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Catalytic solutions to reduce pollutants

J.N. Armor*

Air Products and Chemicals, Inc., 7201 Hamilton Boulevard, Allentown, PA 18195, USA

Abstract

A summary of the type and level of a multitude of atmospheric pollutants is provided. This manuscript will offer an assessment of potential target areas in the area of environmental catalysis and where the author believes attention needs to be focused. In particular, the area of CO_2 emissions and their conversion to useful chemicals as well as the need for cheap and abundant H_2 will be discussed. There is no simple solution to the CO_2 problem. The production of chemicals from CO_2 offers little impact, while increased energy efficiency offers only a partial solution to the current imbalance of CO_2. Some brief remarks will be offered on assessing current experimental strategies (especially for NO_x removal) as well as identifying particular atmospheric pollutants for more intensive research efforts.

Keywords: Environmental catalysis; CO_2; Hydrogen; NO_x; Sulfur oxides

1. Introduction

Catalysis has offered and will continue to offer attractive, economical solutions to improving our environment. One clear example is the role of auto-emission catalysts in reducing NO_x, hydrocarbons, and CO. After years of use, the presence of catalytic converters on most automobiles in the USA is beginning to make a visible improvement in the atmosphere over major metropolitan cities. Worldwide, selective catalytic reduction of NO_x by ammonia over a vanadia-on-titania catalyst is the preferred choice of industries emitting NO_x (NO and NO_2). Production of CFCs has now been eliminated by most major industrial nations of the world.

Significant atmospheric pollutants include: CO_2, CO, CH_4, non-CH_4 VOCs, NO_x, SO_2 and N_2O. A summary of the level and source of most of these pollutants will be provided, and followed by some perceptions of where the most significant problem areas remain, especially with regard to finding catalytic solutions to avoiding or preventing the production of these atmospheric pollutants. Due to the limitations of space, focus of this analysis will be on the problem of CO_2 production and the interest in converting CO_2 to chemicals. Thus, other important areas for research such as removal of NO_x and SO_2, as well as H_2 production, will receive little attention, while important areas such as waste-water treatment and waste minimization will not be discussed at this time. Aspects of the latter topics were discussed in an earlier review [1].

2. Identifying the problem

An excellent summary [2] of the volume and sources of major atmospheric pollutants was recently

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*Corresponding author. Tel.: (1-610) 481-5792; Fax: (1-610) 481-2989; e-mail: armorjn@apci.com

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published by the US Department of Energy. Highlights of their report can be broken down into the types, namely volumes and sources of a variety of pollutants.

- CO_2

Natural and human sources – in millions of metric tons (mmt) of CO_2 per year:
160 000 generated naturally, worldwide
8000 from human derived sources, global
165 000 absorbed by earth
the balance is a global increase of ~3400 mmt
1375 mmt CO_2 from energy production in the USA

- CO: > 107 mmt, globally

– 79 mmt in the USA, 80% from mobile engines!

- Non-CH_4 VOCs

– 79 mmt in the USA, 87% from stationary and mobile engines

- NO_x emissions: > 30 mmt, globally

– 21 mmt in the USA, 95% from vehicles and power sources

- SO_2 emissions: > 42 mmt, globally

– 22 mmt in the USA

- CH_4 (global) sources in mmt

– 160 from natural sources (rice, animals)
– 370 from human derived sources (cars, refineries, coal mines, andfills)
27.2 mmt from US human sources
but only 0.12 mmt of CH_4 from US industry
– 500 adsorbed by the earth

- N_2O (Global) Sources in mmt

– 11 from natural sources
– three from human sources (fertilizer, fuel oil, cars)
– 10 adsorbed by the earth

From this listing it is apparent that CO_2, CO, VOCs, NO_x, and SO_2 represent major sources of pollutants. Although the source of N_2O is small, it is important as a pollutant. This is because the earth only has a limited capacity to absorb N_2O since it has a lifetime [3] of over 150 years in the upper atmosphere.

