Computer-Aided Molecular Design of Catalysts Based on Mechanism and Structure

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A bridge theory including a mathematical expression for the process of catalysis is proposed. A catalytic reaction can be expressed as ||reactant matrix|| × ||bridge matrix|| = ||product matrix||. The physicochemical bases of computer-aided molecular design of catalysts are discussed. Five variations on both structure and mechanism are identified as important in the process of catalyst design. An expert system of molecular design of catalysts (ESMDC) including a knowledge base and a reasoning scheme has been developed and is described.

1. INTRODUCTION

The catalytic process has been playing an increasingly important role in many fields of modern science and industry. Development of a commercial industrial catalyst however is a task requiring much time (7−10 years) and money because thousands of experimental tests are involved. As a consequence, the task of developing more effective catalysts has come into focus in recent years. Trimm,[1] a pioneer in catalyst design, has analyzed the causes of success and failure in practical design of some industrial catalysts published before 1980 and has suggested a scientific basis for catalyst design. Cusumano,[2] Zamaraev,[3] and Likolobov[4] have each provided a perspective on the molecular design of industrial catalysts, and, since 1970, significant work on catalyst design has also been published by Liao,[5] Hegedus,[6] and Graziani.[7]

More recently, advances in computer power have led to the development of reliable bases and useful tools for the design of catalysts at the molecular level, but, to date, no practical expert system for molecular design of catalysts has been reported. The main difficulties facing computer-aided molecular design of catalysts are the absence of a uniform mechanism and mathematical representation for all catalytic reactions. It is also uncertain which variations in structure and mechanism are important to catalyst design. Thus it is a problem to decide on the knowledge rules and reasoning process to be used for a specific catalytic reaction.

In the next section of this paper, we propose a bridge theory with a mathematical expression for the catalytic process. In section 3, the physicochemical bases of molecular design of catalysts and catalytic processes from the periodic properties of elements and compounds are discussed, and, in section 4, using the oxidative coupling of methane (OCM) as an example, a practical expert system, ESMDC-1995, including a knowledge base and a reasoning algorithm, for the design of metal oxide catalysts is described.

2. BRIDGE THEORY AND MATHEMATICAL EXPRESSION FOR CATALYSIS

The development of catalysis theory can be regarded as having gone through several periods: (1) an initial hypothesis of "magic" catalytic force, (2) the early pure chemical, physical, and physicochemical theories of catalysis, (3) recent theory of catalysis, and (4) the modern theory of catalysis. All these various theories and hypotheses attempted to explain the phenomenon of catalysis, but a uniform theory of catalysis is still elusive. Modern techniques however have provided a deep insight into the nature of catalysis and catalysts, but the search for a general and common principle of catalysis remains a paramount problem.

An individual catalytic reaction can be described at the molecular or the atomic level. A hypothesis of "frequency catalysis" involving a relationship between motion, frequency, and energy was proposed by Liao who also recently proposed a new hypothesis for microcatalysis and information catalysis in the life science.[8] Catalysis, in nature, is both a physical and chemical process. A complete explanation of catalysis however also requires a mathematical view, and efforts to provide this have been reported by Balaban,[9] Ugi,[10] Koca, and Kvasnicka et al.[11] who have examined the applicability of graph theory to the chemical problem. A program, COMSYCAT, developed by Likolobov and co-workers,[12] is a mathematical model of the structural chemistry implied by the sequence $\{X + M^*\} \rightarrow \{ZM^*\} \rightarrow \{Y + M^*\}$ in which the molecular system $\{X + M^*\}$ is described as a structural bond-electron matrix. Other attempts to clarify the catalysis problem have been made. Hoffmann has attempted to build bridges between inorganic and organic chemistry, Fukui has studied reaction pathway, and Taube has examined the rate at which electrons are transmitted through the bridge of a metal ligand. In this paper, we develop a bridge theory for which we provide a mathematical representation which deals with three distinct species.

In the bridge theory, the catalyst is treated as a bridge between reactants and products. Any reactant or catalyst can be represented as a mathematical set, and any component of either is defined as an element of the set to which it belongs. All reactants and catalysts can be defined as a product of these sets. Thus the bridge representation of a catalytic process corresponds to a map. The mathematical meaning of a map is a rule, ϕ. Only one element d of a set D can be obtained by the operation of a rule upon any element of a set $(a_1, a_2, ..., a_n)$ $(a_i \in A_i)$, and it can be expressed as follows:

$$\phi; (a_1, a_2, ..., a_n) \rightarrow d = \phi(a_1, a_2, ..., a_n)$$

The reverse catalytic process can be expressed as ϕ^{-1} in bridge representation. An active center and an active adsorption can be also represented as a subset and a mapping, respectively.

