Frontiers & Tasks of Catalysis Towards the Next Century

Frontiers and Tasks of CATALYSIS TOWARDS THE NEXT CENTURY

PROCEEDINGS OF THE INTERNATIONAL SYMPOSIUM IN HONOUR OF PROFESSOR TOMOYUKI INUI

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Frontiers and Tasks of Catalysis Towards the Next Century

Professor Tomoyuki Inui

FORWORD

This special issue is dedicated to Professor Tomoyuki Inui of Kyoto University to celebrate his retirement in March 1998. The 41 contributions constitute either invited talks or invited posters, which will be presented at the International Catalysis Symposium on Frontiers and Tasks of Catalysis towards the Next Century. The Symposium has been organized to honor Professor Inui, with the help of financial assistance from the Ministry of Education, Science, Sports and Culture, Japan and will be held at the Kyoto International Conference Hall on the 20th and 21st March 1998.

Professor Tomoyuki Inui graduated from the Department of Fuel Chemistry, Faculty of Engineering, Kyoto University in 1957 and finished his M.S. and Ph.D. courses at the same university in 1959 and 1962, respectively. Since 1962, he has worked for the same department as a Research Associate until 1978 and as an Associate Professor until 1983, after which he became a full Professor. From 1986 to 1994 he also served as a Professor of the International Corporation Center for Science and Technology, Tokyo Institute of Technology.

Professor Inui has long been widely admired for his distinguished mastery of experimental techniques and his innovative and skillful approach to catalysis research, which have made great contributions to the development of the petroleum chemical industry and to the solutions of energy resource and global environmental problems. He is recognized not only for outstanding research achievements, but also for his superb educational talents and his caring attitude which have resulted in the nurturing of many students into established, respected figures in academia and industry.

Professor Inui's research has always focused on the synthesis of novel catalysts and their practical performance. These contributions include the selective oxidation of lower hydrocarbons, the high-rate synthesis of chemical feedstocks and fuels from non-petroleum resources, the high-rate transformation of carbon dioxide to important chemical intermediates, the purification of exhaust gases, catalytic combustion, effective separation of mixed gases, high-grade purification, and the elucidation of the structure and dynamic behavior of heterogeneous catalysts. In addition, his recent research has shown the importance and validity of non-linear phenomena in catalysis in the analysis of the reaction kinetics and in the improvement of catalytic performance. He is the author of more than 310 technical papers and more than 100 review articles and books and also holds many patents for his work in heterogeneous catalysts.

During his career, Professor Inui has received many honors: the Progress

Award in the Fuel Society of Japan (1983), the Chemical Society of Japan Award (1989), Catalysis Society of Japan Award (1992), the Japan Institute of Energy Award in Academic Division (1994), and the Japan Petroleum Institute Award (1995). He has served on the editorial boards of Applied Catalysis, Catalysis Letters, Zeolites, and Catalysis Surveys form Japan. In addition, he has served as President of the Catalysis Society of Japan, and the Japan Association of Zeolites, and as a member of many important Advisory Committees of the Ministry of Education, Science, Sports and Culture and the Ministry of Industrial Trade and Industry.

It is our greatest pleasure and honor to publish this special issue as Guest Editors for Research on Chemical Intermediates and we are indebted to the editors of the journal, Professors M. Anpo, M. C. Depew, and J. K. S. Wan who kindly gave us this opportunity. We would be very grateful if this issue could help us recognize Professor Inui's outstanding contributions to catalysis science and technology, including a successful research and teaching career in Kyoto University, and his friendly and attractive personality. Most importantly we would like to thank very much all of the authors for their significant contributions in the production of this special issue.

