Metalasiloxanes: New Structure Formation Methods and Catalytic Properties

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Abstract—This article is a review of present-day methods of the formation of the structure of various metalasiloxanes (MS's). Methods of designing the structure of catalytically active MS's are discussed. In the description of synthetic methods and catalytic properties, the MS's are divided into two groups, namely, individual and oligomeric MS's. The first section of the review is devoted to MS's with coordinatively unsaturated metal sites and to cagelike MS's. The methods of formation of MS-based catalytic surfaces are analyzed, and synthetic methods converting these surfaces into ordered inorganic catalytic systems are discussed. The second section of the review presents the methods of synthesis of MS oligomers, the ways of regulating the structure of these compounds, and the use of the MS's as the basic component of catalytic systems for petrochemical syntheses and halohydrocarbon conversion.

Metalasiloxanes (MS's) are organosilicon compounds whose structure has an RSi−O−M (M = metal atom) fragment. The synthesis and properties of these compounds are reported in a number of monographs [1−6] and reviews [7−13].

Synthetic methods suggested to date allow one to obtain both individual MS's (cyclic and cagelike) and oligomers. The latter are amorphous substances with a molecular mass of 3500−30 000.

Interest in MS's as catalytic systems stems from a number of circumstances. The existing synthetic procedures make it possible to introduce almost all metal atoms and various metal atom pairs into the siloxane chain. In most cases, the catalytic properties of MS's are governed by the nature of the metal whose atoms serve as catalytic sites. Therefore, MS's open up great opportunities to vary the catalytic properties of catalytic systems:

(1) The siloxane groups surrounding the metal atom allow the structure of the catalytic site to be formed in different ways.

(2) Owing to their solubility in organic solvents, MS's are usable as homogeneous catalysts.

(3) In heterogeneous catalysis, reactive groups at the silicon atoms ensure strong bonding between the catalyst and the inorganic support (silica or alumina). Recent studies have demonstrated that the siloxane matrix of MS's can serve as an inorganic support as well. Below, we will separately describe the catalytic properties of individual and oligomeric MS's.
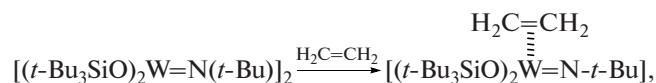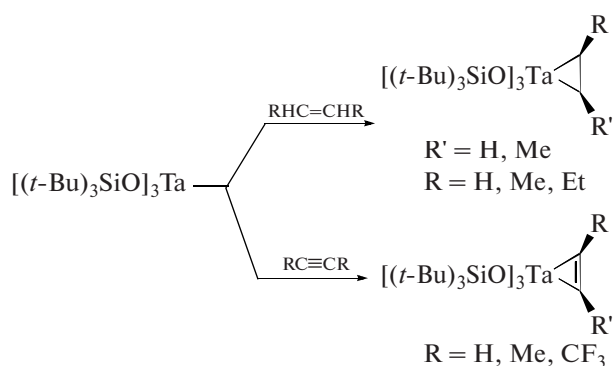
I. CATALYTIC PROPERTIES OF INDIVIDUAL METALASILOXANES

Comprehensive study of the catalytic properties of MS's has shown four promising ways of creating new catalytic systems.

## *Metalasiloxanes with Coordinatively Unsaturated Catalytic Sites*

In most cases, the variety of reactions that can be catalyzed by a given MS is determined by the catalytic properties of the metal in this MS. There have been many works devoted to the catalytic properties of MS's in olefin conversion.

Most present-day studies in this field are primarily oriented toward use of low-coordination-number complexes, whose synthesis requires bulky triorganosiloxy groups. For example, it was established that compounds of tricoordinated W(IV) and Ta(III) with triorganosiloxy groups can form complexes with olefins and alkynes [14, 15]:
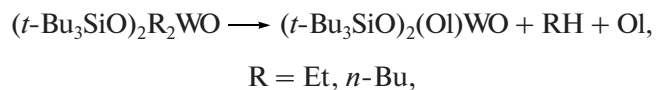
$$[(t\text{-}Bu_3SiO)_2W=N(t\text{-}Bu)]_2 \xrightarrow{H_2C=CH_2} [(t\text{-}Bu_3SiO)_2\overset{\parallel}{W}=N\text{-}t\text{-}Bu],$$

Of equal interest are the cases in which olefin generation is accompanied by catalyst conversion. For example, the thermolysis of alkylsiloxy derivatives of tungsten is accompanied by the disproportionation of alkyl groups at the W atom and by the simultaneous formation of olefin complexes:

$$(t\text{-}Bu_3SiO)_2R_2WO \longrightarrow (t\text{-}Bu_3SiO)_2(Ol)WO + RH + Ol,$$

$$R = Et, \ n\text{-}Bu,$$

where Ol = olefin.

