Available online at www.sciencedirect.com

SCIENCE DIRECT®

Catalysis Today 100 (2005) 95–100

CATALYSIS TODAY

www.elsevier.com/locate/cattod

A view on the future of mixed oxide catalysts The case of heteropolyacids (polyoxometalates) and perovskites

Makoto Misono

Department of Environmental Chemical Engineering, Kogakuin University, Nishi-shinjuku, Tokyo 163-8677, Japan

Abstract

Recent progress of mixed oxide catalysts has been surveyed briefly, and future opportunities of catalytic technology are discussed, taking for example solid heteropolyacid and perovskite catalysts, where some promising signs for the future are noted. It was stressed that much more efforts should be directed to develop useful catalysts in practical applications, in order to accelerate the progress of catalytic science and technology.

Keywords: Heteropolyacids; Polyoxometalates; Perovskites; Catalyst design; Mixed oxides

1. Introduction

The development of high-performance catalysts is still very important for chemical technologies that supply useful substances to the society and assist keeping the environment healthy. However, it recently appears that the progress of catalytic science and technology is slower and epoch-making innovations in catalytic technology are fewer, particularly in heterogeneous catalysts, although the number of papers maintains a high rate of increase. The slow progress and few innovations may be connected with each other. In my view, a catalyst can be called a catalyst only when it catalyzes useful reactions in practical application. This is the same as that a technology is called a technology when it works well in the real world. Hence, the reason why the progress of catalytic science and technology is recently slow is probably because sufficient efforts are not devoted to develop novel catalysts for practical applications. We may lack more than before the collaboration between fundamental and applied researches, and probably our selections of target reactions have not been good enough.

In the above respect, the value of R&D on practical catalysts (these are important as described above) may be expressed, for example, by

$$\text{value} = \frac{I}{1 + D} \tag{1}$$

where I is the impact on catalytic technology, such as novelty, expected profit, greenness, etc., and D is the distance (length of period) to the realization in the real world. This equation is conceptual, just indicating that the value, V, increases with the impact, I, and decreases with the distance, D. A similar equation may be proposed for fundamental research for practical catalysts, as well.

In this short article, the progress of mixed oxide catalysts is surveyed focusing on heteropolyacid and perovskite catalysts. It is also attempted to pick up several achievements that may lead to future innovative catalytic technologies and important problems to be solved by basic research for the progress of the technologies.

My personal belief is that the breakthroughs in the design of heterogeneous catalysts (undoubtedly for practical applications) can be brought about by the design at the atomic/molecular level. Although this is not an easy task, our efforts have been devoted to construct the basis for

---

E-mail address: misono@cc.kogakuin.ac.jp.

0920-5861/$ – see front matter © 2004 Elsevier B.V. All rights reserved.
doi:10.1016/j.cattod.2004.12.010

this design by choosing crystalline heteropolyacid and perovskite mixed oxides, as described in our recent accounts [1–3]. Our basic concept is that mixed oxides having well characterized structure, at least in the solid bulk, are suitable for the catalyst design at the atomic/molecular level.

2. Solid heteropolyacid (polyoxometalates) catalysts

2.1. General remarks on solid heteroplyacid (HPA) catalysts

Fundamentals that make possible the design of solid HPA catalysts at the atomic/molecular level have been fairly well established. First, several groups including our group showed that the molecular nature of heteropolyanion is maintained in the solid state, if necessary caution is paid, and that their acid and redox properties can be controlled in a regular way by changing the atomic composition. Second, we found that the presence of hierarchical structures (primary, secondary and tertiary structures) and three different modes of catalysis (surface-type, pseudoliquid (bulk-type I), and bulk-type II) [1,4,5]. We demonstrated that these are the indispensable basic concepts for the understanding and design of solid HPA catalysts. For example, due to the pseudoliquid behavior that we first reported in 1979 and summarized in 1987 [5], not only very high catalytic activities are obtained, but also reaction mechanisms are elucidated at the molecular level. Recently the locations and dynamic behavior of acidic protons have been spectroscopically clarified [6,7]. In addition, precise control of pore size was made possible for Cs and K salts through the understanding of their nanostructures [1,4].

