

## [Review Paper]

# Design of Solid Catalysts by Sol-gel Method Using Organic Polydentate Ligands and Their Catalytic Performance

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Advantages and effectiveness of using an organic polydentate ligand in the sol-gel process were discussed. The sol-gel method using the ligand was presented herein for preparation of metal oxides including mixed oxides. Design of metal oxide particles using organic polydentate ligands, *i.e.*, control of specific surface area, particle size, pore size, and structure, was examined for silica, alumina, iron oxides, and some mixed oxides. Furthermore, regarding the mixed oxides, the dispersibility of constituent particles and homogeneity of the composition were compared among the sol-gel, coprecipitation, and kneading methods. The mixed oxides prepared using the sol-gel method showed the highest dispersibility and homogeneity. Reflecting this, the sol-gel silica/alumina was much more acidic and effective for alkylation of aromatics than the coprecipitation and kneading ones. The sol-gel method also yielded thermostable alumina and alumina mixed oxides that were useful as combustion catalyst supports; platinum-loaded or palladium-loaded sol-gel alumina, and alumina mixed oxides showed high performance for model purification reactions of exhaust gas. Regarding the supported metal catalysts prepared using the sol-gel method, ruthenium/silica and palladium/silica catalysts activated in hydrogen without calcination, respectively showed high performance for partial hydrogenation of benzene to cyclohexene and for conversion of acid chlorides to the corresponding aldehydes. Furthermore, ruthenium/tin/alumina catalysts activated in a similar manner converted unsaturated fatty acids to corresponding alcohols through hydrogenation while maintaining carbon-carbon double bonds. This type of ruthenium/tin/alumina catalyst was also effective for conversions of aromatic acids and dibasic acids, respectively, to the corresponding alcohols and diols *via* hydroxycarboxylic acids.

**Keywords**

Solid catalyst, Catalyst design, Sol-gel method, Thermostable metal oxide, Hydrogenation

**1. Introduction**

The structure, pore size, surface area, and homogeneity of solid catalysts are important factors governing heterogeneous catalytic reactions. Because a solid catalyst generally consists of several microparticles, the particles' shape, structure, size, pore, and dispersibility determine major characteristics of the catalyst, including the factors described above. Consequently, how to design the particles, or how to prepare the particles with desired properties, and how to assemble the particles to give a desired catalyst are important. Traditionally, kneading, impregnation, and coprecipitation, which produce respective solid catalysts with more or less different performances and properties, have been widely used as solid catalyst preparation procedures because of their ease in handling. However, these procedures are not always suitable to design and control the factors described above determining the catalyst performance. Especially, the former two are not methods to design

microparticles but to use particles with properties determined by nature.

Metal oxides, including mixed oxides that have played a major role in the solid catalyst field as constituents not only of the catalysts themselves but also of the catalyst supports, have been commonly prepared *via* hydrolysis of metal salts or complexes, followed by dehydration-condensation reactions (certain polymerizations), or so-called sol-gel processing. The stability of the metal salts and complexes for hydrolysis depends on ligands surrounding the metal ions by coordination; therefore, the ligands influence subsequent polymerizations, *i.e.*, the formation of metal oxide microparticles, which indicates that ligands can not only control sol-gel process for the formation of metal oxides but also be effective for design of metal oxide particles, as described below.

Another major constituent of the solid catalysts is metal particles, which are generally formed by reduction of the corresponding oxide particles, ions or complexes. In this case, the ligands coordinating to metal ions not only determine the reducibility of the metal particle precursors but also influence the successive

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aggregation of metal particles, as can be inferred from the size control and stabilization of metal particles or colloids. Such control and stabilization are often achieved by surrounding the particles with various surfactants or ligands.

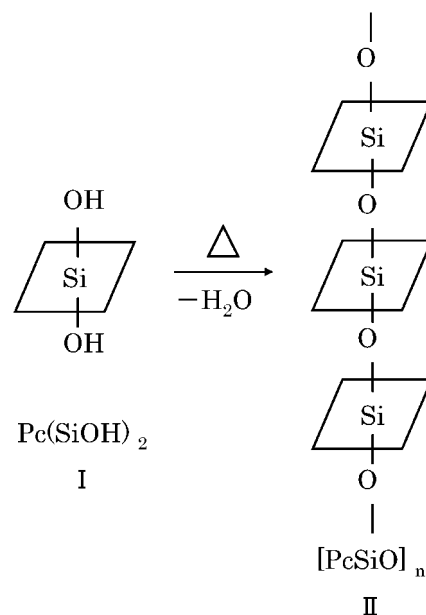
Therefore, as described above, this article discloses the potentiality of ligands, especially organic polydentate ligands, for design of catalyst constituent particles and solid catalysts.

## 2. Design of Solid Catalysts Using the Sol-gel Method

### 2.1. Why and How to Use Organic Polydentate Ligands

A metal ion generally has 4, 6, or 8 bonds, which are known according to the coordination number. Condensation/polymerization to produce metal oxide particles is too complex to enable fine design of the reactions if all of these bonds take part in the reactions. It is therefore necessary to control the number of bonds participating in the reaction, which might be achieved using the action of the appropriate ligand on the metal ion involved in the reaction. In other words, it is possible to control the metal ion reactivity, and to activate or deactivate special positions around the metal ion through action of an appropriate ligand on the ion because these ions form complexes in solution. The stability of the complexes and of respective bonds around the ions depends greatly on the ligand characteristics<sup>1)</sup>. As an example, we consider a metal ion that can have six coordination bonds to form an octahedral structure. In this case, if the ligand is polydentate, the ligand can occupy multiple positions among the six coordination positions in the octahedral structure. Consequently, because polydentate ligands generally form stronger bonds than unidentate ligands<sup>1)</sup>, the positions occupied by the polydentate ligands are blocked or deactivated by them. In other words, the coordination bonds formed by the unidentate ligands are weakened or activated. Two axial positions above and below the plane are generally reactive when the polydentate ligand is a terdentate ligand that occupies four positions forming a square plane in the octahedral structure. Therefore, if such a metal complex is hydrolyzed, the hydrolysis reaction takes place preferentially at the apical positions and then dehydration/condensation/polymerization proceeds with heating to give a one-dimensional polymer. Actually, such a polymer has been prepared from a dihydroxy silicon complex with a phthalocyanine derivative as the ligand (**Fig. 1**)<sup>2),3)</sup>, which indicates that polydentate ligands can not only strongly affect hydrolysis of the coordination bonds but also control the structure of the product formed in the dehydration/polymerization process.

Furthermore, many metal and mixed metal oxide



Pc ≡ phthalocyanine ≡

Fig. 1 Polymerization of  $\text{PcSi}(\text{OH})_2$  to  $(\text{PcSiO})_n$ <sup>2),3)</sup>

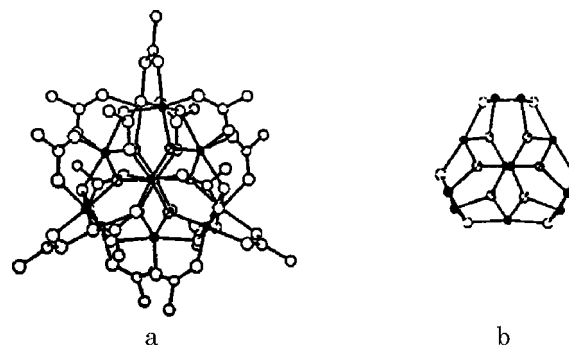


Fig. 2 Structure (a) of  $[\text{Fe}_{11}\text{O}_6(\text{OH})_6(\text{O}_2\text{CPh})_{15}]$  and Core Skeleton (b) Consisting of Iron (●) and Oxygen (○)<sup>5)</sup>

clusters<sup>4)~7)</sup> with frameworks or core structures comprising metal ions and oxygen anions bridging between metal ions and which are surrounded by certain polydentate ligands such as carboxylic anions have been known (**Fig. 2**<sup>5)</sup>). The clusters' structure and size are dependent on the ligand used and its amount. Because the bridging oxygen anions are easily formed by the dehydration between hydroxyl groups bonded to metal ions, the clusters can be regarded as products generated in the dehydration/condensation/polymerization (sol-gel) process proceeding under the influence of carboxylic ligands. Therefore, polydentate ligands can control the degree of dehydration/condensation/polymerization or the size as well as the structure of metal oxide particles produced in the sol-gel process.

