-billion dollar business. Also, there are many small sources of NO_x emissions, such as methane fired water heaters [7]. Thus, the need to remove NO_x is driven by a significant, long-term health benefit with a huge economic incentive for a timely solution. The purpose of this manuscript is to alert the reader and future investigators to the needs and opportunities that remain considering the wealth of information recently gathered on this topic.

2. Approaches to reducing NO_x emissions

2.1. Use of a reductant

There are really only two approaches to removing NO_x from the atmosphere: either treat the NO_x at the source or do not produce it at all! There are a number of commercial approaches [8] to NO_x removal which include adsorptive, thermal [9], and catalytic. The thorough review in 1988 by Bosch and Janssen is an excellent source for further details [3]. Thermal processes require an excess of methane [10,11] and demand much higher operating temperatures. Among the catalytic approaches (which offer much lower operating temperatures), SCR (Selective Catalytic Reduction) is growing in application and is considered the best available control technology [12]. SCR uses a catalyst to facilitate reactions between NO_x and NH₃ in the presence of oxygen; although there are a complicated sequence of reactions, it can best be represented by:

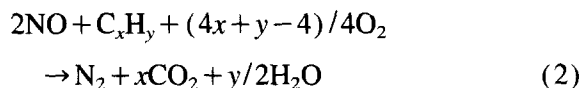


There are a number of variants of this technology depending on the supplier. First generation plants were built in Japan and newer facilities in Germany [13] and the USA. In the USA, the Clean Air Act of 1990 will prompt wider use of SCR; SCR is already in use in California. Standards for NO_x emission vary with the fuel and the type of utility (ca. 300 ppm for coal, 150 ppm for oil, and 10 ppm for gas). In the USA, this provides an enormous business opportunity, but there is a tight

window of opportunity which is being defined by government regulations set to take effect near the turn of the century. Once power plants commit huge levels of capital to meet these regulations, the business opportunities will be reduced, but there will continue to be an on-going need for NO_x removal technology, especially in developing economies.

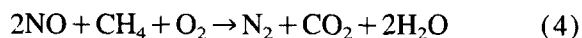
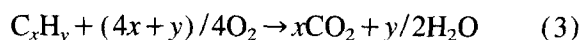
In an earlier review [1], this author outlined several particular problems that limit SCR application. In order to control NO_x to ca. 80% of inlet values, NH₃ is injected into the flue gas prior to the catalyst. This requires a sophisticated distribution system of pipes and nozzles. The addition of ammonia to reduce NO_x ultimately releases about 5–20 ppm NH₃, another pollutant. There are added equipment costs with injection of ammonia and additional issues with regard to corrosion and plugging which arise with the presence of sulfur oxides in the exhaust stream. The large volumes of exhaust being treated necessitate the shipment of NH₃ (not readily available at the power plants) through residential neighborhoods, where the public is beginning to object for safety reasons. Also it often means that anhydrous ammonia needs to be transported and stored near the SCR unit. Sulfur contamination, oxidation of SO₂ to SO₃, pore plugging, and erosion are potential catalyst problems [3]. With SO₂ containing flue gas, ammonium sulfates form at <350°C which coat the downstream process equipment. Additional catalyst and process information on SCR technology are available in two excellent reviews [3,14].

Other reductants besides NH₃ include H₂, CO, carbon, and hydrocarbons. H₂ and CO have too much value as chemical feedstocks. The competitive oxidation of H₂ to water by the excess air in most exhausts and concerns with regard to safe handling and storage of the flammable H₂ often rule out the use of H₂. Carbon is consumed when it is used as a reductant, and higher hydrocarbons can be expensive, since they often have greater value as chemicals or feedstocks. The current, popular approach with hydrocarbons envisions the use



of the unburned hydrocarbons in the exhaust, supplemented by post injection of the fuel to reduce the NO_x (Eq. 2). This will depend on the concentration and type of hydrocarbon available.