The advantage of the bulky triorganosiloxy environment manifested itself most clearly in the study of the catalytic properties of Nb- and Ta-containing MS's. The widely known metathesis catalysts synthesized by R. Schrock (Nobel laureate in chemistry in 2005) contain these metals surrounded by t-butoxy groups, which impart stability to the carbenes resulting from these catalysts. Recent studies have demonstrated that this stabilization can be achieved via a simple synthetic route using t-butylsiloxy groups. Moreover, this route gives better results, allowing a larger number of bulky organic groups to be added to the catalytic site. The triorganosiloxy derivatives of Nb and Ta can add olefins to yield metallacarbenes [18] catalytically active in metathesis:

Similar properties are shown by organosiloxy-substituted titanium(III) hydride (activated by trimethylphosphine), which can form a coordination compound with ethylene [16],
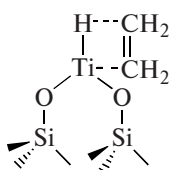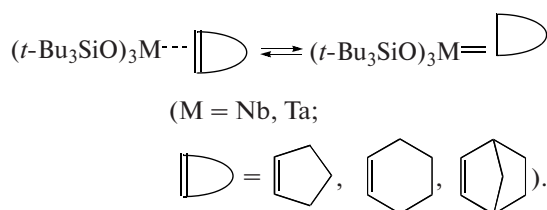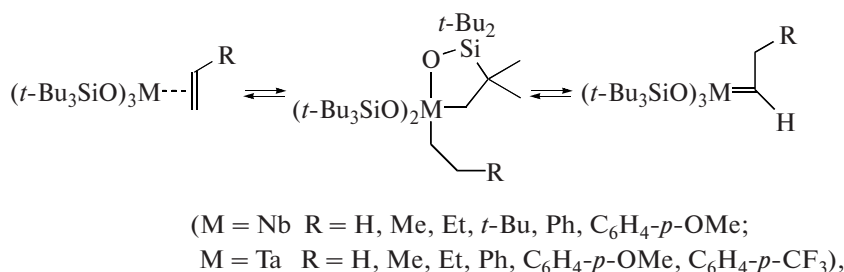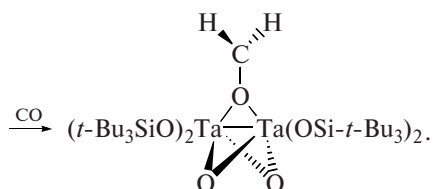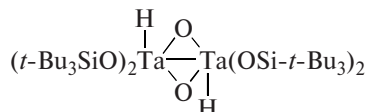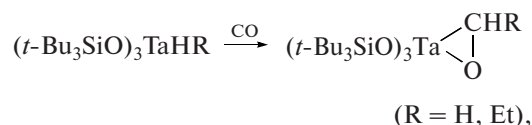
and catalyzes ethylene oligomerization into but-1-ene and higher ethylene oligomers.

(M = Nb R = H, Me, Et, t-Bu, Ph, C$_6$H$_4$-p-OMe;
M = Ta R = H, Me, Et, Ph, C$_6$H$_4$-p-OMe, C$_6$H$_4$-p-CF$_3$),

(M = Nb, Ta;

The great opportunities opened up by the bulky R$_3$SiO groups for the synthesis of some unreadily available MS's gave birth to the conception according to which these groups are alternatives to the Cp ligand because they have a similar geometry and similar electron donor properties [19].

Some MS-based catalytic systems are similar in properties to the Ziegler–Natta catalysts. For example, spirocyclic MS's containing V(IV) [20] and Cr(II) [21],

(L, L$_1$ = Py, THF)
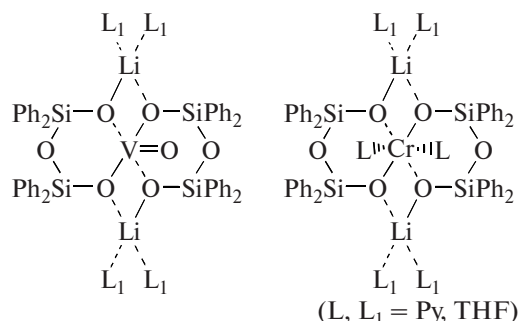
in combination with $AlMe_3$ catalyze ethylene and propylene polymerization.