3. The CO_2 problem

The perceived[1] CO_2 problem exists because huge quantities of CO_2 are produced worldwide. The imbalance noted above is largely a result of economic progress resulting from consumer and industrial demands for more power and mobile vehicles. Large amounts of CO_2 are absorbed (165 000 mmt) by the earth mainly via the capacity of our oceans. If the natural emissions of CO_2 (160 000 mmt) were our only concern, the earth should easily absorb this amount of CO_2, and there would be no imbalance. However, an additional 8000 mmt of CO_2 are produced from human-derived sources, which causes an imbalance of about 3400 mmt of CO_2 per year. The major portion of this imbalance is due to huge amounts of CO_2 emitted by power plants and mobile engines. The US accounts for only a part of this imbalance. What is distressing is that CO_2 levels will continue to grow as an increasing number of emerging nations demand the advantages of growth and with that new sources of CO_2.

A number of solutions have been proposed to reduce this imbalance, including the establishment of a 'carbon tax', efforts to minimize CO_2 emissions (already underway) [4], demand for zero emissions of CO_2 (solar, hydroelectric, wind, nuclear, or geothermal), bury CO_2 by deep storing in ocean pools [5] or use it for enhanced oil recovery [4], absorb it for re-use or purification (already done using monoethanolamines) and, finally, to consider it as a feedstock for valuable chemicals. The carbon tax is highly unpopular; emerging nations certainly cannot accept curtailing growth, there is only a limited need for CO_2 as a bottled gas, so there is intense interest in converting this excess CO_2 into chemicals. Absorption technologies are available and are used to a limited extent, but they are expensive and highly energy-intensive [6].

Rostrup-Nielsen pointed out [7] in 1994 that it is "questionable whether C_1 chemistry can contribute

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[1] There is some disagreement about global warming and the role of CO_2; also the value of 3400 mmt is the difference between two very large numbers.

significantly to solve the greenhouse problem created by CO_2." For example, the present world production of acetic acid is about 5 billion pounds per year. If one were to use $CO_2 + CH_4$ to produce acetic acid, this would amount to the CO_2 emission from only ONE 500 MW coal-fired power plant. The world production of methanol is approx. 20 billion pounds per year which would correspond to the CO_2 emitted from an approx. 4500 MW coal-fired power plant. Thus, it is apparent that even these large-volume chemicals cannot be used to substantially reduce the imbalance of CO_2 produced globally.

If one had sufficient volumes of H_2, one could consider reducing CO_2 back to methanol, CH_4 or CO and consider these as future feedstocks; however, there is a major supply/demand crunch now for H_2. H_2 is needed by refineries [8] to process the nitrogen and sulfur components as well as to make up for the loss of H_2 from the former reforming approaches.

H_2 is produced primarily [9] from steam methane re-forming (SMR) as well as partial oxidation (PO) of fossil fuels, and to a lesser extent, electrolysis. Electrolysis is a very expensive approach for producing H_2, and it is only used when there are nearby and cheap sources of electric power. Both SMR and PO produce CO_2 as a co-product [9], so it does not seem to make sense to co-produce CO_2 when making H_2 and then use the same H_2 to re-reduce CO_2! Thus, if we want large volumes of H_2 to remove CO_2, we must come up with new approaches to making H_2 without co-producing CO_2. Considering the huge quantities of water available on this planet, it would appear that the photodecomposition of water to H_2 and O_2 offers one potential solution for producing the quantities of H_2 necessary to remove CO_2. Some investigators are pursuing the use of a photocatalyst which allows one to use the solar radiation to efficiently dissociate water to produce H_2. This is a very difficult challenge, which many have struggled with for decades.