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With this preamble, we can use matrix algebra to explain the mechanism of catalytic reactions and in the design of catalysts. This done by introducing the concept of both set and group into the mathematical representation of catalysis. A bridge matrix can be defined as consistent with the following expression:

$$\|\text{reactant matrix}\| \times \|\text{bridge matrix}\| = \|\text{product matrix}\|$$

The key step in determination of the matrix representing the target species is the determination of the bridge matrix given that the following expression is thermodynamically reasonable:

$$\|\text{species A}\| \; \|\text{species B}\|...\|\text{species M}\| = \|\text{species 1}\| \; \|\text{species 2}\|...\|\text{species N}\|$$

For example, if suppose species 1 is a target product, we can use the following expression to represent the catalytic process:

$$\|\text{species A}\| \; \|\text{species B}\|...\|\text{bridge matrix}\| = \|\text{target species 1}\|$$

where the bridge matrix includes matrix of active center, promoter matrix, and matrix of reaction conditions and so on.

For an easy understanding of the above matrix expression, here we show a mathematical example. For example, if we use a matrix

$$\begin{Vmatrix} 1 & 1 \\ 2 & 1 \end{Vmatrix}$$

for representing a H_2 molecule and a matrix

$$\begin{Vmatrix} 7 & 3 \\ 14 & 3 \end{Vmatrix}$$

for a N_2 molecule and

$$\begin{Vmatrix} 42 & 42 \\ 42 & 42 \end{Vmatrix}$$

for a NH_3 molecule, it can be shown that the best bridge matrix is

$$\begin{Vmatrix} 6 & 7 \\ 3 & 14 \end{Vmatrix}$$

because

$$\begin{Vmatrix} 1 & 1 \\ 2 & 1 \end{Vmatrix} \begin{Vmatrix} 7 & 3 \\ 14 & 3 \end{Vmatrix} = \begin{Vmatrix} 7 & 14 \\ 6 & 3 \end{Vmatrix} \text{ and } \begin{Vmatrix} 7 & 14 \\ 6 & 3 \end{Vmatrix} \begin{Vmatrix} 6 & 7 \\ 3 & 14 \end{Vmatrix} = \begin{Vmatrix} 42 & 42 \\ 42 & 42 \end{Vmatrix}$$

It is not so simple, of course, for a catalytic process, in which various codes are used to represent matrix elements and both algebraic and logic operations are used to calculate them. Likholobov and his co-workers suggested an alternative coding in which the matrix representations for CO, H_2, and metal surface are

$$\begin{Vmatrix} 2 & 2 \\ 2 & 4 \end{Vmatrix}, \begin{Vmatrix} 0 & 1 \\ 1 & 0 \end{Vmatrix} \text{ and } \|1\|$$

respectively.

How is a catalytic process expressed in a mathematical method of bridge theory? Consider the synthesis of ammonia on an iron catalyst, $N_2 + 3H_2 = 2NH_3$, as an example. All molecules of nitrogen and all molecules of hydrogen can be expressed as a set, $N_2 = \{N_2^a, N_2^b, ..., N_2^\alpha\}$ and $H_2 = \{H_2^a, H_2^b, ..., H_2^\beta\}$, respectively. Let us suppose that the catalyst is simply composed of only element Fe which is expressed as a set $Fe_n = \{Fe_n^a, Fe_n^b, ..., Fe_n^\gamma\}$. The promoter is not considered for the moment. The set Fe_n is a subset of a set Fe. We can note ϕ: $N_2^a \rightarrow N_2^a$ and ϕ: $H_2^a \rightarrow 2H^a$ or H_2^a for chemisorption of N_2 and H_2 molecule, respectively. For a complete set, however, we can note ϕ_1: $N_2 \rightarrow N_2$ and ϕ_1: $H_2 \rightarrow 2H$ or H_2, respectively. Both set N_2 and set H_2 do not map fully to ϕ_1 which corresponds to the set Fe. Only for the map ϕ_2 corresponding to the subset Fe_n, the set N_2 and set H_2 are fully mapped one by one. In chemical language, nitrogen and hydrogen can be actively chemisorbed and combined with each other only if they are adsorbed on an active center of Fe_n cluster. So we have $\phi_2 : N_2 \rightarrow N_2$ and $\phi_2^{-1} : N_2 \rightarrow N_2$ as well as ϕ_2: $H_2 \rightarrow 2H$ or H_2 and $\phi_2^{-1} : 2H$ or $H_2 \rightarrow H_2$. The adsorption and desorption are in equilibrium.