Triorganosiloxy-substituted tantalum hydrides can add CO and are, therefore, candidate catalysts for the Fischer–Tropsch synthesis [22–25]:

$$(t\text{-}Bu_3SiO)_3TaHR \xrightarrow{\ CO\ } (t\text{-}Bu_3SiO)_3Ta\diagup\!\!\diagdown\!\!\!\!\!\!\!\!\!\!{\substack{CHR\\O}}$$

$$(R = H, Et),$$

$$\xrightarrow{\ CO\ } (t\text{-}Bu_3SiO)_2Ta\!-\!Ta(OSi\text{-}t\text{-}Bu_3)_2.$$

Platinum-family elements are commonly used as hydroformylation and hydrogenation catalysts. For example, the rhodium triorganosiloxy derivative $[Ph_3SiORh(CO)_2]_2$ is a more efficient hydroformylation catalyst than $[XORh(CO)_2]_2$ (X = Cl, PhO, $o\text{-}MeC_6H_4COO$) [26]:

$$CH_3CH{=}CH_2 \xrightarrow{\ CO,\ H_2,\ Cat/80°C\ } H_3CCH_2CH_2CHO.$$
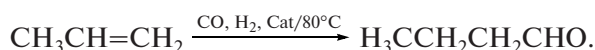
In hydrogenation reactions, the $RMOSiPh_3 \cdot 2L$ (M = Pt, Pd; R = Me, Et, Ph; L = cyclooctadiene) are more efficient than $R_2M \cdot 2L$ or H_2PtCl_6/SiO_2 [27]. The triorganosiloxy groups in these compounds enhance the stability of the catalyst in multiple runs.

Cross-coupling, a reaction widely used in organic chemistry, was also carried out with organosilicon reactants. The catalytic action of palladium complexes on organosilanolates yields the Si–O–Pd fragment as an intermediate [28]. A specific feature of this process is that, because of the low polarizability of the C–Si bond, the organosilicon component needs activation to stimulate the transfer of the organic group from Si to Pd. For this purpose, the silanol group SiOH is converted into the silanolate group SiOM. NaH, Me_3SiOK, $t\text{-}BuONa$, and some other compounds are used here as the activator. The organosilanolate reacts with the palladium complex to yield a palladium siloxane (**I**). Intramolecular rearrangement in **I** results in the transfer of the organic group from Si to Pd. This

eventually yields an oligodiorganosiloxane (**II**) and a palladium complex (**III**). The decomposition of the latter yields the initial PdL_2 compound and the cross-coupling product R–R' (**IV**) (Scheme 1).

Depending of the nature of the R and R' groups, the conversion in this process is 40–80% (between 20 and 50°C). The process is attractive because it makes the variety of cross-coupling "partners" wider by involving organosilicon compounds. In addition, the resulting by-products (oligodiorganosiloxanes) are environmentally friendly substances. This fact is significant for industrially promising processes.

