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Recent progress in the practical applications of heteropolyacid and perovskite catalysts: Catalytic technology for the sustainable society

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ABSTRACT

Recent progresses in practical applications of (i) supported heteropolyacid and (ii) Pd/perovskite catalysts are described. (i) Two industrial catalytic processes, ethyl acetate and acetic acid syntheses both from ethylene, utilize silicotungstic acid, alone and together with Pd, respectively, carefully supported on silica, and exhibit high performance from green chemical and economical viewpoints. The layer structure of heteropolyacid on silica and physical properties of silica are among the key factors of the high performance. (ii) Pd/perovskite catalyst is applied for the treatment of automotive emission, where the catalyst life is very much elongated by embedding Pd into the perovskite lattice and hence resulted in much reduced usage of Pd. These are good examples of green catalytic technology that will contribute to the sustainable society.

1. Introduction

In this article, progresses in practical applications of heteropoly and perovskite catalysts since the previous review about the same classes of catalysts (Catal. Today 100 (2005) 95) are briefly reviewed. These two types of catalysts (heteropoly and perovskite) have been the main subjects of our research aiming at the design of practical catalysts based on structurally well-defined mixed oxides. Moreover, the applications of both catalysts fit the idea of green and sustainable chemical technology.

1.1. Green and sustainable technology

Catalysts are indispensable tools for the green and sustainable chemical technology, but are meaningful only when they are beneficially used in practical applications. In other words, catalytic technology can be a key technology for the sustainable society only by demonstrating its usefulness in the society by the improvements of human welfare and the environment. In this respect it is regrettable that there have recently been very few novel innovations having posed a great impact on the society. In the present article, the successful efforts made by the Japanese companies in collaboration with academia will be described, where heteropolyacid and perovskite catalysts (see Fig. 1) were used to develop chemical processes that are green and sustainable. Even though the achievements may not be very great, the author believes that continuing efforts to innovate practically useful catalysts are very important for the progress of catalytic science and technology.

Consider the following simple equation that always holds:

$$\text{Environmental Impacts or Chemical Risks (EI or CR)} \\ = \{(\text{EI or CR})/(\text{GDP})\} \times (\text{GDP/Population}) \times (\text{Population}) \quad (1)$$

For the suppression of the left hand side of the equation, namely, environmental impacts, EI, or chemical risks, CR, it is necessary to reduce the first term on the right hand side of the equation, that is, (EI or CR)/(GDP), where GDP = Gross Domestic Production = human economical activities, because the second and third terms on the right side, (GDP/Population) and (Population), will continue to grow in the future particularly among developing countries. So-called Environmental Kuznets Curve represents essentially the same idea, where EI or CR [ordinate] is plotted against GDP/Population [abscissa] and an inverse U-type curve (initially upward, but downward in the later stage) is expected.

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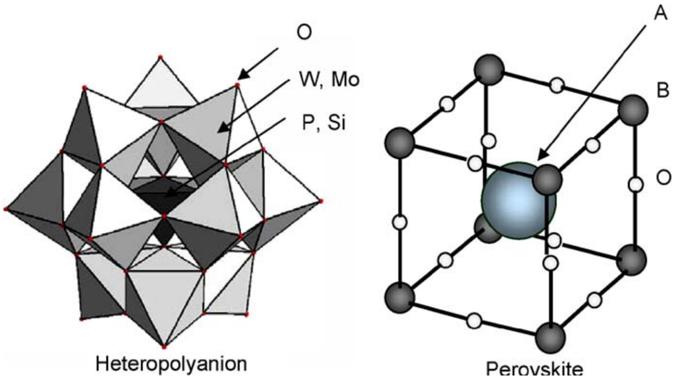

Fig. 1. Heteropolyanion structure (Keggin-type polyoxometalate anion) and perovskite unit cell (ABO_3, cubic).

As the economy grows, (EI or CR) increases in general concurrently with GDP/Population, or the living standards. Developed countries attempt to separate the two axes, (EI or CR) vs. (GDP/Population), and make a U-turn in the curve (to the downslope of the curve). NO_x and SO_x emissions, for example, tend to show the U-turn by applying regulations and technical measures, but the emission of CO_2 in most developed countries still continues to rise, in spite of various efforts. In developing countries, all of these are sharply growing.

Green Chemistry is defined by the utilization of a set of principles that reduces or eliminates the use or generation of hazardous substances in the design, manufacture and application of chemical products [1], where precautionary efforts made at the design stage are stressed rather than end-of-type treatments. The term, Green Chemistry (GC), was first introduced in US in the 1990s, but the idea of Green Chemistry is not new and there were many early examples in line with this idea.