Define a merge set $N_2 \cup H_2 = \{N_2^a + H_2^a, N_2^b + H_2^b, ..., N_2^\alpha + H_2^\beta\} = $ set $NH_3 = \{NH_3^a, NH_3^b, ..., NH_3^\delta\}$. Suppose the set Fe_n is an empty subset corresponding to the set N_2 and H_2. We can note that $N_2 = \{N_2^a, N_2^b, ..., N_2^\alpha, Fe_n^a, Fe_n^b, ..., Fe_n^\gamma\}$ and $H_2 = \{H_2^a, H_2^b, ..., H_2^\beta, Fe_n^a, Fe_n^b, ..., Fe_n^\gamma\}$. Therefore, we have a merge set $NH_3 = \{NH_3^a, NH_3^b, ..., NH_3^\delta, Fe_n^a, Fe_n^b, ..., Fe_n^\gamma\}$. Mathematically, this means that the catalyst is unchanged after the reaction. If the symbol "∘" is used to express a set operation, we can note $(N_2, H_2) \rightarrow {}^1/_2 N_2^3/_2 H_2 = {}^1/_2 N_2 \circ {}^3/_2 H_2$. Also, $(N_2, H_2, Fe_n) \rightarrow {}^1/_2 N_2^3/_2 H_2 Fe_n = ({}^1/_2 N_2 \circ {}^3/_2 H_2) \circ Fe_n$ can be expressed as the following matrix expression:

$$\frac{1}{2} \begin{vmatrix} N_{2,a1} & N_{2,a2} & \cdots & \cdots & N_{2,ai} \\ N_{2,b1} & N_{2,b2} & \cdots & \cdots & N_{2,bi} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ N_{2,n1} & N_{2,n2} & \cdots & \cdots & N_{2,ni} \end{vmatrix} \frac{3}{2} \begin{vmatrix} H_{2,a1} & H_{2,a2} & \cdots & \cdots & H_{2,ai} \\ H_{2,b1} & H_{2,b2} & \cdots & \cdots & H_{2,bi} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ H_{2,n1} & H_{2,n2} & \cdots & \cdots & H_{2,ni} \end{vmatrix}$$

$$\begin{vmatrix} Fe_{2,a1} & Fe_{2,a2} & \cdots & \cdots & Fe_{2,ai} \\ Fe_{2,b1} & Fe_{2,b2} & \cdots & \cdots & Fe_{2,bi} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ Fe_{2,n1} & Fe_{2,n2} & \cdots & \cdots & Fe_{2,ni} \end{vmatrix} = \begin{vmatrix} NH_{3,a1} & NH_{3,a2} & \cdots & \cdots & NH_{3,ai} \\ NH_{3,b1} & NH_{3,b2} & \cdots & \cdots & NH_{3,bi} \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ \cdots & \cdots & \cdots & \cdots & \cdots \\ NH_{3,n1} & NH_{3,n2} & \cdots & \cdots & NH_{3,ni} \end{vmatrix}$$

The mathematical expression including map, group, and matrix is useful and helpful for the computer-aided design of catalysts.

3. PHYSICOCHEMICAL BASES FOR MOLECULAR DESIGN OF CATALYSTS

Ioffe et al.[13] have carried out excellent work in application of pattern recognition to catalytic research. More recently, Kuntz et al.[14] summarized their experience with the DOCK program in the drug discovery process and the challenges that lie ahead for structure-based design. We have investigated molecular design of metal oxide catalysts for oxidation coupling of methane (OCM). Based on the periodic properties of elements and compounds, five physicochemical variations, namely, (1) geometric topology, (2) electronic structure, (3) magnetic property, (4) other physicochemical

properties, and (5) catalytic active model, are identified as important for the computer-aided molecular design of catalysts.