There has been a huge effort into the use of hydrocarbons as reductants for the removal of NO_x , and this has been summarized elsewhere [15]. Hydrocarbons could offer an attractive, alternative reductant to ammonia. The use of hydrocarbons as reducing agents for NO_x was first reported in the 70's [16,17]. These earlier catalysts generally catalyze hydrocarbon combustion (Eq. 3), thus requiring the use of a large excess of hydrocarbon. Recently, several groups reported interesting results on NO_x reduction by zeolite based catalysts in the presence of excess O_2 with non-methane hydrocarbons, e.g., propane, propene, and ethylene. This work has been summarized elsewhere [18,19], and companion manuscripts in this special issue. Additional activity would be desirable for these catalysts; however, one serious factor is their hydrothermal and thermal stability. However, none of these early studies were able to use methane as a reducing agent in an O_2 rich atmosphere. Additional work has also focused on the use of methane as a reductant [20–22]. The best catalyst to



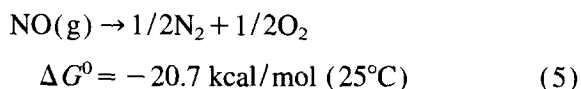
date is estimated to be about a factor of four too low in activity in wet streams [23]. While Co-ZSM-5 seems to offer the hydrothermal stability, it still suffers from a reduction in activity due to the large levels of water vapor in real exhaust streams, which block and inhibit effective NO_x reduction. More improvements are needed with these methane based catalysts and these are reviewed in a separate manuscript [24].

While it is undesirable to carry around another fuel just to destroy the NO_x from mobile engines, it may be possible to design engines to use the

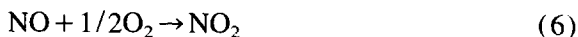
unburned hydrocarbons in the exhaust with post injection using small amounts of gasoline to destroy the NO_x . This will entail the use of more sophisticated engine control technology. Where LPG is the fuel (in a relatively small number of cases), one could readily use the fuel to also control NO_x exhaust emissions. Methane is plentiful, often a source of H_2 , often flared (rather than making a billion dollar investment to ship and store it), and readily available in many parts of the world. Where it is also used as the fuel for mobile engines (a relatively small number) or stationary engines (a large number), one could simply use CH_4 to control NO_x levels (Eq. 4) via post injection of a CH_4 after the combustion chamber.

2.2. NO decomposition

Another approach to NO_x control is the direct decomposition of NO into its elements. This is highly desirable because it does not demand the use of a reductant. The direct decomposition of NO to its elements (Eq. 5) has been a significant challenge to scientists for decades [25–27]. This reaction, although thermodynamically favorable by (see also Ref. [28])



> 20 kcal/mol at 25°C, had not been demonstrated in any substantial yield until recently by Iwamoto et al. [5]. They noted in about 1980 that Cu-Y desorbs large amounts of O_2 at 373°C. For successful NO decomposition, O_2 desorption must occur at < 500°C. This work ultimately led to the breakthrough in 1986 that Cu-ZSM-5 is capable of significantly decomposing NO into its elements at 500°C. No deactivation of the catalyst occurs after 30 h of service. His early work reported incomplete, yet substantial, conversion of NO to O_2 (60%) and N_2 (85%), and it was suggested that NO_2 was produced (Eq. 6); this work represented a step out



improvement over what others had tried for decades to achieve. To date the level of activity exhibited by Cu-ZSM-5 is unique.

Several technical challenges remain for improving this catalytic reaction with respect to its application to NO_x control for stationary and mobile source emissions. The catalyst must be optimized for high-activity operation at the lower operating temperatures (ca. 350°C) and at high space velocities typically encountered in flue gas streams. Unfortunately, Cu-ZSM-5 is not very stable to even 2% water vapor for extended periods of time. Since combustion exhaust streams are rich in water vapor (10–16%), any catalyst must ultimately be able to operate in the presence of high levels of water vapor. Given the fact that NO_x levels are often <2% (and often at the ca. 50 ppm level), it is very difficult to find a catalyst whose active sites needed for NO sorption won't also be overwhelmed by this huge excess of water. Because of the high exhaust velocities (>30000 GHSV), it is impractical to try to separate such large quantities of water from such a huge volume of gas. The thermal and hydrothermal stability of any catalyst will be an important part of any successful NO_x decomposition technology. Since diesel and natural gas contain sulfur components, the critical issue of SO_x resistance of the catalyst still must be addressed. It is probably not cost effective to carry large amounts of an adsorbent to scrub the sulfur from the fuel. Opportunities for improvement will be discussed in Section 4.