A polydentate ligand can link metal ions of different kinds as well as identical ions because it has two or

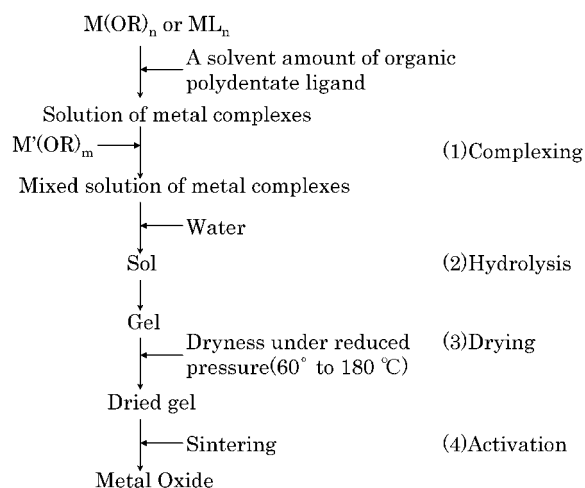
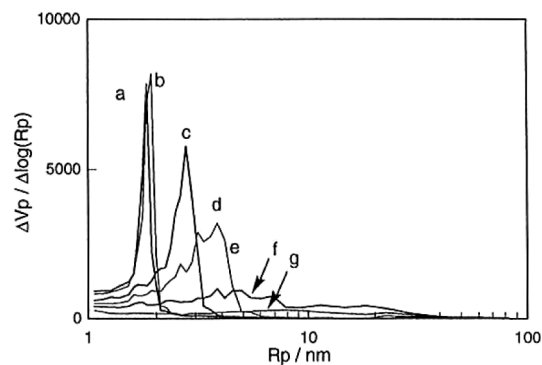


Fig. 3 Typical Procedure of Sol-gel Method Using an Organic Polydentate Ligand

more than two functional groups, which can coordinate respectively to metal ions. Accordingly, polydentate ligands can contribute to the production of particles comprising different metal ions such as mixed metal oxides homogeneous, *i.e.*, to disperse respective constituent particles as fines. As explained above, a polydentate ligand can generally be coordinated to a metal ion more strongly than a unidentate ligand. For that reason, the hydrolysis/dehydration/polymerization proceeds preferentially around the unidentate ligands and polydentate ligands tend to remain in the networks of metal oxide polymers produced in the sol-gel process, or in the oxide particles. The remaining polydentate ligands can be removed using calcinations to give pores with sizes corresponding to the molecular sizes of the ligands used.

## 2. 2. Procedures of Sol-gel Method Using Organic Polydentate Ligands

Based on the description given above, we have proposed an advanced sol-gel process<sup>8)</sup> using organic polydentate ligands actively as a solid catalyst preparation method. In this process, generally metal alkoxides, metal nitrates, metal chlorides etc., which are soluble in organic solvents such as alcohols, ethers and acetone, are used as the raw materials of solid catalysts; polyalcohols, polycarboxylic acids, polyethers, carboxylic acids, hydroxycarboxylic acids, amino acids etc. are commonly used as the ligands. **Figure 3** shows that this sol-gel process consists of roughly four steps, (1) complex formation, (2) hydrolysis, (3) drying, and (4) activation. The selection of an organic polydentate ligand used at the complex forming step is a key because the ligand is expected to play various important roles, such as an agent, to control the hydrolysis rate and the degree of dehydration/condensation/polymerization, a mold that determines the structures of metal oxide polymers or particles, an adhesive agent to combine metal



a,  $r=1.17$ ; b,  $r=1$ ; c,  $r=0.83$ ; d,  $r=0.67$ ; e,  $r=0.50$ ; f,  $r=0.33$ ; g,  $r=0.17$ . Calcination: 450°C, 3 h.

Fig. 4 Pore Size Distribution Curves of the Calcined Gel at Different Malic Acid/TEOS ( $r$ ) Ratios<sup>9)</sup>

ions, and a core that determines the micropore size and shape. That is, it is expected to function as a tool for designing the structure, pore size, surface area, and ultimately the homogeneity of solid catalysts, as illustrated by the concrete examples presented below.

## 2. 3. Control of Particle Size, Pore Size, and Specific Surface Area

As described above, metal oxides have been commonly prepared *via* hydrolysis, followed by dehydration/condensation/polymerization, which is controllable using organic polydentate ligands, and therefore by the molecular weight of a metal oxide. In other words, the particle size of a metal oxide is expected to be related directly to the degree of condensation/polymerization. Furthermore, because gaps resulting between particles with their aggregation, so-called mesopores, depend on the particle size, the mesopores based on the gaps are also strongly affected by the degree of condensation/polymerization. According to this consideration, regarding preparation of silica from tetraethylorthosilicate (TEOS) using the sol-gel method with malic acid as the polydentate ligand, the relationships between the particle size or mesopore distribution of silica obtained and the amount of malic acid used were investigated<sup>9)</sup>. In this procedure, TEOS was mixed first with malic acid to give certain silicon complexes containing malic acid moieties as the ligand by substitution of the ethoxy groups with malic acid moieties (complexing step). Then it was hydrolyzed with water, with subsequent dehydration/condensation/polymerization (hydrolysis step) to give silica sol; it was then turned to gel. Finally the gel was dried under reduced pressure (drying step) and calcined at 450°C for 3 h (activation step). The pore distribution or mesopore size and the specific surface area of the silica obtained respectively decreased and increased with increased amount of malic acid used, as shown in **Figs. 4** and **5**. This relationship is explainable by the mechanism portrayed sche-

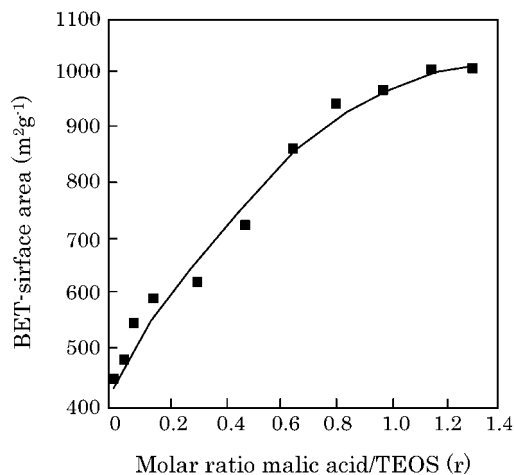


Fig. 5 Effect of Malic Acid/TEOS ( $r$ ) Ratio on Specific Surface Area of Silica Gel Calcined at  $450^{\circ}\text{C}$  for 3 h<sup>9)</sup>

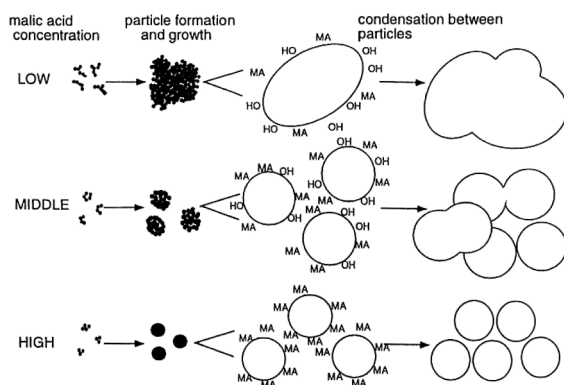
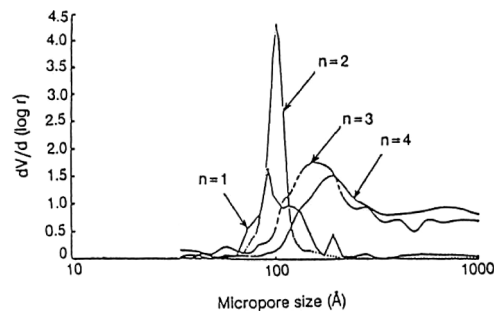


Fig. 6 Influence of Malic Acid on Silica Particle Growth<sup>9)</sup>

matically in **Fig. 6**: A great amount of malic acid prevents condensation between particles in the growth process by covering them.

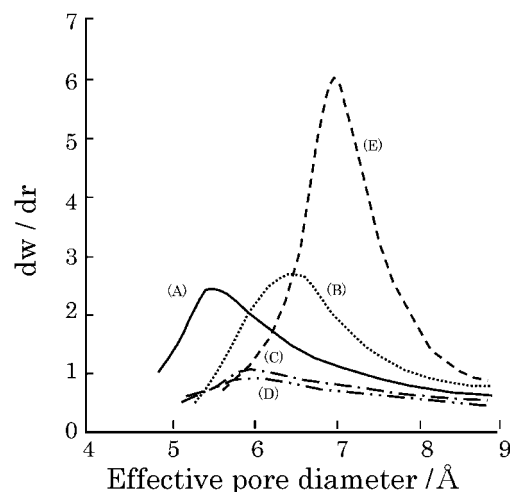
Similar results were obtained for silicas prepared using other polydentate ligands such as tartaric acid<sup>10,11)</sup>, and diols<sup>12)</sup>; furthermore, for alumina obtained from the isopropoxide using polyethers as the organic polydentate ligands (**Fig. 7**<sup>13)</sup>) and silica-alumina<sup>14)</sup> from the corresponding alkoxides using diols as the ligands.

In addition to mesopores, micropores can be designed using organic polydentate ligands because the organic ligands tend to be enclosed in metal-oxygen bond networks formed in the sol-gel process. The pores seem to be generated by burning the ligands. **Figure 8**<sup>15)</sup> depicts the micropore distributions of silica/alumina prepared from TEOS and aluminum isopropoxide using ethylene glycol, 2-methyl-1,2-pentanediol and 2-methyl-2,4-pentanediol as the ligands. Silica-alumina of three types have peak tops at 0.55, 0.63, and 0.67 nm, which correspond approximately to the kinetic sizes of the ligands used. However, most micropores formed in such a manner



Ligand:  $\text{Me}(\text{OCH}_2\text{CH}_2)_n\text{OMe}$ .

Fig. 7 Effect of Ligand Chain Length ( $n$ ) on Micropore Distributions of Alumina Prepared Using Sol-gel Method<sup>13)</sup>



(A) sol-gel (diol = ethylene glycol,  $\text{Al/Si} = 0.04$ ), (B) sol-gel (diol = 2-methyl-2,4-pentanediol,  $\text{Al/Si} = 0.04$ ), (C) coprecipitation ( $\text{Al/Si} = 0.04$ ), (D) commercial alumina/silica (Nikki N-631).

Fig. 8 Micropore Distributions of Silica/alumina: (A)-(D) and NaY Zeolite (E) as Reference<sup>15)</sup>

have insufficient mechanical strength for handling: They are fragile.