The variations of (1) to (4) can be represented and evaluated with a series of relative periodic properties of elements and compounds which are components of a catalyst. The following properties, as suggested by Trimm,[1] are usually important and useful in the process of design of oxide catalysts: radius of ion, acidity, and basicity, affinity for gases, the parameter $d\%$, electronic structure of d^0 and d^{10}, coordination model, electronegativity, ionization potential, work function, magnetic susceptibility, lattice parameter, surface energy, adsorption heat, valence state, partial charge of oxygen, stability, melting point, entropy of fusation, melting heat, and formation heat, etc.

The exchange of ions with similar radius, cation with cation, or anion with anion may have an effect on a significant change for both catalytic activity and selectivity. An active catalyst for OCM is mostly composed of the alkali and alkaline earth metal compounds and, also, rare earth metal compounds or other metal compounds, especially with variable valence. A pair of matching cations usually has a close or similar radius, as in the case of Li^+ (0.068 nm) vs Mg^{2+} (0.074 nm) and Na^+ (0.098 nm) vs Ca^{2+} (0.104 nm). The replacements between cations or between anions with different valence states, in this case, may take place and cause such change on the surface lattice as the generation of holes and so on.

In general, acidity is favorable for dehydration, but basicity is favorable for dehydrogenation. It is a continuous property and generally related to catalytic activity. Also, acidity favors carbonization, but basicity favors protection against carbonization. The oxide with less partial charge on oxygen has stronger acidity. The electronegativity of metal ions also corresponds to their acidity.

If a metal element has an affinity for a gaseous molecule, generally, the metal and its compounds can catalyze the catalytic reaction involving the gaseous molecule. The magnitude of affinity usually can be expressed as heat of adsorption. Obviously, a gaseous molecule with larger affinity for a metal is more active.

The parameter $d\%$ usually is related to the adsorption and catalytic selectivity. It represents the contribution of d orbitals to dsp hybridized orbitals for a transition metal. An metal oxide with electronic structure of d^0 or d^{10} usually has good selectivity for catalytic oxidative reaction.

A coordination model of adsorbed species on surface of solid catalyst generally relates to the activity of a catalyst. The adsorption model usually can be divided into two types, namely, associate and dissociate or molecular and atomic. The chemisorbed species may be electrically neutral, positive, or negative.

The direction and pathway of transfer of both electrons and charges in catalysis usually may be correlated with the electronegativity of the catalyst components, and the electronegativity can be divided into electronegativity of elements, orbitals, ions, or groups. The ionization potential also has an effect on the transfer of electrons in catalysis and is related to the electronegativity and work function. The orbitals of an element with a larger ionization potential are more occupied. The exit of electrons from surfaces of metal with less work function into vacuum is facilitated.

Magnetic susceptibility, a very important factor in magnetic catalysis, is often related to f electrons. Paramagnetism or diamagnetism are also important parameters in magnetic catalysis. The lattice parameter is an important parameter in molecular design of catalysts based on structure. Catalytic activity and selectivity generally relate to the stereo structure of catalysts. The geometric topology usually has a considerable effect on catalysis.

The catalytic active model is the most complex and difficult in the process of catalyst design. It mostly depends on the type of a catalytic reaction and its catalysts. Fortunately, the development in the field of catalysis in the past decades has provided a lot of useful information. We can find almost all types of catalytic reactions and catalysts as well as their mechanisms from various handbooks and literatures as a reference for the catalyst design. However, the individual knowledge and experience of experts in catalysis are often the most important and decisive factor.

The first four variations provide physicochemical bases for catalyst design based on structure, but the last variation provides the bases of design based on mechanism. A good design should be based on both structure and mechanism.

4. CONSTRUCTION OF AN EXPERT SYSTEM FOR MOLECULAR DESIGN OF CATALYSTS

Based on above physicochemical bases in both structure and mechanism and the mathematical expression method, an expert system for the molecular design of heterogeneous oxide catalysts has recently been developed in our group. Using this system, we can predict and theoretically prepare a catalyst for a desired catalytic reaction catalyzed by oxidic catalysts. We also can find information useful to an explanation of the mechanism of a known catalytic reaction. Figure 1 shows the system flow diagram for computer-aided molecular design of catalyst components. The system structure of our Export System of the Molecular Design of Catalyst (ESMDC) is shown in Figure 2.