In the absence of sufficient volumes of cheap H_2 to reduce CO_2, it has been suggested that one could consider using this CO_2 as a feedstock for various chemicals [5,10]. The difficulty is that CO_2 is relatively inert – it represents a highly stable form of carbon; any attempts to convert CO_2 to value-added chemicals will demand added energy in the form of added heat, light, or some chemical. It is a matter of the fundamental thermodynamics of the problem: CO_2 cannot be converted to more value-added products without substantial inputs of energy [11]. It is possible to react CO_2 with CH_4 to produce H_2, but this is a highly energy-intensive reaction that does not proceed without eventual deposition of carbon, unacceptably fouling any current commercial catalyst. One can treat CO_2 with NH_3 to produce urea, but there are limited demands for urea which, in turn, is controlled by the price of NH_3. (NH_3 plants are largely H_2 plants!) One can react CO_2 with H_2 to produce valued-added products such as methanol or methane, but again this requires cheap H_2. All these technical hurdles would need to be solved, and if so, the chemical industry worldwide (not just regionally) would have to universally accept CO_2 as a feedstock in order to begin to significantly reduce some of this imbalance.

Even if one could find sufficient levels of H_2 to convert CO_2 to value-added chemicals, one must remember that there will be significant (and probably economically nonviable) demands upon the quality of the CO_2. One cannot simply use CO_2 being emitted from a power plant without further cost. There are issues of purity, continuous availability, transportation, pressure, and reactivity that must be considered. The purity of the CO_2 will be absolutely critical: one cannot use CO_2 contaminated with traces of NO_x, SO_2, N_2O, or even water vapor. Any feedstock must be continuously available: the volume of CO_2 from power plants is often produced as a function of peak power demands, that is to say more is available during certain times of the day, but a chemical plant does not operate on a partial-day basis. The CO_2 must be produced at the site of its intended use: it would no longer be 'free' if it had to be transported to another location. Some storage (tank farms) or piping systems would be necessary to ensure a continuous supply and to move the CO_2 to the site of use. Most importantly, because of its inherent stability and low chemical reactivity, if one is going to react CO_2, it must be available at elevated pressures. Again, CO_2 emissions are often diluted with air, or water vapor, which means these components would have to be removed before their pressurizing the CO_2 [12]. Concentrating and pressurizing the CO_2 adds two costly steps.

Regrettably, there seems to be no simple, even long-term solution to the CO_2 problem. There are small steps that can be taken such as replacing coal-based sources with natural gas. CH_4 yields about 70% more energy for each unit of CO_2 [13]. Only small gains toward reducing the CO_2 imbalance can result from more use of CO_2 as a feedstock. Increased energy conservation, thus leading to less CO_2 emissions, offers another partial solution. In the long term, the production of H_2 from nonfossil fuel sources of energy, such as the solar photocatalytic decomposition of water, may offer one catalytic approach to a partial solution. There are other creative noncatalytic solutions that have been proposed. Attempts to partially solve the CO_2 problem need to appreciate the issues of CO_2 purity and pressure for its use as a chemical feedstock. However, simply removing CO_2 from one point source in our atmosphere will not significantly reduce the equilibrium concentration of CO_2; it will only make a small dent in the total global level of CO_2 in our atmosphere.

4. Targets for environmental catalysis

Certainly, not all our environmental problems can be resolved by catalysis, but a major portion of these could potentially be reduced if appropriate catalytic solutions are discovered. My belief is that there are certain topics which deserve more attention than others. These include:

- SO_2 removal
- NO_x removal
- Waste-water cleanup
- Waste minimization
- Catalysts for increased energy efficiency
- H_2 production without co-product CO_2

There are other pollutants, not on my list because there are already known and/or acceptable solutions to CO, VOCs, N_2O, CH_4, particulates and ozone. The CO_2 problem has already been addressed in the prior section. As an impurity, it can readily be removed by absorption; as a co-product, our best approach without nonfossil fuel sources of power or H_2 is increased energy efficiency, which can be impacted by waste minimization [1].