The properties of metal oxides described earlier are derived mainly from the primary particles' characteristics. In the sol-gel method using organic polydentate ligands, the size of the secondary metal oxide particles can be controlled as well as that of the primary particles. **Figure 9**<sup>16)</sup> shows silica spheres obtained from TEOS using tartaric acid as the polydentate ligand. The sphere size is controllable by changing the stirring speed: It decreases with increased speed. This control and good relationship between the sphere size and the stirring speed was attained in the presence of tartaric acid and not in its absence.

#### 2. 4. Structural Regulation of Metal Oxides

Based on the fact that organic polydentate ligands strongly affect the structures of metal oxide clusters and precursors, we considered that a specific structure or

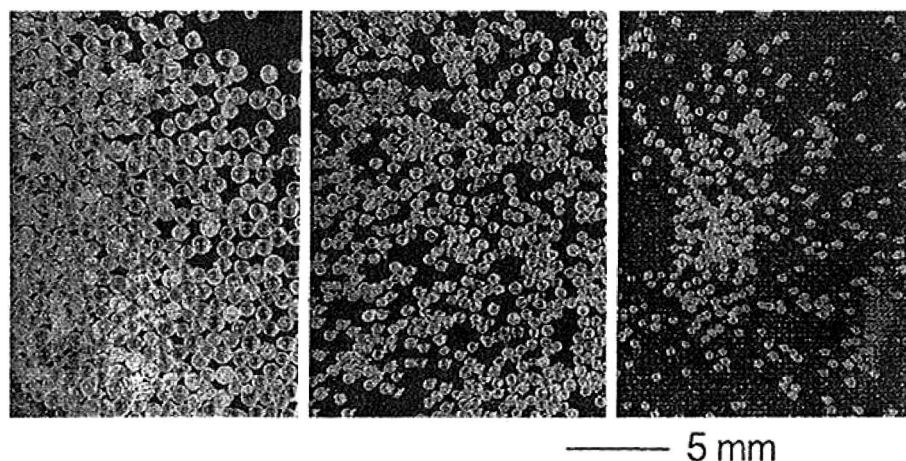


Fig. 9 Photographs of Dried Silica Spherical Particles Prepared from TEOS in the Presence of Tartaric Acid with Various Stirring Speeds<sup>16)</sup>

Table 1 Effect of the DEMM Fraction on Components of the Calcined Powders<sup>17), a)</sup>

Calcination temp. [°C]	a (2 equiv.)	b (1.5)	c (1)	d (0.8)	e (0.67)	f (0.5)	g (0.25)
1000	$\alpha$ -C, $\mu$ -C	$\alpha$ -C, $\mu$ -C	$\alpha$ -C, $\mu$ -C	$\alpha$ -C, $\mu$ -C	$\beta$ -Q, Spn	$\beta$ -Q, Spn	Spn (broad)
1100	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\beta$ -Q, Spn $\alpha$ -C	$\beta$ -Q, Spn	Spn
1200	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -Q, Sap Cb, $\alpha$ -C	$\alpha$ -Q, Sap Cb	Sap
1300	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C, Sap	$\alpha$ -C, Sap	$\alpha$ -C, Sap
1400	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C	$\alpha$ -C

a)  $\alpha$ - or  $\mu$ -C =  $\alpha$ - or  $\mu$ -cordierite;  $\alpha$ - or  $\beta$ -Q =  $\alpha$ - or  $\beta$ -quartz; Spn = spinel ( $\text{MgAl}_2\text{O}_4$ ); Sap = sapphire ( $\text{Mg}_{3,5}\text{Al}_9\text{Si}_{1,5}\text{O}_{20}$ ); Cb = cristobalite.

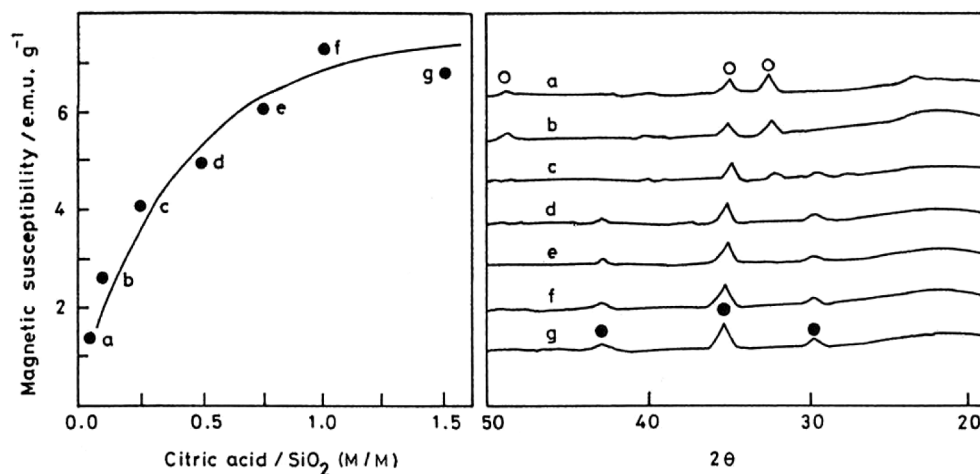
crystal phase among some possible structures of a metal oxide can be formed preferentially using a special ligand; alternatively, this sol-gel method might let a mixed metal oxide take a desired structure at a much lower temperature if a ligand used is suitable for the formation of the precursor producing the structure compared to formation of the structure from the constituent metal oxide powders using the corresponding traditional mixing method.

Therefore, low-temperature synthesis of cordierite, which is a typical thermostable ceramic and which is well known as the honeycomb support for the automobile exhaust gas purification catalyst, was tried from alkoxides of silicon, aluminum, and magnesium using diethylene glycol monomethyl ether (DEMM) as the polydentate ligand. **Table 1**<sup>17)</sup> shows the relationship between the calcination temperatures of the powders obtained after the drying step and the amounts of the ligand used, based on the appearance of the crystal phases. When the amount of DEMM used is greater than four-fifths equivalent in moles to the total amount of alkoxides used, a cordierite structure that, according to the phase diagram, is a stable phase, preferentially appears, even at 1000°C, which is 300°C lower than the calcination temperature required for cordierite synthesis

from the constituent metal oxide powders using traditional powder mixing. Actually, if the DEMM used is 2/3 equivalent amount or less, cordierite phase appears at calcination temperatures over 1300°C, as consistent with the temperature required for the powder mixing method.

Preferential formations of a stable crystal phase at a lower temperature have also been recognized respectively for syntheses of yttrium iron garnet<sup>18)</sup> and mullite<sup>19)</sup> from nitrates of yttrium and iron and from alkoxides of silicon and aluminum using diols as the polydentate ligands.

The sol-gel process or dehydration/condensation/polymerization can be controlled not only in solution but also on a substrate using organic polydentate ligands. For example, a desired phase of anatase or rutile among the possible three crystal phases for titania can be obtained selectively on a glass substrate or silicon wafer by reacting titanium alkoxide with an appropriate diol of DEMM, triethylene glycol monomethyl ether, or 2-methyl-2,4-pentanediol (diacetone alcohol) by applying the obtained sol on the substrate, then drying and calcining it<sup>20)</sup>. Similarly, magnetic iron oxide with a spinel structure can be formed selectively on a quartz substrate as a transparent thin film<sup>21)</sup>.



Citric acid: SiO<sub>2</sub> are ratios used for preparation of the composites.  
○: corundum iron oxide; ●: spinel iron oxide.

Fig. 10 Magnetic Susceptibilities and X-ray Diffraction Patterns of Iron Oxide/Silica Composites<sup>22)</sup>

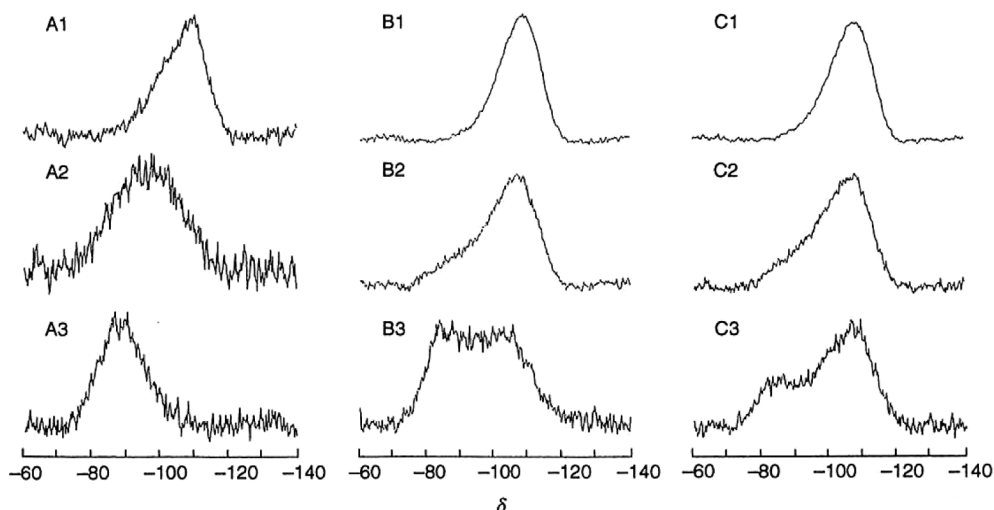
Moreover, structural regulation can be attained on a powder carrier. Silica was first impregnated with citric acid in water and dried; it was again impregnated with iron nitrate in acetone, dried, and burned to form iron oxides on the silica. **Figure 10**<sup>22)</sup> portrays the magnetic susceptibility and powder X-ray diffraction (XRD) patterns of the iron oxide/silica composites obtained as described above. The saturated magnetic susceptibility increased as the amount of citric acid used increased, indicating that the structure of iron oxide on silica transforms from corundum to a spinel form with increased citric acid used, as verified by the XRD pattern, which changes from a corundum pattern to a spinel one according to the citric acid amount. Actually, use of diacetone alcohol instead of citric acid produced the corundum form only. Furthermore, it has been disclosed for this procedure that both the structure and particle size of the iron oxide are controllable by carefully selecting the organic ligand, for example, using a series of saccharides with different molecular weights<sup>23)</sup>.