There are already more than seven large-scale industrial processes using HPA catalysts, mostly in Japan. A recent topic in industry is that remarkable improvement was reported for the process of ethyl acetate production catalyzed by HPA (Showa Denko), although the plant already started several years ago.

2.2. Acid catalysis of HPA

2.2.1. Recent progress

It has been demonstrated that the catalytic activities for surface-type reactions are correlated proportionally to the surface acidity and those for the reactions in pseudoliquid to the bulk acidity [1,4]. In the former case, we found that Cs2.5 ($Cs_{2.5}H_{0.5}PW_{12}O_{40}$) is much more active than the traditional solid acids for many liquid-phase organic reactions of surface-type and that precise control of nanopores of acidic Cs salts brings about remarkable shape selectivity that differentiate the molecular size of reactants [1,4].

The followings are two recent interesting findings for practical application of solid HPA in liquid phase. Efficient solid catalysts are very desirable in the wide range of applications in the syntheses of fine chemicals. Here, the *E*-factors (by-product/main product ratios proposed by Sheldon) are very large (10–100), due to the multi-step syntheses and to mass and energy consumption during separation and purification. An example shown in Fig. 1 [8] demonstrates that usage of solvents is tremendous.

2.2.1.1. Firm immobilization of Cs2.5 on silica [9]. Cs2.5 is almost insoluble in water, but after agitation during reaction the surface layer of Cs2.5 dissolves slightly and also partly comes off as nanoparticles into solution. In addition, the particles of Cs2.5 are so small that their separation by filtration is difficult. Recently, Okuhara et al. found that Cs2.5 nanoparticles bound to the amino group of a coupling reagent, 3-aminopropyltetraethoxysilane (APTS), that is chemically bonded to the surface of silica (APTS:silica = 14:86) (Fig. 2), showed only a loss of less than 0.02% and were easily separable, maintaining more than 90% of the catalytic activity of Cs2.5.

2.2.1.2. Water-tolerant catalysis of Cs2.5 [10]. According to the adsorption of water, the hydrophobicity was presumed to be in the order of HZSM-5 (Si/Al = 628) $>$ HZSM-5 (Si/Al = 40) = Cs2.5 $>$ silica–alumina. Owing to the moderate hydrophobicity, Cs2.5 shows a high catalytic activity for organic reactions in water like hydration of alkenes and hydrolysis of oligosugars (Table 1).

2.2.2. Important problems and a topic

(a) Crystalline bulk HPA catalysts (without supports or additives) are very talented catalysts for various organic reactions. But as they show rather ‘‘strong and unique character’’, fine-tuning of acidity and choice of adequate reaction systems (reactions themselves and reaction conditions) are crucial.

(b) The structure and acidic properties of supported HPA are very important for practical applications, but they have little been clarified. The control of the HPA–

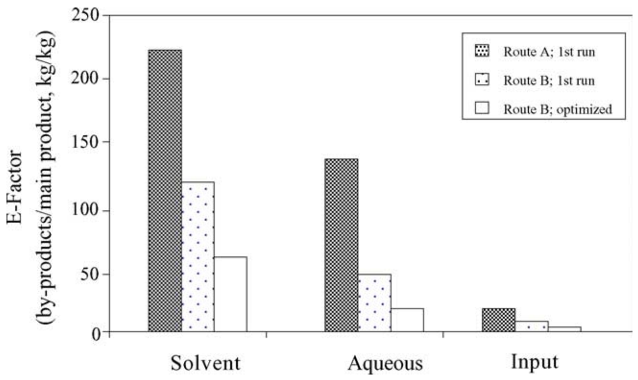


Fig. 1. Reduction of *E*-factor (by-products/main product ratio) by the optimization of synthetic route from A to B’s.