2.3. Avoid NO_x production

Perhaps the most attractive approach to the NO_x problem, is the simplest approach, but most complex technically. If one does not make NO_x in the first place, no post-treatment units are necessary. One can envision destroying the NO_x as it is produced by some type of secondary reaction that consumes NO_x, or operating the combustion process so that NO_x is not produced [1]. One can try to minimize NO_x formation with more efficient burner designs or the addition of more O₂ to the fuel.

The generation of NO_x by combustion arises from the high temperatures during combustion which oxidize either the N₂ in the air or the nitrogen containing components of the fuel to NO_x. A lot of progress to avoiding NO_x production is being made using non-catalytic, engineering based approaches such as fluid bed combustion or improved burner designs [29,30]. Fluidized-bed combustion processes offer lower emissions of NO_x and SO₂. The lower NO_x emission is partly due to lower combustion temperatures and to staged combustion [31]; unfortunately, this often means higher levels of N₂O production. If one can initiate combustion catalytically at a lower temperature and continuously carry the heat away from the catalyst surface, than the amount of NO_x produced is small [32]. Catalytica Inc. has made additional progress in the design of such a cool combustor using a metal monolith [33]. Any such operation will be dependent upon the efficiency of the combustion at these lower temperatures, the amount of capital, the operating costs, etc.

3. Current effectiveness of new catalytic technology

In the US (and most of the world), SCR with NH₃ is the current best approach that balances economic, technical, and regulatory concerns. In the absence of a better technical and economic solution and in view of the strides made to reduce the level of NO_x emissions to ca. 5 ppm, SCR with NH₃ will continue to be the solution of choice. A large amount of work (for example see [18,19,34–37]) has appeared on the Cu-ZSM-5 system. The level of Cu is crucial to optimal performance, with the highest activity for NO decomposition on apparently over-exchanged Cu²⁺. Ion exchange with a large number of other cations was not productive. ZSM-5 is unique in activity vs. MOR, Y, or X type zeolites. Presently, it appears [19] that the Cu-ZSM-5 system lacks sufficient activity (by about a factor of 2–4 even in a dry environment) for commercial applications. Long-term hydrothermal testing [38] and engine testing

[39,40] have proven that the current composition displays relatively rapid and irreversible deactivation and thus will not withstand the rigors of mobile or stationary engine demands. Given the huge level of research on this approach, it seems unlikely that slight modifications of Cu-ZSM-5 will provide an acceptable solution. Recent research has shifted to NO reduction by hydrocarbons. Hydrocarbons do provide more activity with regard to NO_x reduction, but that activity is dependent on the type of hydrocarbon. Interestingly, the optimum level of copper in Cu-ZSM-5 is not the same for NO_x decomposition vs. hydrocarbon reduction. For Cu-ZSM-5, the catalyst is still very sensitive to the presence of water vapor at high temperatures for extended periods of time. Co-ZSM-5 does offer comparable activity with these higher hydrocarbons, and it does appear to be much more hydrothermally stable [22,41]. The use of hydrocarbons holds promise, but companies probably would prefer not to add another compound or new fuel (which has its own cost and transportation costs) to remove NO_x, unless one can use on-board fuel (for mobile engines) to efficiently control NO_x as well.

4. What opportunities remain?

The gradual understanding of the limits of Cu-ZSM-5 for NO_x decomposition, has diverted investigators to seek solutions with other systems, especially via reduction of NO_x with hydrocarbons. What many seem to have forgotten, or perhaps pushed aside, is that NO decomposition still offers a very attractive approach to NO_x removal. The world waited over 20 years (from the conclusion that NO_x decomposition was catalytically unattainable at any substantial level in the 1960's) until Iwamoto's breakthrough in 1986. Ultimately, more active NO decomposition (rather than reduction) catalysts may be discovered which may have commercial significance. *Creative scientists need to focus their wisdom on inventing new catalyst compositions that will allow one to break away from the current limits*