## 2.5. Homogeneity of Mixed Metal Oxides, and Dispersibility of Components

Hydrolysis/dehydration/condensation/polymerization of metal ions or complexes often produce mixed metal oxides with uneven composition because the rates of hydrolysis and dehydration/condensation and the optimum pH region for formation of metal oxide precipitates frequently differ greatly between the metal ions or complexes. During the sol-gel process using organic polydentate ligands, however, the ligands can stabilize the metal ions or complexes to adjust their reactivities and also bridge between different metal ions through coordination bonds. Consequently, the copolymerization of different metal ions at the atomic level seems to

be accelerated to produce homogeneous mixed oxides in which the components are highly dispersed from each other.

Actually, although the hydrolysis and dehydration/condensation rates of TEOS are much slower than those of aluminum isopropoxide (AIP), homogeneous silica/alumina in which the respective components are well mixed is obtainable using an organic polydentate ligand in the sol-gel process. **Figure 11**<sup>24)</sup> portrays <sup>29</sup>Si MAS NMR spectra of three series of silica/alumina prepared from TEOS and AIP using sol-gel (A), coprecipitation (B) and kneading (C) methods. During the sol-gel procedure, 2-methyl-2,4-pentanediol was used as the polydentate ligand. During coprecipitation, hydrolysis of the alkoxides was carried out using nitric acid as the catalyst. For kneading, TEOS and AIP were first hydrolyzed to the respective hydrogels separately; then hydrogels of two kinds were kneaded. After drying under identical conditions, silica/aluminas of all three types were calcined at 550°C for 8 h. Great differences were apparent among the three series of NMR spectra of silica/alumina, although the starting materials and the calcinations conditions were identical. In the A series, as the aluminum content or Al/Si ratio increases, the peak top shifts continuously from -110 ppm assigned to Si(OSi)<sub>4</sub> signal to -85 ppm assigned to Si(OAl)<sub>4</sub> signal via a broad signal attributed to Si(OSi)<sub>1-x</sub>(OAl)<sub>x</sub>, but such a continuous peak shift is not observed for the other two series of NMR spectra. In both the B and C series, the signal attributed to Si(OSi)<sub>4</sub> is always strong; especially in C, it is highest even when the Al/Si ratio is 4 or the aluminum content is four times higher than the silicon content, which indicates that formation of Si-O-Al bonds proceeds smoothly in the A series, but not in the B and C series. This smoothness of the proc-



A, sol-gel; B, coprecipitation; and C, hydrogel kneading.  
Al : Si = 0.08 (A1, B1, C1), 1 (A2, B2, C2), and 4 (A3, B3, C3).

Fig. 11  $^{29}\text{Si}$  MAS-NMR Spectra of Alumina/Silicas Calcined in Air at  $550^\circ\text{C}$  for 8 h<sup>24)</sup>

Table 2 Acid Amount of Alumina/Silicas Calcined in Air at  $550^\circ\text{C}$  for 8 h<sup>24)</sup>

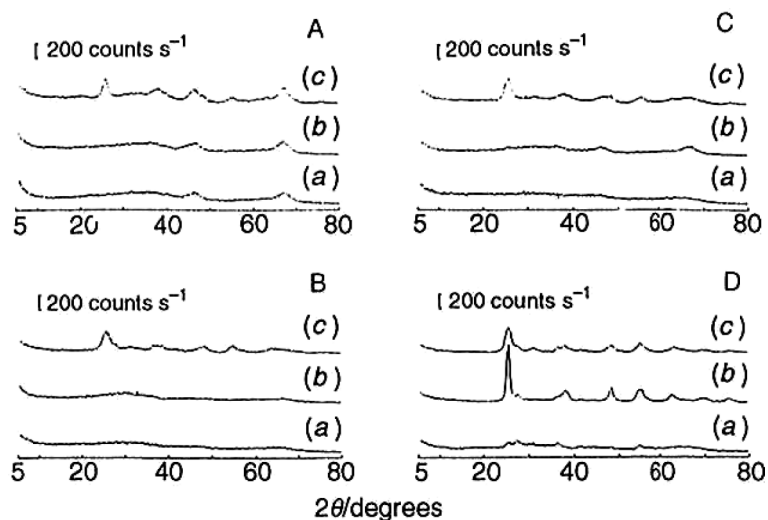
Al/Si	Acid amount [mmol/g]		
	Sol-gel	Coprecipitation	Hydrogel kneading
0	0.021	0.011	—
0.08	0.130	0.005	0.005
1	0.212	0.075	0.044
4	0.372	0.282	0.179
$\infty$	0.471	0.172	—

The acid amounts were measured by  $\text{NH}_3$  TPD method.

ess reflects the difference in mixing or dispersibility between silica and alumina particles. It is therefore considered that, in the A series, mixing between silica and alumina is attained at a very fine level or at an almost atomic level, on the other hand, in the B and C series, the mixing is neither so fine nor homogeneous, and silica and alumina particles tend to be maintained in their original shapes during calcination; therefore, the formation of Si-O-Al bonds does not proceed deep inside of the particles, especially in the C. The formation of Si-O-Al bonds is performed only on the inter-surfaces between original silica and alumina particles. Corresponding with this,  $^{27}\text{Al}$  MAS NMR spectra disclosed that in the silica/alumina with Si/Al ratio over 1, the content of 4-coordination aluminum, which originates the Brønsted acidity, is much more in the sol-gel silica/alumina than in the coprecipitation and kneading ones. Reflecting these, the silica/alumina types obtained using the sol-gel procedure are much higher in the amount of solid acid than those from the coprecipitation and kneading methods, as presented in **Table 2**<sup>24)</sup>.

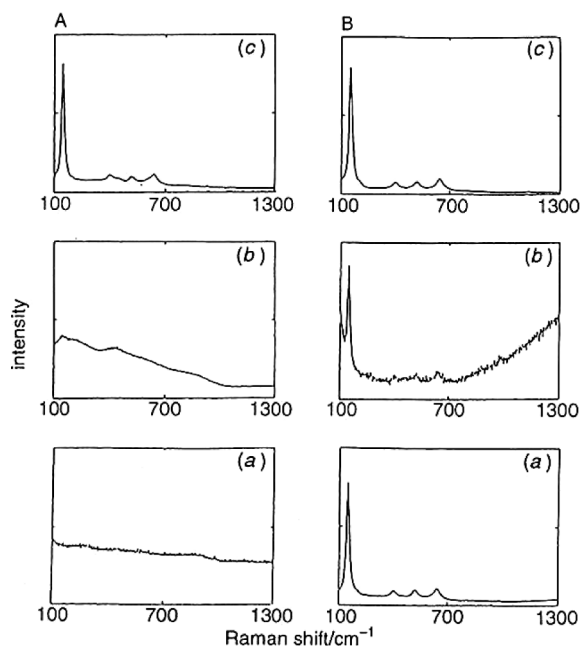
Similar phenomena to those described above for silica/alumina have been observed for titania/silicas<sup>25)</sup>, zirconia/silicas<sup>26)</sup>, and alumina/titanias<sup>27)</sup> obtained using sol-gel, coprecipitation, and kneading processes. However, in these cases, the dispersibility of the constituent metal oxide particles has been deduced based not only on MAS NMR spectra, but also on XRD and Raman spectra because titania and zirconia particles readily transform from amorphous to crystal phases during calcination if their dispersibility is low, *i.e.*, if the particles are sufficiently large to be detected in crystallization. For example, when the titania of alumina/titania composites is dispersed nonuniformly or aggregated, the crystal phases of titania readily appear by heating, as portrayed in **Figs. 12**<sup>27)</sup> and **13**<sup>27)</sup>.

Luminescence and excitation spectra sometimes reflect the homogeneity of mixed metal oxides. **Figure 14**<sup>28)</sup> shows spectral patterns of an aqueous solution of uranyl acetate (a), and two uranium oxide/silica composites (b and c). Composite (b) was prepared from TEOS and uranyl acetate using the sol-gel procedure with ethylene glycol as the organic polydentate ligand. Composite (c) was obtained by impregnating silica derived from TEOS with the aqueous solution of uranyl acetate. Before spectral measurements, both composites were dried under identical conditions and calcined at  $550^\circ\text{C}$  for 5 h. All three samples show only the spectra relevant to the uranyl ion. The spectral patterns of (b) are much more similar to those of (a) than to those of (c), despite the fact that composites (b) and (c) have identical composition. As might be expected, uranyl ions in the solution are uniformly dispersed because of the homogeneous solution. Therefore, the similarity in the spectral patterns of (a)



Ti : Al = A, 0.05; B, 0.2; C, 0.5; and D, 1.  
(a) sol-gel; (b) coprecipitation; (c) hydrogel kneading.

Fig. 12 Effect of Preparation Method on X-ray Diffraction Patterns of Alumina/Titania Calcined at 550°C for 8 h<sup>27)</sup>



Light source, Kr laser 647.1 nm.  
A, sol-gel; B, coprecipitations. Ti : Al = (a) 0.2, (b) 1, (c) 2.