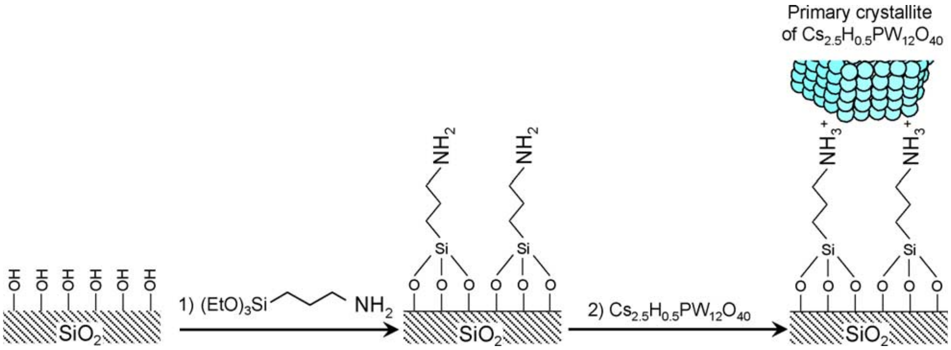


Fig. 2. Cs2.5 nanoparticles firmly fixed on silica via a coupling reagent (APTS).

support interactions was likely the key factor for the remarkable improvement of the ethyl acetate process mentioned above.

(c) Another serious problems often encountered for solid HPA catalysts are deactivation caused by by-products. As the thermal stability is not very high, coke deposits can hardly be removed by combustion. Control of acidity is one possible solution. In certain reaction systems, these problems are not serious and those reactions have been commercialized.

(d) Other mixed oxides. Recently gas-phase Beckmann rearrangement of caprolactam was commercialized by Sumitomo Chemical (2003) [11], and awarded several prizes including that of the Minister of Economy, Trade and Industry of Japan. The process that replaces the traditional process using concentrated sulfuric acid has been a long-period dream of researchers in the field of solid acid catalysts. The fact that the dream was realized by using ‘‘non-acidic’’ zeolite with extremely high Si/Al ratio was unexpected. This indicates that very weak acids can catalyze reactions that require strong acidity at a low temperature, and will provide many future opportunities in organic reactions catalyzed by weak solid acids at high temperature.

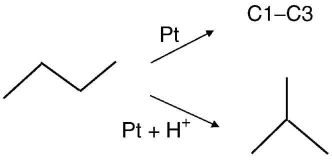
2.3. Oxidation catalysis of HPA

In my previous account [2], it was stated that in spite of extensive attempts using HPA for alkane oxidation, the performance was considerably below the level of commercialization. Regrettably, this appears still true, although some improvements were reported recently [12]. One of the reasons of the difficulty is thermal instability, particularly of Mo-polyanions having mixed addenda atoms. Unless outstanding breakthroughs are made for high-temperature selective oxidation, the potential targets of research on catalytic oxidation using HPA catalysts may be limited to the followings [2].

(a) Reactions at low temperatures where the polyanion structures are maintained (homogeneous and heterogeneous). Polyanions having novel structures and compositions (including fixation of these polyanions on elaborate supports) have been reported for selective oxidation in liquid phase [13].
(b) Stabilization of polyanion structure, for example, by forming stable salts.
(c) Combination of stable polyanions and functional counter cations.
(d) Combination of HPA and noble metals. Direct synthesis of acetic acid from ethylene was industrialized with a Pd–HPA catalyst [1]. An interesting example, although this is not an oxidation reaction, is that the presence of acidic proton dramatically changes the reaction path in the reaction of a mixture of *n*-butane and hydrogen; Pt on Cs3 (non-acidic) shows mainly hydrogenolysis, while selective hydroisomerization to isobutane takes place over Pt on Cs2.5 (acidic) [1] (Scheme 1).

Table 1
Catalytic activities of solid acids for acid-catalyzed reactions in excess water [10]

Catalyst	Hydration of 2,3-dimethyl-2-butene	Hydrolysis of oligosugars
Cs2.5	10.5	51.0
HZSM-5 (Si/Al = 40)	5.7	1.7
SO_4–ZrO_2	0	0
H-mordenite	0	0
Silica–alumina	0	0
Nafion-H	1.8	52.0



Scheme 1. Contrast between the reactions of a mixture of *n*-butane and hydrogen catalyzed by Pd/Cs3 (non-acidic) and Pd/Cs2.5 (acidic).