Now, we take the design of composition of metal oxide catalysts for OCM as an example. If the alkali metal cation Li^+, Na^+, and K^+, respectively, is selected as a reference ion, the recommended matching ions in catalyst for OCM are as follows. (1) For alkali metal ion Li^+, we can find that alkaline earth metal ion Mg^{2+}, rare earth metal ions Lu^{3+}, Yb^{3+}, Sc^{3+}, transition metal ions Ti^{3+}, Ti^{4+}, Ti^{2+}, V^{3+}, V^{2+}, V^{4+}, Nb^{4+}, Nb^{5+}, Ta^{5+}, Cr^{2+}, Cr^{3+}, Mo^{4+}, W^{4+}, W^{6+}, Mn^{3+}, Mn^{2+}, Fe^{2+}, Fe^{3+}, Ru^{4+}, Os^{3+}, Co^{3+}, Co^{2+}, Rh^{3+}, Rh^{4+}, Ni^{2+}, Ir^{4+}, Pt^{4+}, Cu^{2+}, Zn^{2+}, etc., other metal ions Al^{3+}, Ga^{3+}, Ga^{2+}, Sn^{4+}, As^{3+}, Pb^{4+}, Bi^{5+}, Sb^{5+}, and anions O^{2-}, F^- may be a good matching ion. (2) For alkali metal ion Na^+, alkaline earth metal ions Ca^{2+}, Sr^{2+}, rare earth metal ions La^{3+}, La^{4+}, Ce^{3+}, Ce^{4+}, Y^{3+}, Pr^{3+}, Nd^{3+}, Pm^{3+}, Sm^{3+}, Eu^{3+}, Gd^{3+}, Dy^{3+}, Th^{4+}, Pa^{3+}, Pa^{4+}, Nb^{3+}, Pu^{3+}, Am^{3+}, transition metal ions Mn^{2+}, Ti^{2+}, Zr^{4+}, Cr^{2+}, Hf^{4+}, Ag^+, Cu^+, Hg^{2+}, other metal ions In^{3+}, Cd^{2+}, Ti^{3+}, Sn^{2+}, Sb^{3+}, Te^{4+}, and anions Cl^-, Br^- may be a good matching ion. (3) For alkali metal ion K^+, alkaline earth metal ions Ba^{2+}, Sr^{2+}, Ra^{2+}, rare earth metal ions Ac^{3+}, transition metal ions Ag^+, other metal ions Bi^{3+}, Tl^{3+}, Pb^{2+}, and anions F^-, O^{2-} may be a good matching ion. Again, if the La^{3+} is selected as a reference ion, we can find only the Ca^{2+} ion as a recommended matching ion among the alkaline earth metal ions. The selection should follow some physicochemical rules in both structure and mechanism. Figure 3 shows the procedure of system design for combination of different ions with specific properties to form a complex oxide with a defect lattice.
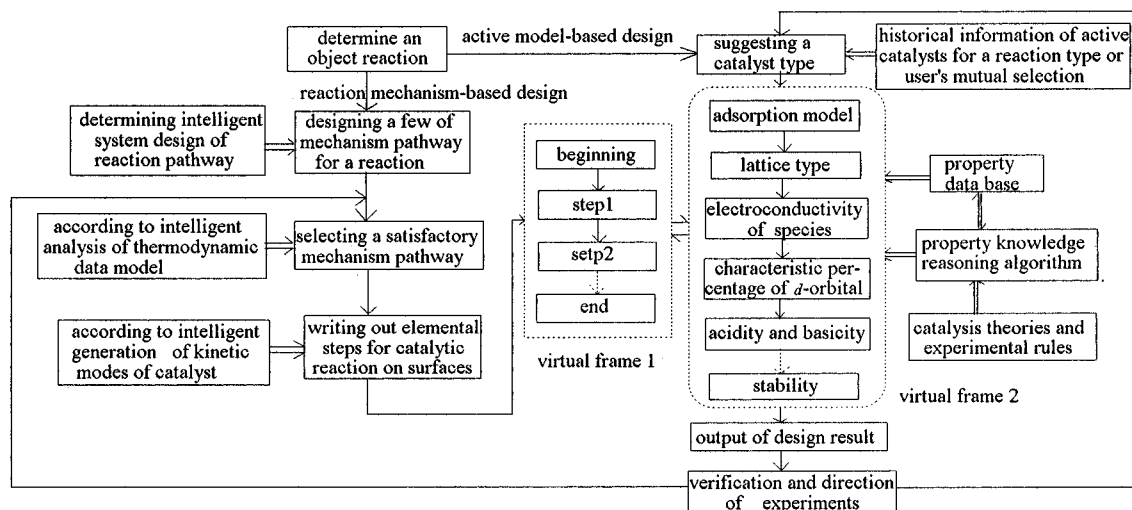
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Figure 1. System flow diagram for computer-aided molecular design of catalyst components.
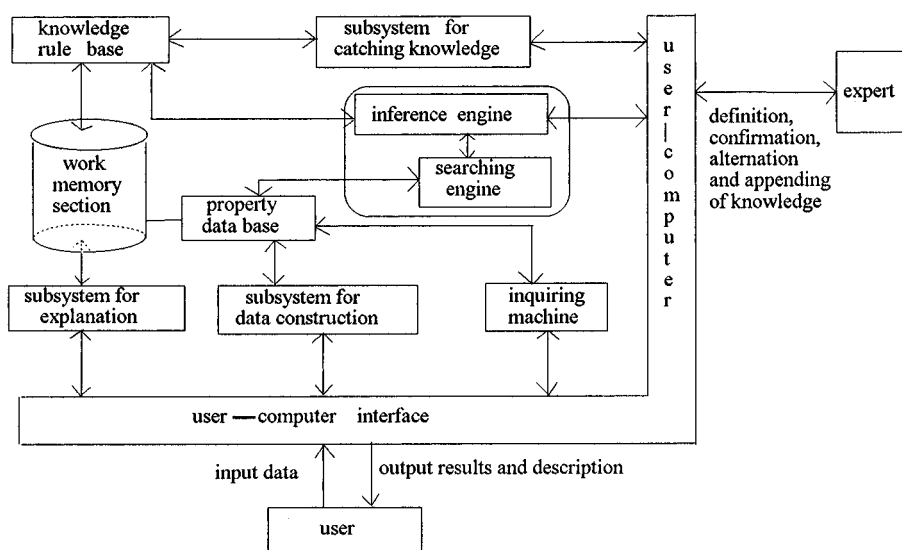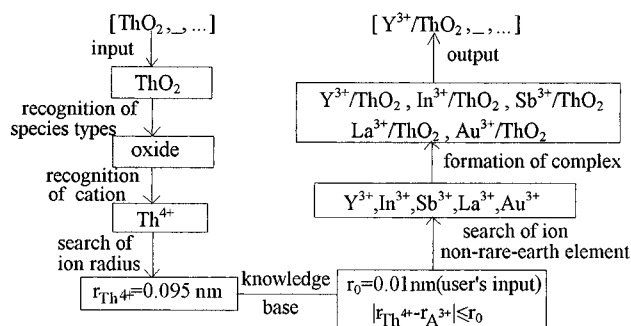