Fig. 13 Raman Spectra of Alumina/Titania Calcined at 550°C for 8 h<sup>27)</sup>

and (b) suggests that uranyl ions are highly dispersed in the silica in composite (b).

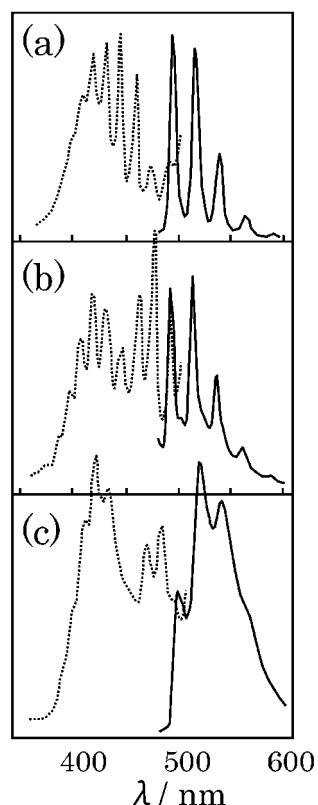
### 3. Catalytic Performance of the Composites Prepared Using the Sol-gel Method

In most cases, solid catalysts prepared using the sol-gel method with organic polydentate ligands show higher performance than the corresponding catalysts obtained using a traditional preparation method such as impregnation or coprecipitation. Such catalysts often display unique properties. Among them, typical examples are introduced below.

#### 3.1. Silica/Alumina

Table 3<sup>14)</sup> shows conversion of methanol catalyzed by different aluminosilicates including the sol-gel silica/alumina. For preparation of the sol-gel silica/alumina, TEOS and  $\text{AlCl}_3$  were used as the raw materials, and 2-methyl-2,4-pentandiol (1), pinacol (2), 1,2-propanediol (3), 2,3-butanediol (4), and ethylene glycol (5, 6, 7) were used as the organic polydentate ligand. The methanol conversion ability of a kneading silica/alumina is poor; although the commercial silica/alumina (N632HN) can convert methanol to dimethyl ether, its hydrocarbon producing ability is low. Compared to these samples of silica/alumina, the sol-gel samples show much higher hydrocarbon producing abilities, which are comparable to that of FCC containing Y-zeolite as the main component. Especially, the sol-gel silica alumina with the Si/ $\text{Al}_2$  ratio of 50 prepared using ethylene glycol as the polydentate ligand shows comparable ability for production of ethylene and propylene to that of ZSM-5. Moreover, sol-gel silica/alumina obtained from TEOS and AIP in a similar manner shows higher activities for alkylation of aromatics than the conventional silica/alumina<sup>29)</sup>. These phe-





(a) uranyl acetate dihydrate; (b) sol-gel uranyl-silica; (c) the impregnated uranyl-silica at  $-196^{\circ}\text{C}$ .

Fig. 14 Fluorescence (solid line) and Excitation (dotted line) Spectra of the Aqueous Solution<sup>28)</sup>

nomena seem to be attributable to the high acid amount and/or Brønsted acidity of the sol-gel silica/alumina.

Actually, as described above, the sol-gel procedure using organic polydentate ligands can produce more homogeneous silica/alumina than conventional procedures can, which suggests that the sol-gel procedure can provide excellent starting powders for the solid state transformation<sup>30)~34)</sup> of amorphous silica/alumina to zeolite. Actually, the silica/alumina powder containing tetrapropyl ammonium hydroxide prepared using the sol-gel procedure was more rapidly transformed to the MFI type of zeolite at lower temperatures than the conventional hydrothermal synthesis of the zeolite<sup>35)</sup>. A great advantage exists in this solid state transformation of amorphous silica/alumina to zeolite. From traditional zeolite synthesis, zeolite is generally obtained as powder and is difficult to shape into a disk or pellet for the catalyst without a binder. However, in such a transformation, a disk or pellet made of the starting silica/alumina powder containing an appropriate amine can be crystallized to zeolite as it is: The shaped body of amorphous silica/alumina can be transformed directly to the shaped zeolite<sup>35)~38)</sup>. The H-MFI type of zeolite disk membrane catalyst obtained using this solid state

transformation shows a higher selectivity for the formation of *p*-xylene in the methylation of toluene with methanol than the corresponding powder catalyst<sup>36)~38)</sup>.

### 3. 2. Thermostable Catalysts

As described above, the sol-gel method using organic polydentate ligands can produce homogeneous mixed oxides in which the components are highly dispersed from each other or in which the constituent particles are fine and well mixed. Based on that fact, if the reaction between the components constituting the mixed oxide is feasible, the oxide smoothly transforms into another compound or crystal. In contrast, if the components are not so mutually reactive, the aggregation or particle growth of one component tends to be hindered by that of another component: The respective crystal growth and sintering processes of the constituent particles are suppressed because of their high dispersibility. Accordingly, the sol-gel method can yield thermostable mixed oxides that are resistant to sintering, *i.e.*, effective as supports for combustion catalysts. Based on this consideration, different alumina mixed with metal oxides were prepared using the sol-gel procedure. Their respective thermostabilities were investigated using XRD, TG-DTA, and BET nitrogen adsorption<sup>39),40)</sup>.

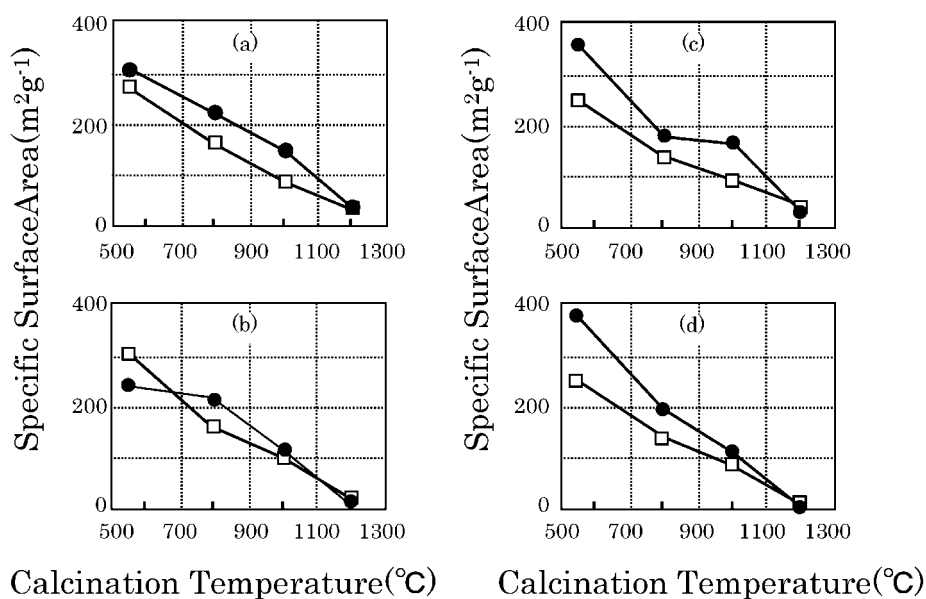
**Figure 15**<sup>39),40)</sup>, displays the specific surface areas of 10 wt% metal oxide/alumina prepared using sol-gel and coprecipitation methods. Raw materials of alumina and other metal oxides were all alkoxides; alcohol was used as the solvent to mix alkoxides of two kinds. In addition, in the sol-gel procedure, 2-methyl-2,4-pentanediol was used as the organic polydentate ligand. Calcination was carried out at temperatures of 550-1200°C for 3 h. Generally speaking, the sol-gel  $\text{La}_2\text{O}_3/\text{Al}_2\text{O}_3$ ,  $\text{SrO}/\text{Al}_2\text{O}_3$ ,  $\text{BaO}/\text{Al}_2\text{O}_3$ , and  $\text{ZrO}_2/\text{Al}_2\text{O}_3$  show higher surface areas than the corresponding coprecipitation ones, although almost no differences were apparent between the corresponding two kinds of mixed alumina calcined at temperatures higher than 1100°C. All four kinds of sol-gel mixed alumina calcined at 1000°C or lower temperatures showed no clear XRD peaks, indicating that all are amorphous; when further calcined at 1200°C, only  $\text{BaO}/\text{Al}_2\text{O}_3$  was amorphous and the others showed clear XRD peaks. Reflecting this, among the 10 wt% metal oxide/alumina of four kinds,  $\text{BaO}/\text{Al}_2\text{O}_3$  showed the highest specific surface area and thermal resistance. The specific surface area and thermal resistance of  $\text{BaO}/\text{Al}_2\text{O}_3$  are, of course, dependent on the BaO content. The optimum content of BaO was 10 wt%, as presented in **Tables 4**<sup>39),40)</sup> and **5**<sup>39),40)</sup>. This 10 wt%  $\text{BaO}/\text{Al}_2\text{O}_3$  retains a high specific surface area of 139 m<sup>2</sup>/g and shows no clear XRD peaks after calcination at 1000°C for 100 h<sup>39)</sup>.