3. Perovskite catalysts

3.1. Catalyst design based on perovskites

We previously proposed basic principles for the design of perovskite catalysts [14]. Later, we added an additional principle (i.e. (e)) [3,15]:

(a) Selection of transition element at B-site of perovskite structure (ABO_3), that primarily determines the catalytic behavior.
(b) Valency control of B-site elements (and vacancy control at B site and of oxygen). Redox property very much depends on these values.
(c) Synergistic effect of two different B site ions. For example, Cu and Mn located at B-site in 1:1 atomic ratio exhibits a very high catalytic activity for CO oxidation.
(d) Enhancement of surface area by forming thin layers or nanoparticles of perovskite on support materials [16,17]. Perovskites prepared by the ordinary methods usually have very small surface areas.
(e) Combination of noble metals with perovskites. This will be described below.

3.2. Applications of perovskite catalysts

To my knowledge, perovskite catalyst was commercialized for the first time for the catalytic removal of odor and smoke from cooking table in the kitchen [18]. Recently, according to the principle (e) of catalyst design described in the previous section, a new automobile catalyst was successfully developed by Daihatsu Motor [19] (see below). Other promising applications are the oxygen-reducing electrode of fuel cell and diesel particulate filter [20]. In spite of low surface area and high sensitivity to SO_x, perovskites can find novel applications. Teraoka's group of Kyushu University is developing a wide range of R&D activities aiming at practical usage of perovskite catalysts, in a CREST Project of Environmental Nano-catalysts [20]. The key is to understand the character of perovskites and apply them to appropriate applications.

4. Pd combined with mixed oxides

4.1. Interactions between noble metals and metal oxides under oxidizing conditions

Behavior of noble metals supported on oxide supports has extensively been investigated. However, most works were devoted to that in reducing atmosphere like hydrogenation and hydroisomerization. Important concepts such as ligand versus ensemble effect, geometric versus electronic factor, and support effects (e.g., electron-donating or withdrawing of supports) are all concerned with noble metals in the reduced state. In contrast, knowledge on the behavior of noble metals in oxidizing atmosphere is very limited, although this is very necessary, for example, for the development of practical automobile catalysts, wet oxidation of waste water and catalytic combustion.

4.2. Pd-zeolite

We discovered remarkable contrasts between Pd on HZSM-5 and Pd on NaZSM-5 for the reduction of NO in $NO–CH_4–O_2$ mixture: the former is very active for both reduction of NO and oxidation of methane, but the latter is active only for methane oxidation, while the rate of methane oxidation is almost the same for both catalysts [21]. The reason was that isolated Pd ion in HZSM-5 is active for NO reduction and is stabilized in oxidizing atmosphere, because Pd metal clusters can be redispersed to Pd ions under the oxidizing conditions [22]. On the other hand, Pd metal clusters on NaZSM-5 is only oxidized to PdO particles under the oxidizing conditions. This behavior is illustrated in Fig. 3. The oxidation of Pd cluster on HZSM-5 proceeds in two steps as shown by Eq. (2). The behavior of Pd on HZSM-5 very much resembles what we found a long time ago for Cu on hydroxyapatite; Cu cluster (on the surface) → CuO (on the surface) → Cu^{2+} (in the lattice), upon oxidation and Cu^{2+} → Cu cluster (via Cu^+), upon reduction [23]

$$\text{Pd(0) on HZSM-5} \xrightarrow{O_2} \text{PdO on HZSM-5} \xrightarrow{O_2} \text{Pd(H)ZSM-5} \qquad (2)$$

The activity and durability of Pd-ZSM-5 are high enough for practical applications, but only in the absence of water. In the presence of water, it deactivates significantly, due to the crystal growth of Pd or PdO. Our efforts to suppress the deactivation were not successful so forth. Here is another important problem to be clarified and solved.