Figure 2. System structure of ESMDC.

Figure 3. Procedure of system design for combination of different ions with specific properties to form complex oxide with defect lattice.

The system includes a user-computer interface, a knowledge collection scheme, a property data base, a knowledge rule base, an explanation scheme, a memory scheme, and a reasoning scheme. The general knowledge base is divided into two bases. The property data base is composed of periodic properties of elements and compounds. The knowledge rule base is composed of the knowledge rules from the field of catalysis.

The collection and expression of data and knowledge should be consistent with the reasoning performance. The knowledge in catalysis can be classified as follows: (1) data

type knowledge which involves periodic properties of elements and compounds, etc. and can be collected mostly from various handbooks such as CRC and literatures and can be expressed in a frame structure, (2) descriptive type knowledge which involves the principle, mechanism, and structure, etc. in catalysis and can be collected from the facts and experimental results in literature and experience of experts, (3) solution type knowledge which is an ambiguous and blurring judgment and can be collected from literature and experience, and (4) process type knowledge, which is a knowledge of a control scheme, is a comprehensive knowledge of principles, facts, and experiences and forms a reasoning frame. The last three types of knowledge can be expressed as a generative expression and predicate logic expression. For example, we can write down the following rules of knowledge:

[Rule 1] (Catalyst has active phase) $\wedge$ (Catalyst has promoter) $\rightarrow$ (The catalyst is an active catalyst)

[Rule 2] (Component has defect structure) $\wedge$ (Component has CaF_2 type lattice) $\rightarrow$ (The component is an active phase)

[Rule 3] (complex, active phase) $\wedge$ {(complex, promoter) $\vee$ (complex, stabilizator) $\vee$ (complex, inert diluter) $\vee$ (complex, quencher)} $\rightarrow$ (It is an active complex catalyst)