Combustion catalysts are known to produce much steam or water while working. Therefore, the resistance of 10 wt%  $\text{BaO}/\text{Al}_2\text{O}_3$  to water was examined by

Table 3 Methanol Conversion with Various Silicas/Alumina and Aluminosilicates<sup>14)</sup>

Catalyst	Si/Al <sub>2</sub>	320°C <sup>a)</sup>			360°C <sup>a)</sup>			380°C <sup>a)</sup>		
		Methanol conv. [%]	Yield [%]		Methanol conv. [%]	Yield [%]		Methanol conv. [%]	Yield [%]	
			T.H.C.	C2' + C3'		T.H.C.	C2' + C3'		T.H.C.	C2' + C3'
Sol-gel silica-alumina										
1 (HG)	50	83.6	3.8	0.0	83.9	4.3	0.1	83.5	4.4	0.1
2 (Pinacol)	50	86.3	5.2	0.1	83.8	9.2	0.7	82.9	11.5	2.7
3 (1,2-PD)	50	86.1	5.8	0.1	84.5	10.2	1.6	83.9	13.8	2.6
4 (2,3-BD)	50	85.9	12.7	1.3	85.1	21.6	4.0	84.0	26.2	5.7
5 (EG)	50	85.8	14.2	1.8	85.7	23.1	4.6	84.6	27.2	6.1
6 (EG)	25	85.9	10.2	0.1	85.3	21.9	1.4	85.0	31.2	3.6
7 (EG)	5	85.7	8.3	0.1	84.6	9.9	0.2	84.0	10.7	0.3
Kneading	50	1.9	1.9	0.0	3.0	3.0	0.0	3.3	3.3	0.0
Nikki (N632HN)	4.4	85.8	4.3	0.0	85.0	4.5	0.0	83.4	4.4	0.1
FCC (MRZ-204)	—	84.3	13.1	2.9	83.7	10.8	2.9	83.2	8.5	1.5
ZSM-5	40	no data			99.7	99.7	6.3	99.7	99.7	7.2

Sol-gel silica-alumina 1-7 were prepared from TEOS and aluminium trichloride anhydride using 2-methyl-2,4-pentanediol (HG), pinacol, 1,2-pentanediol (1,2-PD), 2,3-butanediol (2,3-BD) and ethylene glycol (EG) as the organic polydentate ligand and calcined at 550°C for 12 h.  
a) Reaction temperature, T.H.C.; total hydrocarbons, C2': ethylene, C3': propylene.



(●) sol-gel, (□) coprecipitation. M<sub>x</sub>O<sub>y</sub>: (a) La<sub>2</sub>O<sub>3</sub>, (b) SrO, (c) BaO, (d) ZrO<sub>2</sub>.

Fig. 15 Specific Surface Areas of 10 wt% M<sub>x</sub>O<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub> Prepared Using Sol-gel and Coprecipitation Procedures<sup>39),40)</sup>

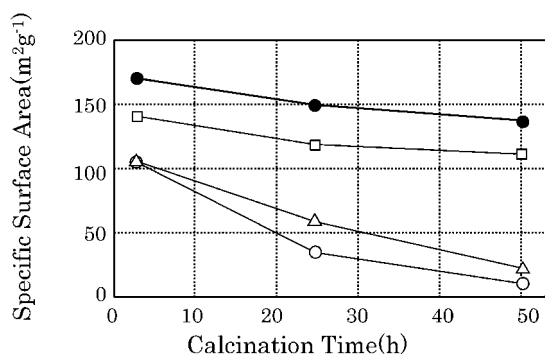
soaking it in water. Results showed that BaO in BaO/Al<sub>2</sub>O<sub>3</sub> is dissolved gradually in water. However, the mixed alumina, after being soaked and washed several times with water, retained a high specific surface area after calcination at 1000°C despite a large decrease in the BaO content. This fact suggests that the thermostability of alumina is increased not only by the addition of BaO but also by the preparation procedure itself. Therefore, alumina was prepared from AIP using the

sol-gel method with 2-methyl-2,4-pentanediol as the polydentate ligand<sup>40)–43)</sup>, and compared them with alumina of two kinds obtained using conventional methods (double decomposition<sup>44)</sup> of aluminum sulfate with sodium aluminate and simple hydrolysis of AIP in isopropanol) and a commercial alumina (CK-300; Nippon Ketjen Co., Ltd.) as the reference. Among the four alumina types, the sol-gel alumina showed the highest specific surface area in calcination of 600–1000°C and

Table 4 Influence of BaO Content on Specific Surface Areas of BaO/Al<sub>2</sub>O<sub>3</sub> Prepared Using the Sol-gel Procedure<sup>39,40)</sup>

Calcination temp. [°C]	550	800	1000	1200	1450
Calcination time [h]	3	3	3	3	5
BaO [wt%]	Specific surface area [m <sup>2</sup> /g]				
5	444	162	111	17	4
10	375	219	171	96	7
15	488	227	176	32	8
20	340	202	141	13	11
25	364	111	75	10	6

Raw material: Al<sub>2</sub>O<sub>3</sub>, Al(Opr<sup>r</sup>)<sub>3</sub>; BaO, Ba(Obu<sup>n</sup>)<sub>2</sub>.



● sol-gel (a), □ conventional precipitation from the alkoxide (b), △ double decomposition (c), ○ Ketjen, CK-300 high purity (d).

Fig. 16 Effect of the Time of Calcination at 1000°C on the Specific Surface Area of Alumina<sup>40)</sup>

retained the highest value (136 m<sup>2</sup>/g) even after calcination at 1000°C for 50 h, as depicted in **Fig. 16**<sup>40)</sup>. Therefore, the sol-gel alumina can retain not only high specific surface area but also good durability with no additives.

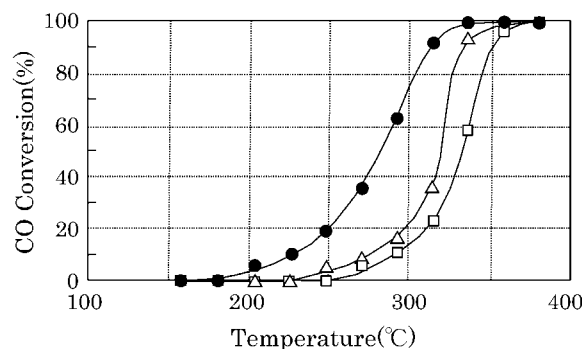
We prepared 1 wt% platinum catalysts of three kinds using a conventional impregnation technique with the sol-gel alumina described above, a commercial alumina derived from an aluminum alkoxide, and the above sol-gel 10 wt% BaO/Al<sub>2</sub>O<sub>3</sub> as supports. We tested for the oxidation of carbon monoxide as a model reaction for exhaust gas purification<sup>40,45)</sup>. The three supports were calcined at 1000°C for 20 h before impregnation with an aqueous solution of dinitro diammine platinum complex. After drying, 1 wt% platinum catalysts of three types were calcined at 400°C for 3 h, then at 1000°C for 20 h, and activated in a hydrogen stream at 400°C for 1 h. Finally, we tested for the CO oxidation. The Pt contents of the three catalysts prior to the activation were confirmed by chemical analyses as equal within experimental error. **Figure 17**<sup>40)</sup> portrays CO oxidation profiles for the three catalysts. The catalyst activity decreases in the order of the sol-gel BaO/Al<sub>2</sub>O<sub>3</sub> > the sol-gel alumina > the commercial alumina. **Figure 18**<sup>40)</sup> depicts SEM micrographs of the surfaces of the three

Table 5 Structures of the Sol-gel BaO/Al<sub>2</sub>O<sub>3</sub> Calcined at Different Temperatures<sup>39,40)</sup>

Calcination temp. [°C]	1000	1200	1450
Calcination time [h]	3	3	5
BaO [wt%]	Structure		
5	a > c	c > m > s	c > m
10	a	a	c = m
15	a	c < m	c < m
20	a	m	m
25	a > s	m = s	m

Structure: a, amorphous; c, α-Al<sub>2</sub>O<sub>3</sub>; s, BaO·Al<sub>2</sub>O<sub>3</sub> (spinel); m, BaO·6Al<sub>2</sub>O<sub>3</sub> (magnetoplumbite).

Raw material: Al<sub>2</sub>O<sub>3</sub>, Al(Opr<sup>r</sup>)<sub>3</sub>; BaO, Ba(Obu<sup>n</sup>)<sub>2</sub>.

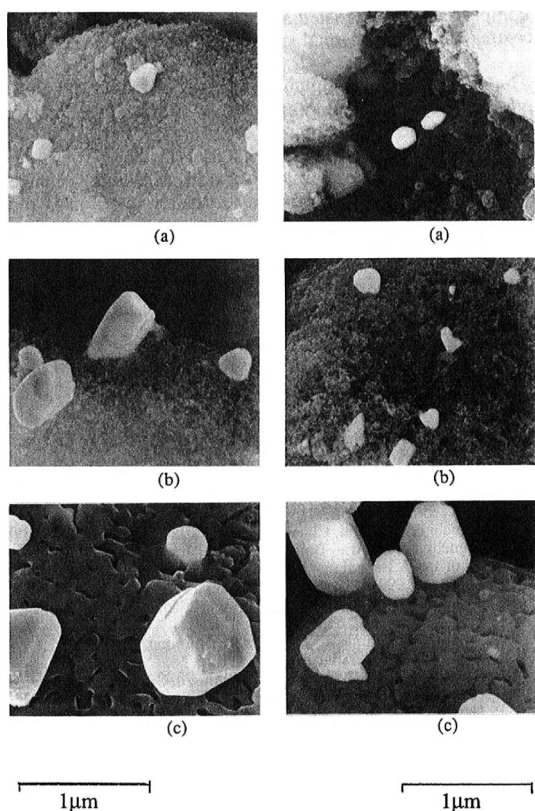


● Pt/sol-gel 10 wt% BaO-Al<sub>2</sub>O<sub>3</sub>, △ Pt/sol-gel alumina, □ Pt/commercial alumina derived from alkoxide.