Cagelike Metalasiloxanes

Among the numerous cagelike MS's described to date [13], there are compounds with a cubane structure in which one vertex of the siloxane cage is occupied by a catalytically active metal.
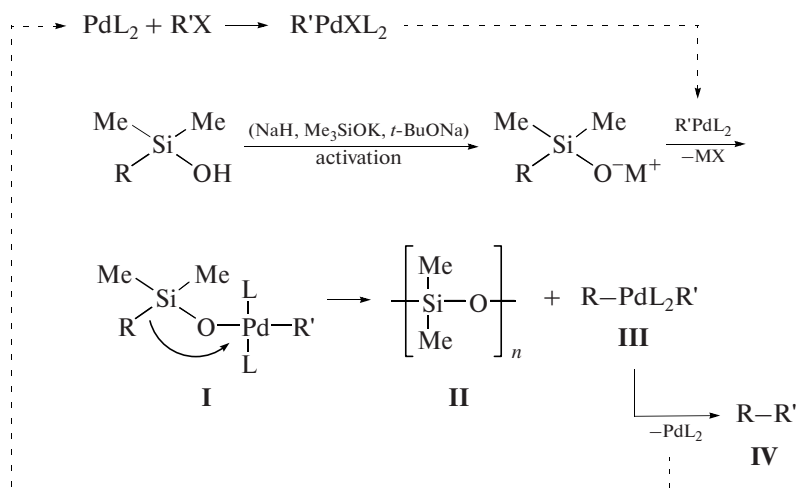
The synthesis of a wide variety of these compounds has been possible owing to the earlier syntheses of incompletely condensed cubic silsesquioxane structures that are not closed at one vertex and have Si–OH functional groups in its place [29–33]:
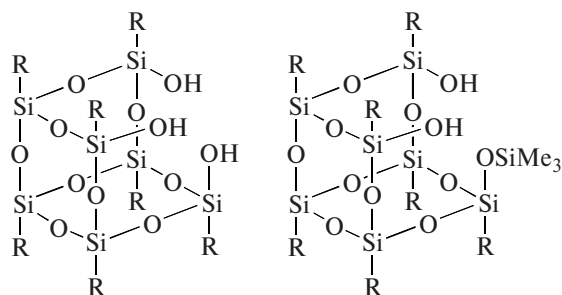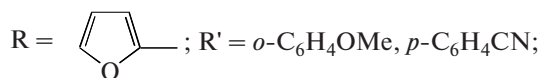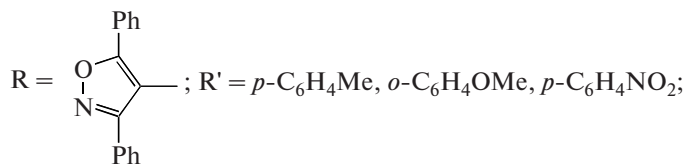

$$(R = cyclo\text{-}C_5H_9, cyclo\text{-}C_6H_{11}).$$

These compounds are exceptionally convenient precursors for metalation with various metals. Cubane structures containing Ge [33], Ti [33–35], Zr [36], Al [37, 38], Bi [39], Sn [40], V [34, 41], Cr [34], Os [42], Mo [43], or W [43] in a vertex of the polyhedron were obtained using similar procedures (Scheme 2).

The above dimers form in many cases. Cocrystallization can yield dimers simultaneously containing different metal atoms [34]. This result can also be obtained by directed synthesis [44]:

$PdL_2 + R'X \longrightarrow R'PdXL_2$

$$\text{Me}_2(R)Si\text{-OH} \xrightarrow[\text{activation}]{(\text{NaH, Me}_3\text{SiOK, }t\text{-BuONa})} \text{Me}_2(R)Si\text{-O}^-M^+ \xrightarrow[-MX]{R'PdL_2}$$