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CONTENTS

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IMPORTANT TARGETS IN ENVIRONMENTAL CATALYSIS©

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Abstract– Catalysis has offered and will continue to offer attractive, economical solutions to improving our environment. The focus of this manuscript will be on the opportunities for catalysis research to provide solutions for improving our environment, some of which are described in an earlier review article [1] which will be updated. Some of the big emissions/environmental problems that remain are NOx cleanup [current approaches are not sufficient to meet intended emissions' standards], SO_2 removal, waste water cleanup, increased energy efficiency, H_2 production without co-product CO_2, and waste minimization. Among these topics there seems to be an over-emphasis on NOx removal at the expense of other important topics also needing a solution. In some areas such as mobile engine emissions control, we need to shift the balance our research efforts to better match the fuel choices of the future. Comments are offered with respect to solid acid research opportunities and also the large scale conversion of CO_2. This manuscript reviews some catalytic solutions and highlights opportunities for others. An assessment will be offered about what the problem areas are, where the author believes more attention needs to be focused, as well as identifying new opportunities for research in applying catalysis to the control of undesirable waste products.

INTRODUCTION

Catalysis offers a clear opportunity to provide realistic solutions to many environmental issues. There are at least two approaches to consider in reducing undesirable emissions. They are to treat the pollutant being emitted or better still don't produce the pollutant at all! Often we seek the former because we have no easy and economically acceptable approach which avoids producing the pollutant. Examples of the former are the three way auto exhaust catalyst and selective catalytic reduction of NOx by NH_3, according to equation 1.

$$4NO + 4NH_3 + O_2 \rightarrow 4N_2 + 6H_2O \qquad (1)$$

Examples of approaches where we already avoid making the pollutant include various types of waste minimization, the design of new catalysts for alternative, less polluting products, or new routes to valuable products without the formation of

undesirable coproducts.

Historically, catalysis has provided economical solutions to auto emissions control, emissions from stationary engines for power plants, volatile organic compounds [VOCs], and CFCs. This article attempts to highlight where opportunities exist beyond the current popular emphasis on NOx removal. First we need to understand the types of pollutants we are considering and then focus on areas which could receive much more attention.

Levels of pollutants

Past articles [2,3] have described the various levels of undesirable pollutants, which include CO_2, NOx, SO_2, CFCs, N_2O, CO, VOCs and CH_4.

CO_2 emissions. This particular emission has received a lot of recent attention, so I shall only summarize what has already been said. For CO_2, it is estimated that 160,000 million metric tons (mmt) are generated naturally, worldwide: 8,000 mmt from human derived sources, globally: 165,000 mmt are absorbed by earth, with the balance being a global increase of ~3,400 mmt. There is some disagreement about the accuracy of the latter number since it is based on the difference of two large numbers. Further, a small group of scientists contend that global warming is not related to CO_2, but to other factors such as water vapor. An earlier manuscript [4] described solutions being considered for CO_2 removal, the chemical and political limitations on use and reduction of CO_2 levels, and the role of H_2 in effecting a solution.

Other emissions. The level of CO amounts to >107 million metric tons emitted globally, of which it is estimated that the USA accounts for 79 mmt. 80% of the latter number is ascribed to mobile engine emissions. For non methane VOCs, it is estimated that the USA generates 79 mmt with 87% coming from stationary and mobile engines. NOx emissions amount to >30 mmt globally with 21 mmt coming from the USA and 95% of the latter comes from vehicles and power sources. SO_2 emissions amount to 42 mmt globally.

IMPORTANT TARGETS FOR ADDITIONAL RESEARCH

At the very beginning of this manuscript, I would like to point out those topics which I believe deserve particular attention for additional R&D, and in this regard are particularly amenable to catalysis providing a practical approach. They include catalysts for

- Increased energy efficiency

- Waste minimization
- Waste water cleanup
- NOx removal [>30 million metric tons/yr]
- SO_2 removal [>42 million tons/yr]
- H_2 production without co-product CO_2

One may note that CO, hydrocarbons, N_2O, CH_4, particulates, and ozone are not listed. This is because we already know of catalytic approaches which are quite suitable for removing these particular compounds. We need to focus on those molecules which are particularly unattractive [bulleted items above] rather than do more work on those where solutions already exist. The balance of this manuscript will provide some commentary to expand on aspects of the bulleted items listed above as well as some other topics dealing with environmental catalysis.