Fig. 17 CO Oxidation Profiles with Three Catalysts Activated after Calcination at 1000°C for 20 h<sup>40)</sup>

catalysts calcined at 1000°C for 20 h. Large white masses correspond to platinum; their sizes increase in the order of the sol-gel BaO/Al<sub>2</sub>O<sub>3</sub> < the sol-gel alumina < the commercial alumina. These orders of two kinds result from the sintering extent of the alumina surfaces, as implied by **Fig. 18**<sup>40)</sup>. Actually, according to the XRD analyses<sup>40)</sup>, the transformation rates of the alumina in the catalysts to α-alumina are 39%, less than 5%, and can not be estimated respectively for the commercial alumina, the sol-gel alumina, and the sol-gel 10 wt% BaO/Al<sub>2</sub>O<sub>3</sub>. Because the sintering of alumina at high temperatures proceeds with the transformation to α-alumina, we infer in this case that the catalytic activity of the catalysts is based on the thermostability of the supports.

Similar comparison between the sol-gel and the commercial alumina supports was carried out for the decomposition of hydrazine with the 30 wt% iridium alumina catalysts prepared using the impregnation technique with ethanol as the solvent<sup>46)</sup>. First, iridium catalysts of two types were heated at 850°C for 4 h under a nitrogen atmosphere; then they were provided for decomposition. The iridium supported by the sol-gel alumina decomposed hydrazine smoothly after



(a) Pt/sol-gel 10 wt% BaO-Al<sub>2</sub>O<sub>3</sub>, (b) Pt/sol-gel alumina, (c) Pt/a commercial alumina derived from alkoxide. Magnification: 30,000.

Fig. 18 SEM Images of the Three Catalysts after Calcination at 1000°C for 20 h<sup>40)</sup>

some induction period, but the iridium supported by the commercial alumina only slightly decomposed hydrazine. This is also attributable to the difference in the thermostability between the two alumina types. Exactly why the alumina obtained using the sol-gel with 2-methyl-2,4-pentanediol as the polydentate ligand possesses high specific surface area and thermostability remains unclear, but both properties can be mostly attributed to its rod-like shape<sup>43)</sup>.

A similar investigation was performed for oxidation of CO and hydrocarbons and the conversion of NO<sub>x</sub> with platinum<sup>45),47),49)</sup>, rhodium<sup>47)</sup> and palladium<sup>45),50)</sup> catalysts supported by different alumina types<sup>45)</sup> and alumina-based mixed oxides such as CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub><sup>47)</sup> and CeO<sub>2</sub>/M<sub>x</sub>O<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub><sup>48)~50)</sup> which were prepared using the sol-gel method and conventional impregnation consisting of one step or two steps. When the support was only alumina, the sol-gel alumina prepared using 2-methyl-2,4-pentanediol as the polydentate ligand yielded catalysts with higher-performance than the commercial alumina and other sol-gel alumina obtained using another polydentate ligands. In both cases of CeO<sub>2</sub>/Al<sub>2</sub>O<sub>3</sub> and CeO<sub>2</sub>/M<sub>x</sub>O<sub>y</sub>/Al<sub>2</sub>O<sub>3</sub>, the sol-gel supports always gave higher performance catalysts than the cor-

responding impregnation ones.

### 3.3. Supported Metal Catalysts for Hydrogenation

Supported metal catalysts can also be prepared using the sol-gel method with organic polydentate ligands as well as mixed oxides: The raw materials of the active metal and support components building up the final catalyst were dissolved in a polar organic solvent such as alcohol together with an organic polydentate ligand, and complexed, then hydrolyzed to the sol; the gel obtained after drying the sol was activated in a hydrogen stream before or after calcination. The supported metals such as palladium, platinum, ruthenium, rhodium, etc. obtained in this manner are much more finely dispersed in more uniform shape on the supports than those in the conventional impregnation catalysts<sup>51),52)</sup>. In addition to the characteristics, interestingly, the sol-gel supported metal catalysts that were activated directly in hydrogen without calcination show particularly high performance in some kinds of hydrogenations: Those with a certain inhibitor or poison as a reaction controller or promoter requiring a noble metal catalyst, as described below.

A typical catalytic reaction in which a poisonous material is necessary is the partial hydrogenation of benzene to cyclohexene. During the usual hydrogenation of benzene, only cyclohexane is produced because the value of  $\Delta G^0$  for conversion to cyclohexene ( $-23$  kJ/mol at 25°C) is substantially smaller than that for the complete hydrogenation to cyclohexane ( $-98$  kJ/mol at 25°C)<sup>53)</sup>. Accordingly, this partial hydrogenation is quite difficult, but important industrially, because cyclohexene can be the starting material of nylon-6 monomer or  $\epsilon$ -caprolactam<sup>54)</sup>. Therefore, efforts to improve such partial hydrogenation have been made for a long time. Results of earlier studies indicate that ruthenium is the best catalyst for the cyclohexene formation<sup>55)~62)</sup>, but together with the catalyst, considerable amounts of poisonous additives such as sodium hydroxide<sup>59)</sup> and metal sulfates<sup>59),60)</sup> and a large amount of water as the solvent are necessary to obtain cyclohexene in an appreciable yield. Unexpectedly, when ruthenium catalysts are prepared using the sol-gel method with the organic polydentate ligands and directly activated in hydrogen after drying without calcination, high cyclohexene yields are attained without addition of poisonous materials to the reaction solution<sup>51),63)~68)</sup>, as presented in **Table 6**. Actually, the sol-gel ruthenium catalysts that are calcined and then activated in hydrogen only show a poor ability in the production of cyclohexene<sup>65),67)</sup> as well as the usual ruthenium catalysts. According to the FT-IR spectra<sup>67)</sup>, the sol-gel ruthenium catalysts activated without calcinations retained some residues of organic polydentate ligands used in the catalyst preparation. The amount of the residues is a trace, but sufficient to cover the ruthenium metal particles<sup>64),67)</sup>. Therefore, the organic polydentate ligands

Table 6 Partial Hydrogenation of Benzene with Various Ruthenium Catalysts<sup>(63),64)</sup>

Procedure		Catalyst composition	Cyclohexene yield [mol %]	Benzene conversion [%]
Preparation	Organic ligand			
sol-gel	ethylene glycol	2 wt% Ru-SiO <sub>2</sub>	27.0	86.8
sol-gel	ethylene glycol	2 wt% Ru-0.2 wt% Cu-SiO <sub>2</sub>	31.4	83.3
sol-gel	pinacol	2 wt% Ru-Al <sub>2</sub> O <sub>3</sub>	14.2	42.7
sol-gel	pinacol	2 wt% Ru-0.2 wt% Cu-Al <sub>2</sub> O <sub>3</sub>	24.3	74.1
impregnation <sup>a)</sup>		2 wt% Ru-SiO <sub>2</sub>	8.6	64.3
impregnation <sup>a)</sup>		2 wt% Ru-Al <sub>2</sub> O <sub>3</sub>	5.3	54.5
impregnation <sup>a),b)</sup>		2 wt% Ru-Al <sub>2</sub> O <sub>3</sub>	27.2	72.7

Initial reaction mixture: benzene (160 ml), H<sub>2</sub>O (100 ml), catalyst (2 g).

Reaction temperature (180°C), reaction pressure (7 MPa).

a) commercial, b) 5 g of CoSO<sub>4</sub> was added to the reaction mixture.

Table 7 Formation of Aldehydes in the Hydrogenation of Acid Chlorides Catalyzed Using the Sol-gel 3 wt% Pd/SiO<sub>2</sub> at 80°C<sup>72)</sup>

Substrate	Electron density <sup>a)</sup>	Conversion [%]	Selectivity [%]	Maximum yield [%]	Reaction time [h]
Benzoyl chloride <sup>b)</sup>	0.546	94	93	87	9
Benzoic acid <sup>c)</sup>	0.761		no reaction		
<i>o</i> -Anisoyl chloride <sup>c)</sup>	0.678	97	81	80	29
<i>m</i> -Anisoyl chloride <sup>c)</sup>	0.551	100	99	99	62
<i>p</i> -Anisoyl chloride <sup>c)</sup>	0.566	88	98	90	24
Decanoyl chloride <sup>b)</sup>	0.606	97	100	97	17
2-Naphthoyl chloride <sup>c)</sup>	0.575	90	90	81	16
2-Furoyl chloride <sup>b)</sup>	0.592	100	98	98	31
Terephthaloyl chloride <sup>c)</sup>	0.541	99	76	75	25
Adipoyl chloride <sup>c)</sup>	0.632		precipitate		

Type of catalyst used: a<sub>1s</sub>, activated by bubbling hydrogen gas in the reaction solvent at 80°C for 1 h prior to hydrogenation.

a) Calculated by RHF/6-31G\* for the carbon atom of the acyl carbonyl.

b), c) Used cyclohexane and toluene, respectively, as the reaction solvent.

not only contribute by highly dispersing ruthenium ions but also keep the ruthenium metal particles highly dispersed or very small and modify the surfaces of the particles by surrounding them after they turn to residues during activation, which is probably why the sol-gel ruthenium catalysts require no additives such as either a reaction regulator or promoter for cyclohexene formation<sup>67)</sup>.

Synthesis of aldehydes through palladium-catalyzed hydrogenation of acid chlorides is well-known as Rosenmund reduction<sup>(69)~(71)</sup>. In the Rosenmund reduction, generally a large excess of an additive such as quinoline-S (thioquinathrene), pyridine, amines, or acetate is added to the reaction mixtures as a poison to prevent successive hydrogenation of aldehydes. However, the sol-gel silica-supported palladium catalysts prepared using sol-gel method with a mixture of ethylene glycol and 2,4-pentanedione as the organic polydentate ligands and activated without calcinations show high performance for the formation of aldehydes in the absence of the above additives in the reaction solution, as presented in **Table 7**<sup>72)</sup>. In palladium of this type, as described above, the polydentate ligands and/or their residues left in the catalysts not only prevent fine palladium metal particles from aggregating or sintering but also modify their surfaces<sup>52),72)</sup>. In other

words, the polydentate ligands and/or their residues in the sol-gel silica-supported palladium catalysts play a similar role to that of poisons added to the reaction solution.