4.3. Pd-perovskite

Pd can be incorporated in a perovskite structure to a certain extent, in the trivalent state, for example, as $La(Fe,Co)_{0.9}Pd_{0.1}O_3$, under oxidizing conditions. Utilizing

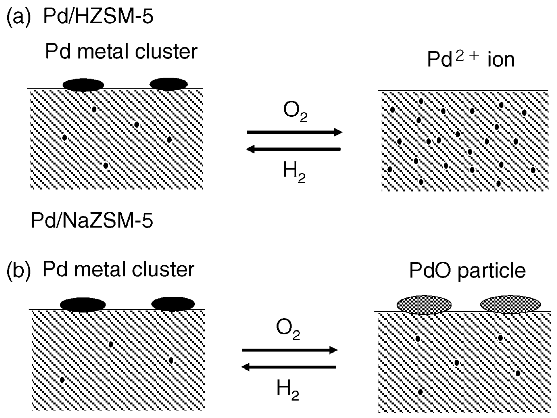


Fig. 3. Contrast between the reversible changes of Pd on HZSM-5 and Pd on NaZSM-5 upon oxidation and reduction.

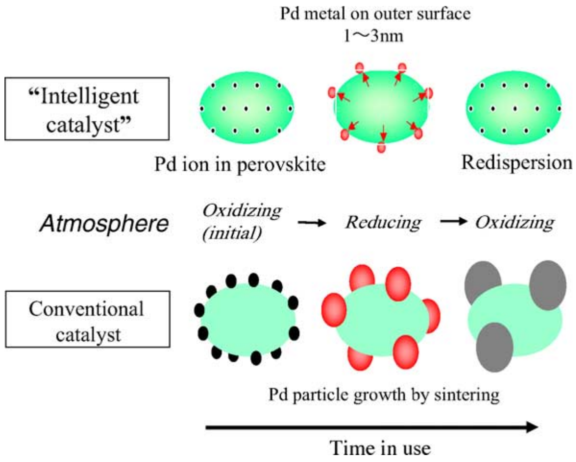


Fig. 4. Contrast between the changes of Pd on perovskite and Pd on ordinary supports upon repeated cycles of oxidizing and reducing atmosphere.

this property, the sintering of Pd nanoparticles on the surface of perovskite is greatly suppressed under the working conditions of automobile exhaust, where the oxidizing atmosphere and reducing atmosphere alternate rapidly [19]. This is illustrated by Eq. (3) and in Fig. 4

$$\mathrm{Pd(0)\ on\ perovskite} \underset{H_2}{\overset{O_2}{\rightleftarrows}} \mathrm{Pd\,(3+)\ in\ perovskite(LaFe(Pd)O_3)} \quad (3)$$

Since the growth of particle size is the major cause of catalyst deactivation of the three-way catalyst (TWC), Pd combined with perovskite developed by Tanaka et al. (Daihatsu Motor) exhibited a dramatically prolonged catalyst life [19]. According to Daihatsu, the amount of Pd usage was decreased to 30% (saving of 70%). They did not detect Pd particles by X-ray diffraction after a long-time use, while Pd(0) was detected by XPS, demonstrating that Pd is present as very fine particles. They called this catalyst an ‘‘intelligent catalyst’’, since it recovers its initial atomic dispersion by itself by sensing the change of atmosphere. The ‘‘intelligent catalyst’’ recorded a huge sale and was awarded several prestigious prizes in Japan.

5. Concluding remarks

Mo–Bi oxides for allylic oxidation, zeolites for catalytic cracking and Co–Mo sulfides for hydrotreatment may be most known examples of mixed oxide (or sulfide) catalysts industrialized in the 1960s and 1970s. We summarized in 1990 and 1993, the industrial catalysts developed in the 1980s in Japan [18,24]. There were a large number of new catalysts and catalytic processes. After our first review, there were similar reports from USA by Armor and Europe by Hoelderich, as well. In those articles, several new types of mixed oxide catalysts are found. But after that we see few new types of mixed oxide catalysts that are really used in practical application. Mesoporous and zeolitic materials are interesting and promising, but we do not see so forth many practical applications except for TS-1.