4.1. NO_x removal

Time does not permit a detailed review and analysis of catalytic approaches to NO_x removal. A recent review by this author provides such a summary and offers some guidance about what areas deserve further attention [14]. Also, one should appreciate that NO_x, SO_2 and CO emissions are often a local problem (often aggravated by high population density and/or geography (such as the Los Angeles basin)), but CO_2 is a long-term global problem. Since many of these critical approaches seem to be ignored in most publications, let me restate them once again.

Most NO_x exhaust streams contain high levels of water vapor. Water vapor has been established [15,16] as a known inhibitor in most NO_x reduction catalysts. Thus, any study announcing new catalysts for NO_x removal must consider and evaluate these same materials in wet NO_x atmospheres of $> 10\%$ water vapor. Unless there is a worldwide reduction of sulfur levels in fuels, NO_x streams will usually have ppm levels of some sulfur compound; thus NO_x-removal catalysts must also be tested for their resistance to sulfur in the form of H_2S or SO_2.

If one is going to use a reductant such as methane or propane to reduce NO_x, it will not be acceptable to add large excesses of hydrocarbon to destroy ppm levels of NO_x. We may recall that a great percentage of NO_x in exhaust streams lies at < 1000 ppm. Stoichiometry for NO_x reduction by any hydrocarbon in the presence of O_2 requires only two atoms of hydrogen for every nitrogen atom as NO. Thus, working with a two- or tenfold stoichiometric excess of a hydrocarbon only ends up polluting the air with excess hydrocarbon (which then must be scrubbed or burnt, to produce more CO_2).

Typical exhaust velocities from power plants are of the order of >30 000 GHSV. The turnover efficiency of NO_x catalysts needs to be evaluated in realistic operating regimes of space velocity or residence time.

Any NO_x-removal catalyst will have to perform for periods of months to years at a time. This demands that reports on NO_x removal clearly state the lifetime of the study and this should exceed 4 h of sustained activity at any reported conversion.

One notices an increasing number of NO_x-removal studies being reported without any reference to previously established catalysts. Catalysts should always be benchmarked against state-of-the-art materials. Reports of improved catalyst life without some reference point to established catalysts under similar operating conditions only adds confusion to the growing literature in this area.

4.2. *Removal of SO_2*

The production and elimination of SO_2 into our atmosphere are a major environmental problem without a completely clean solution so far. Current approaches in commercial use that convert the SO_2 to another material require further disposal or treatment to add value to the sulfur-containing product. There are approaches to oxidize dilute SO_2 to SO_3 and ultimately produce sulfuric acid. However, the acid has little value in the dilute form, and usually must be concentrated, which adds cost and may involve additional transportation costs. SO_2 can be precipitated by the addition of lime to produce gypsum which can be used as a construction material or buried in a landfill. Finally, SO_2 can be treated with H_2S to produce elemental sulfur; however, there is a plentiful supply of elemental sulfur. All these processes produce compounds containing some form of sulfur, these being of little immediate value. We need to think of more creative approaches to catalytically remove or convert this sulfur to a value-added product. Another possible approach is to use SO_2 to remove NO_x [17].

5. Conclusion

It is apparent that some pollutants are more serious than others, just by their sheer volumes. Some, like CO, VOCs and N_2O, already have reasonable catalytic solutions that are being applied. Others, like CO_2 offer major challenges because there is no clear effective and commercially attractive way to catalytically convert CO_2 to value-added compounds. It would appear that one partial key to the CO_2 problem is providing sufficient and cheap sources of H_2 for reduction of CO_2 to value-added products. However, one must keep in mind that CO_2 will need to be concentrated, pressurized and purified if one wants to use it as a feedstock. Another partial solution is to continue to pursue greater energy efficiency in order to reduce power demands.

A great deal of worldwide effort is underway to reduce NO_x, but this should include many more studies incorporating the use of $> 10\%$ water vapor, traces of H_2S, higher GHSV, and adequate bench marking so that the reader can truly appreciate the significance of the reports. Finally, in the area of SO_2 removal, one needs to come up with new and creative catalytic solutions about what to do with all the sulfur produced by current treatment approaches.

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