The conversion of fatty acids, or long-chain aliphatic acids, to the corresponding alcohols is important in the oleochemical industry because fatty acids are main components of natural fats and oils, together with glycerin; also, higher alcohols with a long chain are in great demand as neutral surfactants<sup>73),74)</sup>. Historically, synthesis of such higher alcohols was performed by the hydrogenation of fatty acids or their methyl esters using copper chromite-based catalysts under high pressures (25-30 MPa) and high temperatures (250-300°C)<sup>75)</sup>, but the catalysts tended to deactivate and the lifetime was short because of such severe reaction conditions. Furthermore, to the extent that this type of the catalyst is used, when the fatty acids are unsaturated—containing carbon-carbon double (C=C) bonds while retaining C=C bonds—it is difficult to convert the unsaturated fatty acids to unsaturated alcohols, which are often more valuable than the corresponding saturated alcohols, because the C=C bonds are generally much more easily hydrogenated than the carboxyl and ester groups. Consequently, several catalysts which work under milder reaction conditions and which do not hydrogenate the

Table 8 Effect of Catalyst Preparation Method on Hydrogenation of Oleic Acid<sup>79),a)</sup>

Catalyst	Method of preparation	Reaction time [h]	Conversion [%]	Alcohol selectivity [%]	
				9-Octadecen-1-ol	Total
Ru-Sn-Al <sub>2</sub> O <sub>3</sub>	impregnation	16.5	62.4	67.0	84.3
Ru-Sn-Al <sub>2</sub> O <sub>3</sub>	coprecipitation	17.0	82.2	52.1	84.2
Ru-Sn-Al <sub>2</sub> O <sub>3</sub>	sol-gel	17.0	78.8	79.1	95.5
Ru-Sn-ZrO <sub>2</sub>	impregnation	21.5	65.1	22.4	44.5
Ru-Sn-ZrO <sub>2</sub>	sol-gel	20.0	70.3	13.1	33.4

a) Experimental conditions were as follows: The sol-gel catalysts were prepared using RuCl<sub>3</sub>·*n*H<sub>2</sub>O, SnCl<sub>4</sub>·*n*H<sub>2</sub>O, Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>, and Zr(OC<sub>3</sub>H<sub>7</sub>)<sub>4</sub> as raw materials and hexylene glycol as the solvent. The alumina and zirconia used as supports for impregnation catalyst also were prepared from the same raw materials in a similar manner with the same solvent. Impregnation of RuCl<sub>3</sub>·H<sub>2</sub>O and SnCl<sub>4</sub>·*n*H<sub>2</sub>O onto the support was carried out in the conventional way with ethanol as solvent. The coprecipitation catalyst was prepared from a precipitate deposited by adding ammonia to a solution containing RuCl<sub>3</sub>·*n*H<sub>2</sub>O, SnCl<sub>4</sub>·*n*H<sub>2</sub>O, and Al(OC<sub>3</sub>H<sub>7</sub>)<sub>3</sub>. Ruthenium metal loading was 2 wt% and the atomic ratio of Ru-Sn was about 1 : 2 in all cases. The catalysts were calcined at 400°C for 2 h and then activated in hydrogen at 400°C for 4 h. Reaction conditions: temp., 250°C; pressure, 5.6 MPa; oleic acid, 50 g; and catalyst, 6% by weight.

Table 9 Effect of Support of Ru-Sn Catalyst on Hydrogenation of Oleic Acid<sup>79),a)</sup>

Supports	Reaction time [h]	Conversion [%]	Alcohol selectivity [%]	
			9-Octadecen-1-ol	Total
Al <sub>2</sub> O <sub>3</sub>	17.0	78.8	79.1	95.5
SiO <sub>2</sub>	20.0	66.6	40.5	53.2
TiO <sub>2</sub>	19.0	54.2	18.4	36.7
ZrO <sub>2</sub>	20.0	70.3	13.1	33.4

a) All catalysts were prepared from alkoxides and RuCl<sub>3</sub>·*n*H<sub>2</sub>O using the sol-gel method with 2-methyl-2,4-pentanediol as the organic polydentate ligand. Ruthenium metal loading was 2 wt% and the atomic ratio of Ru : Sn was 1 : 2. Catalyst activation conditions are the same as those shown for Table 8. The catalysts were calcined at 400°C for 2 h and then activated in hydrogen at 400°C for 4 h.

Initial reaction mixture: oleic acid (50 g), catalyst (3 g).

Reaction conditions: temp., 250°C; pressure, 5.6 MPa; reaction time, 17 h.

Total: 9-octadecen-1-ol + stearyl alcohol.

C=C bonds were sought. Results show that the supported ruthenium/tin catalysts found are effective for conversion of fatty acids to corresponding alcohols under milder conditions (4.5 MPa at 270°C)<sup>76)~78)</sup>. Moreover, the alcohol yield and the rate of the C=C bond remaining unhydrogenated are much influenced by the catalyst preparation method and support<sup>79),80)</sup>. **Tables 8 and 9** show results for hydrogenation of oleic acid to 9-octadecen-1-ol (oleyl alcohol) with different ruthenium/tin catalysts prepared from identical raw materials using the sol-gel method with 2-methyl-2,4-pentanediol (hexylene glycol) as the organic polydentate ligand, coprecipitation and impregnation methods. The sol-gel ruthenium/tin/alumina catalyst shows the best performance for alcohol formation and C=C bond preservation. Actually, in this ruthenium/tin/alumina catalyst, the optimum atomic ratio of Sn/Ru was 2.

The catalysts, composed of ruthenium, tin, and alumina, are also effective for hydrogenation of other aliphatic acids, aromatic acids and their esters to the corresponding alcohols. Mostly, the sol-gel catalyst shows the highest or comparable activity and selectivity

for alcohol formation. For example, the sol-gel ruthenium/tin/alumina catalyst described above with the Sn/Ru ratio of 2 converts pentadecanedioic acid monomethylester to  $\omega$ -hydroxypentadecanedioic acid with selectivity of greater than 85% at 91% conversion, and stepwise  $\omega$ -hydroxypentadecanedioic acid to the corresponding diol in a high yield for prolonged hydrogenation<sup>81)</sup>. Furthermore, the catalyst can convert benzoic acid<sup>81)</sup>, dehydroabiatic acid<sup>81)</sup>, and ethyl phenylacetate<sup>82)</sup> to benzyl alcohol, dehydroabietyl alcohol, and 2-phenylethanol, respectively, in about 70%, 80%, and 90% yields.

#### 4. Conclusion

The size and specific surface area of metal oxide particles can be controlled using the sol-gel method with organic polydentate ligands. Thereby, the method can design the size of mesopores and might be useful for micropore design. Furthermore, the sol-gel method can control the structure of metal oxides because organic polydentate ligands can act as the structural regulator of

metal ions. The sol-gel method highly disperses the constituent particles of metal oxides to give homogeneous mixed oxides.

In the supported metal catalysts prepared using the sol-gel method with organic polydentate ligands, the ligands used tend to remain in the catalysts without calcinations and surround the metal particles to prevent them from aggregating, and to keep them in fine. Furthermore, the ligands play a role as a certain modifier of the metal particle surfaces and control the successive steps in reactions with sol-gel supported metal catalysts.

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## 要 旨

### 有機多座配位子を活用するゾルゲル法による固体触媒の設計と触媒性能

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有機多座配位子をゾルゲル過程で活用することによる優位性や効果を論じた。本ゾルゲル法による金属酸化物および複合金属酸化物の調製手順を示すと同時に、シリカやアルミナ、酸化鉄および数種の複合酸化物で本ゾルゲル法による金属酸化物粒子の設計すなわち比表面積、粒子径、細孔径および構造の制御を例示した。さらに、本ゾルゲル法、沈殿法および混練法で調製した複合酸化物に関し、構成粒子の分散性や組成の均質性を比較したところ、本ゾルゲル法による複合酸化物が最も分散性が良く均質であった。これを反映して、シリカ・アルミナでは本ゾルゲル法によるものが沈殿法および混練法によるものに比べ、固体酸量が多く、芳香族化合物のアルキル化反応でも優れていた。本ゾルゲル法により、燃焼触媒の担体として有用な耐熱性の高いアルミナやアルミナ複合酸化物も得ることができ、

実際にも、これらを担体とする白金およびパラジウム触媒はモデル排ガス浄化反応で高性能を示した。担持金属触媒では、本ゾルゲル法によるシリカ担持ルテニウムおよびパラジウム触媒はそれぞれ焼成することなく水素雰囲気下で活性化すると、ベンゼンからのシクロヘキセン合成および酸塩化物からのアルデヒド合成に高性能を発揮した。同様な手法で調製、処理したルテニウム・すず・アルミナ触媒は、炭素-炭素二重結合を保持したままで、不飽和脂肪酸を対応する不飽和アルコールへと変換した。さらに、本ゾルゲル法によるこのルテニウム・すず・アルミナ触媒は芳香族カルボン酸の対応するアルコールへの変換や両末端カルボン酸の対応するヒドロキシカルボン酸およびジオールへの変換にも優れていた。