Increased Energy Efficiency

The reason for my focus on increased energy efficiency is that this would focus research on reduction of power requirements and thus also reduce the emissions [NOx, SO_2, and CO_2] which arise from power generation. In a recent article by M. Carson [5] power generation is a major reason for the huge amounts of CO_2 which are generated and will continue to build into the next century. With the combustion of fossil fuels, also comes the coproduction of NOx and SO_2 which are linked to the combustion process and to the sulfur content of the fossil fuel. What is alarming is the large increases in CO_2 that are forecast over the next twenty years. While those from the USA are projected to grow by less than 30%, those from other existing strong economies are expected to grow by more than 50%, while China is projected [5] to grow by >230% and India by >200%! Thus, simply by focusing on enhanced efficiency in the way we produce power [such as burner designs, combustion efficiency, etc] would offer a big impact on reducing the projections above. Much of the new growth in power demands will come from new construction in these emerging nations where designing improvements to power generation and emissions control will have a great deal of impact on these projections. Catalysis can play a significant role here.

Waste Minimization

Not only does the concept of waste minimization mean reduced by-products, but it also carries with it enhanced energy efficiency [by reduction of the number of process steps and the energy needs associated with that] and also the concept of generating higher product yields per unit of energy used. There are a number of processes which are prone to improvements in yields because their current

efficiencies [selectivities] are much lower than those we typically get for most large scale chemical processes. Many of these include reactions employing oxidation, which often suffer from reduced efficiency due to over oxidation to produce CO_2. Specific opportunities include O_2 oxidation of methane directly to methanol in one step. Other one step oxidations include benzene to phenol, and propylene to propylene oxide. In all such selective oxidations it is important to appreciate that it would be most appropriate to carry out such oxidations with molecular oxygen [either as pure O_2 or with air]. If one uses air, the temperature of the oxidation is important since by-product formation of NOx from the oxidation of the N_2 in the air is an undesirable factor. On the other hand there has been much written and done with using H_2O_2 as a clean, selective oxidant, but one must appreciate that hydrogen peroxide [as is ozone] is a relatively expensive source of oxygen atoms. This is not only because of the added cost of making H_2O_2 from O_2 , but also the fact this is diluted with water which not only reduces its effectiveness but also adds transportation costs. Thus the ideal oxidant of choice would be to use O_2.

Other direct processes offering advantages of waste minimization include the decomposition [as opposed to the reduction of] NOx to N_2 and O_2, an energetically very favorable reaction, but kinetically very difficult to achieve. In addition the use of SO_2 over a wide range of pH to reduce NO to N_2 would be an another interesting approach to NOx removal while simultaneously using the pollutant SO_2.

In any of these waste minimization processes, all of which are characterized by reduction of process steps, one must achieve such reactions with high yield, high selectivity, high rates, and excellent catalyst life with low capital costs. It makes no sense to minimize waste with more costly processes (with extremely cost energy sources or low yield operations demanding enormous recycle costs). Attempts to minimize waste without attention to yields, selectivities, rates, catalyst life and capital costs will only bring about unacceptable solutions and a poor use of potential R&D funds.

The importance of capital costs to new technology R&D is nicely described in a recent article by Tijm, *et al.* [6]. Research groups cannot ignore the impact of capital costs as a simple tradeoff for cheaper feedstocks. Also with regard to use of methane as a feedstock, the low feedstock cost of CH_4 often cannot offset the economic penalty that comes with low yields per pass of some more direct processes. Further, the high cost of capital, heat and mass transfer duty can be major factors in deciding against the use of new technology. Other forces which control process economics include the economies of scale [some larger processes are more efficient to run because one can reduce cumulative capital and feedstock costs and because of better energy management]. There is also a strong relationship between capital costs and the thermal efficiency of fuel manufacturing plants.

Waste Water Purification

Two recent UN sponsored reports [7,8] warn that the world must act now to protect its water. In many regions of the world, people take for granted the real value of the water which we use, while in many other regions water is a limited natural resource because of supply or contamination. We must not just develop new processes for treating water, but also for the processes which use and affect the water we use. This means more efficient use of water, especially in view of the continued global warming which will increase irrigation needs even further. In addition certain types of energy production consume more water than others. Coal gasification or use of oil shales require 20-50 times more water to process these fuel sources than the use of oil or natural gas.