There are quite a few good examples in Japan, as well. One of the examples is shown in Fig. 2 [2]. This is about the emission of BOD (biochemical oxygen demand), or organic waste, into rivers. In 1970, the total amount of the BOD emission was 3.75 million tons, most of which is from industry and the half of it from pulp and paper industry. In about 20 years it dramatically decreased to less than one million tons by the efforts principally made by the industry, including the paper and pulp industry. The decrease realized by the pulp and paper industry, in spite of increased production, was mostly due to the change of the process (from sulfite pulp to kraft pulp) and raw materials (increased usage of recycled paper), and the waste water treatment contributed to only 15% of the decrease. Thus this is an excellent example of Green Chemistry accomplished before 1990.

Another good example of green chemical technology developed in Japan is the electrolysis of NaCl using an ion-exchange membrane. After many technological improvements, the process is now the greenest and most efficient process.

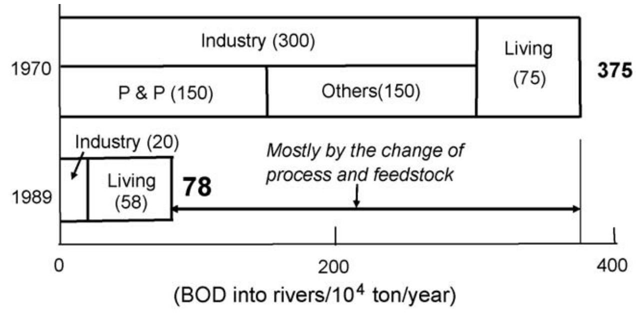

Fig. 2. An example of green chemistry before green chemistry. BOD emission into rivers in Japan.

1.2. Green catalysts and environmental catalysts

If one looks at catalytic technology for the sustainable society, its roles may be two ways: (i) green catalysts that realize green chemical processes, that is, environmentally friendly and non-hazardous processes, and (ii) environmental catalysts that eliminate or diminish hazardous compounds, including so-called end-of-pipe technology. These two are to be developed for the suppression of (EI or CR)/(GDP) of Eq. (1).

In this article, as an example of green catalysts, *heteropolyacid catalysts* will be described and, for environmental catalysts, *perovskite catalysts*. The author's group has studied many years fundamentally the catalyst design based on well-characterized, namely, crystalline or molecular mixed oxides. Heteropolyacids and perovskites are the examples and the major materials we studied. In addition, both were developed successfully for practical applications by industry (Showa Denko and Daihatsu, respectively) in collaboration with the author's group: (1) improvement of the performance of supported heteropolyacid catalysts for the productions of ethyl acetate and acetic acid both from ethylene, and (2) improvement of catalyst life of automotive three-way catalyst by using a combination of noble metals and perovskite. The former made the processes much greener and more profitable, and the latter resulted in dramatic decrease in the amount of usage of noble metals: Pd, Pt and Rh.

2. Heteropolyacid catalysts

Catalytic chemistry of heteropolyacids has been reviewed by several groups [3] and there are already several industrial processes utilizing heteropolyacid catalysts [4]. In relation to the catalyst improvements described in the present article, the concept of three distinctly different types of catalysis present for solid heteropolyacids was important. In particular, the surface acidity and moderate (not too much) contribution of pseudo-liquid catalysis was essential.

As for the heteropoly compounds in the solid state, we have demonstrated from the late 1970s that the solid structure must be understood hierarchically. The primary structure is the molecular polyanion (here, Keggin anion). The secondary structure is three-dimensional crystal of the polyanions and various cations. The tertiary structure is the assembly of the secondary structure, for example, resulting in different particle size and pore structure. Flexible nature of the secondary structure of certain heteropolyacids is the origin of pseudo-liquid catalysis, one of the three types of catalysis of solid heteropolyacids [3a–c].

2.1. Supported heteropolyacids

We have studied mostly unsupported heteropolyacid catalysts, but there have been several studies on supported catalysts including ours [5]. The necessity of supported heteropolyacids in practical applications is evident from the examples described below. We found a very high catalytic activity of $Cs_{2.5}H_{0.5}PW_{12}O_{40}$, so-called Cs2.5, for various surface-type reactions. The reason of the high activity was essentially due to its high surface acidity brought about by its high surface area, in addition to the high catalytic activity of the surface acidic proton. The surface area of Cs2.5 is very high (100–200 m^2/g), because Cs2.5 consists of aggregates of very fine particles. As Cs salts have uniform composition in the solid after heat-treatment, it is possible to estimate the number of protons on the surface from the chemical