Table 1. Some Output of Catalyst Component Design for OCM

with a CaF_2 lattice, n-type metal cation with stable valence melting point > 500 °C, p-type	CaO, ZnO, SrO, CdO, Sc_2O_3, La_2O_3, Bi_2O_3
to be able to form a defect CaF_2 lattice, matching ions with radius of ±0.01 nm, metal cation with variable valences, T_{min} of phase transformation > 500 °C	Na^+/MnO, Cu^+/MnO, Sc^{3+}/ZrO_2, Rh^{3+}/ZrO_2, Sb^{3+}/ZrO_2, Ir^{3+}/ZrO_2, Au^{3+}/ZrO_2, Sc^{3+}/CeO_2, Y^{3+}/CeO_2, In^{3+}/CeO_2, Sb^{3+}/CeO_2, Au^{3+}/CeO_2, Y^{3+}/ThO_2, In^{3+}/ThO_2, Sb^{3+}/ThO_2, La^{3+}/ThO_2, Au^{3+}/ThO_2, Sc^{3+}/UO_2, Y^{3+}/UO_2, In^{3+}/UO_2, Sb^{3+}/UO_2, Au^{3+}/UO_2
to be able to form a defect CaF_2 lattice, matching ions with radius of ±0.01 nm, both n-and p-type electroconductivity, carbonate modified with alkaline-earth metal	$Ca^{2+}/Sm_2O_3/SrCO_3$, $Mn^{2+}/Sm_2O_3/BaCO_3$, $K^+/PbO/BaCO_3$, $Cd^{2+}/Sm_2O_3/SrCO_3$, $Sn^{2+}/Sm_2O_3/CaCO_3$, $In^+/PbO/MgCO_3$, $Mn^{2+}/Gd_2O_3/BaCO_3$, $Rh^{2+}/Gd_2O_3/CaCO_3$, $Hg^+/PbO/BaCO_3$, $Cd^{2+}/Gd_2O_3/BaCO_3$, $Sn^{2+}/Gd_2O_3/CaCO_3$, $Tl^+/PbO/MgCO_3$
to be able to form a defect Ce_2O_3 lattice, matching ions with radius of ±0.005 nm, mp > 500 °C, ionic type electroconductivity, modified with a metal ion being able to form superoxide	$Sc^{3+}/ZrO_2/Na^+$, $Na^+/SnO/Cs^+$, $Cu^+/SnO/Rb^+$, $Sc^{3+}/CeO_2/Ra^{2+}$, $In^{3+}/CeO_2/Sr^{2+}$, $Sb^{3+}/CeO_2/Ba^{2+}$, $Au^{3+}/CeO_2/K^+$, $Rh^{3+}/PbO_2/Sr^{2+}$, $Ir^{3+}/PbO_2/K^+$, $Y^{3+}/ThO_2/Ba^{2+}$, $In^{3+}/ThO_2/Ra^{2+}$, $Sb^{3+}/ThO_2/Na^+$, $Au^{3+}/ThO_2/K^+$, $Sc^{3+}/UO_2/Ba^{2+}$, $In^{3+}/UO_2/K^+$, $Sb^{3+}/UO_2/Ba^{2+}$, $Au^{3+}/UO_2/Cs^+$
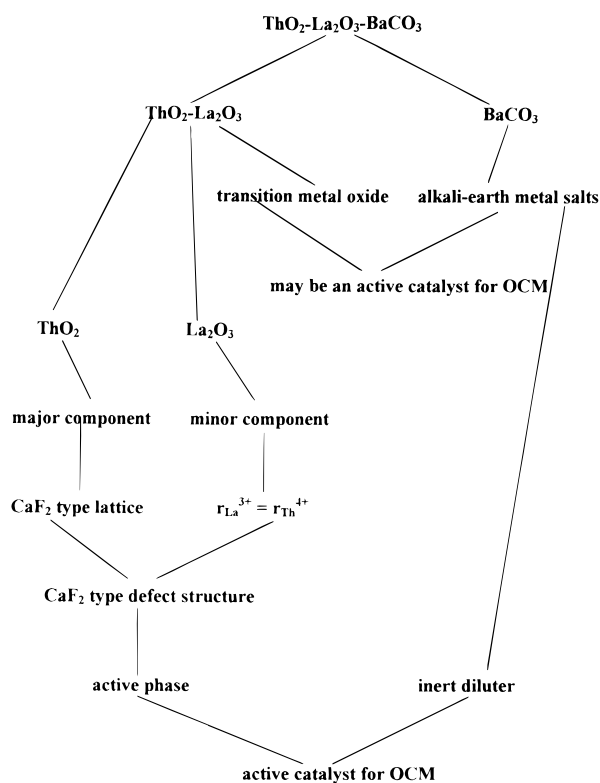
Figure 4. An example of generative reasoning.