Another factor in the quality of our drinking water is the presence of nitrates and nitrates caused by tremendous amounts of runoff from soil where nitrates are used as fertilizers. Some have advocated that a surcharge should be placed on the cost of nitrate fertilizers to reflect the added cost they impose on the local regions for the eventual removal of these nitrates. The use of nitrates as fertilizers also leads to enhanced levels of N_2O, another undesirable emission [8]. This issue is complicated by the fact that the use of NH_3 and nitrate fertilizers is critical for our survival in the production of essential amino acids, urea, DNA, and proteins. It is estimated that one third of the protein responsible for nourishing mankind depends upon the use of synthetic fertilizer. Unfortunately a problem arises from the runoff of nitrates which then accumulates in the water supply.

In attempting to treat waste water we need to appreciate that there are multiple parts to this problem. Not only are nitrates and nitrites present but also many different types of undesirable organic compounds in low levels. Many of the organic compounds cannot be removed by a single, simple, cost effective catalyst. Further, the removal of the organic compound still leaves the nitrates and nitrites in the water. In treating the waste water one has to appreciate that it must be done at low temperatures [preferably <100 °C] because one doesn't want to spend a lot of energy to vaporize water needlessly. Further, such treatment must be done in the presence of an excellent ligating material, water itself. In using catalysts for such operations, they must not only perform efficiently in the presence of large amounts of water, but catalyst erosion and leaching is unacceptable. Thus the problem is not only removing dilute levels of impurities, but also the presence of many different types of pollutants further complicated by the presence of nitrates and nitrites which may still have to be removed by some alternative approach.

Removal of Harmful Gases

Auto emission controls. B. Cooper has summarized some of the opportunities

in auto emissions control. These include improved thermal durability of the catalysts, developing fast light off catalysts, developing thin wall substrate systems, improving methods of dispersion and stabilizing key catalytic components, substituting nickel with other components in order to suppress H_2S emissions, and developing new lean NOx catalysts. Further the problems are different but even more complicated for diesel engine emissions control [9].

NOx removal. Much has already been said about means to remove NOx [1,4], so I don't believe there is a need to repeat much of what has already been written. Let me just summarize some key thoughts in this regard. Additional research on this topic should not focus only on ideal atmospheres. There is a need to operate in the presence of what may seem, but are typically present, large levels of water vapor [>10%]. If one chooses to use a hydrocarbon as a reducing agent, large excesses of hydrocarbons are not acceptable, since they then must be removed. Ethane, ethylene, propane or propylene may be useful model hydrocarbons, but much more work is needed to be done with compounds similar to the components of gasoline or diesel fuels. Mobile vehicle manufacturers do not want to install two fuel systems into new vehicles, rather it is preferred to use the current fuel to treat NOx emission. In evaluating NOx removal catalysts, one needs to add SO_2 or H_2S at ppm levels since some form of sulfur is often present with emissions of NOx. Further, NOx will be present not only at dilute levels but in large volumes of gas at very high space velocities. The means to remove NOx must be demonstrated at very high GHSV, in excess of 30,000. In addition, one should not assume that removal of NOx at percent or thousands of ppms levels can extrapolate to conventional NOx emission levels at the 50-200 ppm level. Any announced breakthroughs in technology for NOx removal must be balanced and benchmarked against sustained long lived activity for hours, not just minutes. Benchmarking of new catalysts becomes increasingly important; reports of new catalysts should be compared against well established materials already reported in order to give readers a scale for comparison. Further, I believe it is necessary for us to refocus efforts away from overly popular catalysts such as Cu-ZSM-5. It is clear that this catalyst needs extensive modification because of its known hydrothermal sensitivity. Finally, NOx decomposition will always be a much more acceptable alternative in the long run because it avoids the use of another reagent, in most cases the hydrocarbons discussed above.

SO_2 removal. The removal of SO_2 is not an easy problem by any means. Many have tried in the past, but with incomplete impact upon the problem which is focused at the extremely high levels of sulfur oxides which are emitted worldwide. These sulfur oxides amount to much more [10] than the level of NOx currently emitted [Figure 1], but certainly the level of research on SOx is small compared to