of Cu-ZSM-5. The Cu-ZSM-5 system almost gave us a very attractive solution. It was a clear breakthrough in the technology, but we need another breakthrough to handle the decomposition of NO_x under the conditions of typical wet, O₂ rich exhaust streams. We need to keep asking the question and to be alert for new catalyst compositions that offer even greater promise. Most of the current research is directed at the use of modified zeolites or simple metal oxides. Clearly simple extensions of these current approaches have not and probably will not lead to satisfactory solutions. Considering the vast amount of past, good work on Cu-ZSM-5, *the focus of research needs to shift to more complex catalyst compositions, or some step out composition that differs substantially from the current formulations being tested.*

We need to learn from the limitations of Cu-ZSM-5 and build upon that knowledge to generate new catalytic approaches. Since any combustion process is going to produce almost 16% water vapor, one must *focus on a catalyst that is stable for long times in such wet environments.* Since combustion operates with excess air, one must look for solutions with catalysts that are stable in excess air at the high temperatures of the exhaust. Further, NO_x is produced at very low levels in exhausts which emerge at high velocities. Research must be reported with *data at long exposures* from hours to days at a time. One ultimately needs to test the catalyst under *actual operating conditions*; in the absence of a true engine exhaust, researchers must study simulated exhaust compositions which include 16% water vapor, ppm levels of SO_x, and ppm levels of NO_x. (It is unwise to assume that studies at 500 ppm to percentage levels of NO_x are acceptable gauges of NO_x removal from ppm level streams.)

Further new catalysts need to be evaluated and tested for performance at relatively high space velocities (e.g., GHSV of > 10000). Automobile companies and power suppliers cannot afford to add control systems which also produce undesirable increases in back pressure. In addition, we need to be able to benchmark the progress of the research. Catalysts that are purported to offer new

activity are useless unless they can perform at these high space velocities over an extended period of time from ambient to short-term exposures at 1000°C (700°C for diesels). The discovery of model catalysts does add fundamental knowledge, but only if that knowledge is pointed to the correct target.

Research that focuses on characterizing and analyzing the Cu-ZSM-5 catalyst has been underway for almost 8 years; we really do not need more research focused at this approach. What is needed now is to understand why these catalysts are unacceptable and then to use this knowledge to design new catalyst systems that meet the demanding conditions described above.

Finally, people need to think more creatively about *avoiding NO_x emissions in the first place*. Oxides of nitrogen are generated in other chemical operations such as the production of HNO₃, the combustion of methane used to heat the steam methane reforming reactors for producing H₂, the synthesis of Nylon 6,6, the burning of coal for chemicals or power, etc. These are a few of the more well-known processes that produce NO_x as a byproduct. The cool combustion approach to catalytic combustors for gas fired engines is one approach at avoiding NO_x emissions. Are there other approaches applicable to NO_x reduction from any of these other NO_x generating processes?

5. Conclusion

Clearly there are enormous health and economic benefits to new technologies for NO_x removal. The reduction of NO_x with hydrocarbons is enjoying a lot of attention, but hydrothermal stability with sustained activity is still a troubling point for many of the current catalysts. Further plant operators and mobile vehicle manufacturers would prefer not to transport, store, and pay for a separate reductant to post treat the exhaust. Stationary engine users will be more concerned with the cost of the hydrocarbon source and any secondary pollutants. Ultimately, the catalytic decomposition of NO into its elements offers the

cleanest and most direct approach to NO_x removal. For this approach another breakthrough is needed to provide a catalyst with substantial activity that can perform in the typical exhaust atmosphere. Scientists need to break away from the heavy emphasis on Cu-ZSM-5 and seek newer, more active catalysts. These catalysts should be tested under realistic feed compositions typical of actual exhaust streams, especially containing high levels of water vapor. Alternatively, new combustion or chemical process technology that does not co-produce NO_x would be an even more desirable alternative. These last two approaches are very difficult and will demand additional creativity and breakthroughs.

Acknowledgements

We thank Air Products and Chemicals, Inc. for the permission to publish this work.

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