[Rule 4] (complex, oxide) ∧ cation (oxide, stable valence) → (It may be an active complex catalyst)

[Rule 5] If $(0.79/1.32) \leq (r_M^{n+}/r_O^{2-}) \leq (1.34/1.33)$ then the oxide M_2O_n can form a lattice CaF_2

[Rule 6] If a complex catalyst is composed of a reducible metal oxide of IV, VA, or IIB group and an alkali metal oxide, then the catalyst may be an active catalyst for OCM

where the symbol ∧ and ∨ represented logic "and" and logic "or", respectively. We can, in this way, write down many knowledge rules for the knowledge base.

The reasoning scheme is the most difficult key problem in the molecular design of catalyst since the catalysis is extremely complex. Different reasoning schemes are designed for different knowledge expression scheme in catalysis, respectively. They include generation reasoning, reasonable inference, graph searching, deductive reasoning, and algorithm reasoning, etc. Figure 4 shows an example of generative reasoning. Table 1 shows some output of catalyst component design for OCM.

5. CONCLUSION

A new and common method for explaining and mathematically expressing a catalytic reaction is proposed in the bridge theory which is favorable for computer-aided molecular design of catalysts. According to the physicochemical and mathematical bases for catalyst design, a practical expert system based on both structure and mechanism, is described with catalyst for OCM as an example. An advanced program for molecular design of catalysts has been developing. We believe that the molecular design of catalysts should play a more and more important role in developing new catalysts and catalytic processes and describing the mechanism of a known catalytic reaction as well as preparing high effective catalysts.

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REFERENCES AND NOTES

(1) Trimm, D. L. *Design of Industrial Catalysts*; Elsevier Sci.: New York, 1980.
(2) Cusumano, J. A. In *IUPAC* Perspectives in catalysis—A Chemistry for the 21st Century Monograph; Thomas, J. M., Zamaraev, K. I., Eds.; Blasckwell Sci.: Oxford, 1992; pp 1−34.
(3) Zamaraev, K. I. In *IUPAC* Perspectives in catalysis—A Chemistry for the 21st Century Monograph; Thomas, J. M., Zamaraev, K. I., Eds.; Blasckwell Sci.: Oxford, 1992; pp 35−66.
(4) Likholobov, V. A. In *IUPAC* Perspectives in catalysis—A Chemistry for the 21st Century Monograph; Thomas, J. M., Zamaraev, K. I. Blasckwell Sci.: Oxford, 1992; pp 67−90.
(5) Liao, D. W. *Chemistry* **1982**, (3), 44−51, 38 (in Chinese).
(6) Hegedus, L. L. et al. *Catalyst Design-Progress and Perspectives*; John Wiley & Sons: New York, 1987.
(7) Proceedings of Workshop on Catalyst Design. In *Advances in Catalyst Design*; Graziani, M., Rao, C. N. R., Eds.; World Sci.: New Jersey, 1991.
(8) Liao, D. W. et al. Study on Micro-catalysis in Life Science (1) Separation of Ginseng Saponins and Quantum Chemical Calculation of Panaxdiol; (2) Isolation of Polysaccharides and Information Catalysis, to be published in *J. Xiamen University (N.S.)*.
(9) Balaban, A. T. *Chemical Application of Graph Theory*; Academic: London, 1976.
(10) Ugi, I.; Wochner, M. *J. Mol. Struct (THEOCHEM)* **1988**, *165*, 229.
(11) Kvasnicka, V.; Pospichal, J. *Int. J. Quant. Chem.* **1990**, *38*, 253.
(12) Likholobov, V. A. et al. *Homogeneous and Heterogeneous Catalysis*; VNU Sci.: Utrecht, 1986.
(13) Ioffe, I. I. *Application of Pattern Recognition to Catalytic Research*; John Wiley & Sons: New York, 1988.
(14) Kuntz, I. D.; Meng, E. C.; Shoichet, B. K. *Acc. Chem. Res.* **1994**, *27*, 117.