Important examples that are not discussed in the above reviews may be CeO_2–ZrO_2 used as the promoter of three-way automobile catalysts and NO_x storage and reduction catalysts for lean-burn automobile exhausts. Both of these new developments originated in the real world of industrial applications. We also note that, although the performances of those catalysts have gradually been improved, fundamental understanding of catalytic function is still poor and the R&D very much depend on trial and error. This situation tempts me to believe that it is now necessary to carry out proper basic research to solve the problems present in R&D of practical catalysts and to make hard efforts to realize new innovative practical catalysts.

In the world of mixed oxides, there are many kinds of fundamental structures (of double oxides and salts of oxoacids) and numerous compositions for each structure, and those mixed oxides exhibit various valuable functions derived from a variety of electronic, magnetic and chemical properties. Therefore, we may expect invaluable future opportunities also for catalytic functions.

Acknowledgments

This article contains rather personal view of the author, but the view is derived from the discussion and experiments done with many colleagues. The author expresses deepest gratitude to them.

References

[1] M. Misono, Chem. Commun. (2001) 1141.
[2] M. Misono, Top. Catal. 21 (2002) 89.
[3] H. Tanaka, M. Misono, Curr. Opin. Solid State Mater. Sci. 5 (2001) 381.
[4] T. Okuhara, N. Mizuno, M. Misono, Adv. Catal. 41 (1996) 113.
[5] M. Misono, Catal. Rev.-Sci. Eng. 29 (1987) 269;
M. Misono, Catal. Rev.-Sci. Eng. 30 (1988) 339.
[6] S. Uchida, K. Inumaru, M. Misono, J. Phys. Chem. B 104 (2000) 8108.
[7] G. Koyano, T. Saito, M. Hashimoto, M. Misono, Stud. Surf. Sci. Catal. 130 (2000) 3077;
M. Hashimoto, G. Koyano, N. Mizuno, J. Phys. Chem. B 108 (2004) 12368.
[8] D.J. Constable, A.D. Curzons, V.L. Cunningham, Green Chem. 4 (2002) 521.
[9] T. Okuhara, Private communication.
[10] T. Okuhara, Chem. Rev. 102 (2002) 3641.
[11] H. Ichihashi, M. Ishida, A. Shiga, M. Kitamura, T. Suzuki, K. Suenobu, K. Sugita, Catal. Surv. Asia 7 (2003) 261.
[12] F. Cavani, R. Mezzogori, A. Pigamo, F. Trifiro, E. Etienne, Catal. Today 71 (2001) 97.
[13] K. Kamata, K. Yonehara, Y. Sumida, K. Yamaguchi, S. Hikichi, N. Mizuno, Science 300 (2003) 964;
N. Mizuno, C. Nozaki, I. Kiyoto, M. Misono, J. Am. Chem. Soc. 120 (1998) 9267.
[14] M. Misono, Stud. Surf. Sci. Catal. 54 (1990) 13.
[15] H. Tanaka, N. Mizuno, M. Misono, Appl. Catal. A 244 (2003) 371.

[16] N. Mizuno, H. Fujii, H. Igarashi, M. Misono, J. Am. Chem. Soc. 114 (1992) 7151.
[17] M. Yuasa, G. Sakai, Y. Teraoka, N. Yamazoe, J. Electrochem. Soc. 151 (2004) 1690.
[18] M. Misono, N. Nojiri, Appl. Catal. A 64 (1990) 1.
[19] H. Tanaka, M. Uenishi, I. Tan, M. Kimura, J. Mizuki, Y. Nishihata, SAE Paper 2001-01-1301 and references cited there in.;
Y. Nishihata, et al. Nature 418 (2002) 164.
[20] Y. Teraoka. http://www.nano-catlaysts.jst.go.jp, http://mm.kyushu-u.ac.jp/lab_04/99index-j.html.
[21] Y. Nishizaka, M. Misono, Chem. Lett. (1993) 1296;
Y. Nishizaka, M. Misono, Chem. Lett. (1994) 2237.
[22] G. Koyano, S. Yokoyama, M. Misono, Appl. Catal. A: Gen. 188 (1999) 301.
[23] M. Misono, W.K. Hall, J. Phys. Chem. 77 (1973) 791.
[24] N. Nojiri, M. Misono, Appl. Catal. 93 (1993) 103.