$$\mathbf{I} \longrightarrow \left[\text{Me}_2Si\text{-O} \right]_n + R\text{-}PdL_2R' \quad \mathbf{III}$$
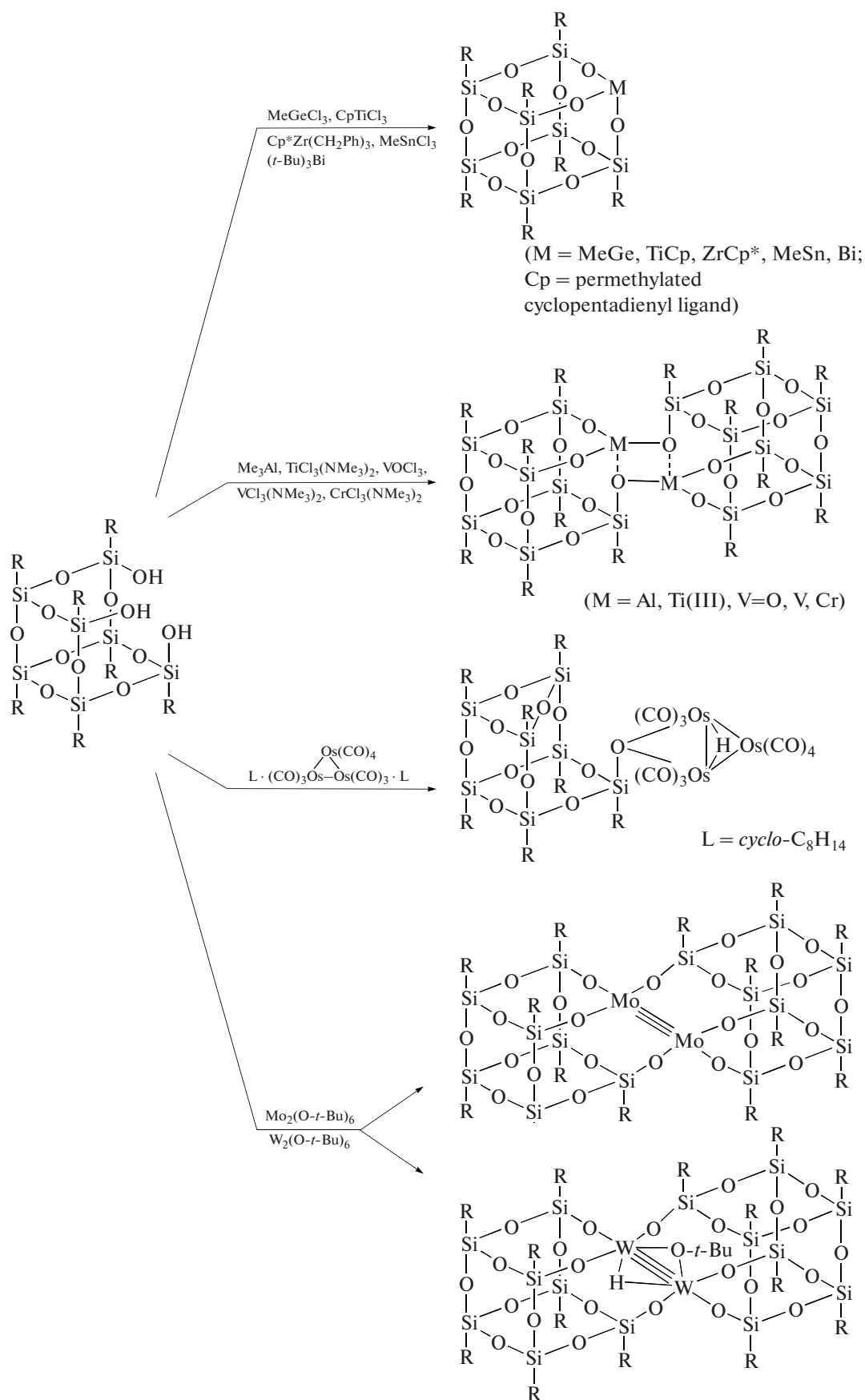
$$\mathbf{II}$$

$$\mathbf{III} \xrightarrow{-PdL_2} R\text{-}R' \quad \mathbf{IV}$$

Scheme 1.

$M = K, Na;$

$X = Br, I;$

$L = \text{dibenzylideneacetone } (PhCH=CH)_2CO;$

$R =$ (2-indolyl, N-Boc) ; $R' = Ph,$ $o\text{-}C_6H_4Me,$ $p\text{-}C_6H_4OMe,$ $p\text{-}C_6H_4CO_2C(CH_3)_2,$ $p\text{-}C_6H_4CF_3,$ $p\text{-}C_6H_4NO_2$

$(Boc = t\text{-butyloxycarbonyl});$

$R =$ (2-indolyl, N-Me) ; $R' = p\text{-}C_6H_4OMe,$ $o\text{-}C_6H_4NO_2,$ $p\text{-}C_6H_4CN,$ (2-thienyl) ;

$R =$ (3,5-diphenylisoxazol-4-yl) ; $R' = p\text{-}C_6H_4Me,$ $o\text{-}C_6H_4OMe,$ $p\text{-}C_6H_4NO_2;$

$R =$ (2-furyl) ; $R' = o\text{-}C_6H_4OMe,$ $p\text{-}C_6H_4CN;$

$R =$ (2-thienyl) ; $R' = p\text{-}C_6H_4OMe,$ $o\text{-}C_6H_4CN,$ $p\text{-}C_6H_4COOEt.$

Scheme 2.

(R = *cyclo*-C$_5$H$_9$)

(R = *cyclo*-C$_5$H$_9$)
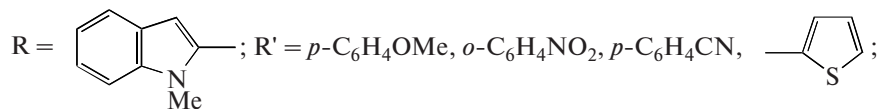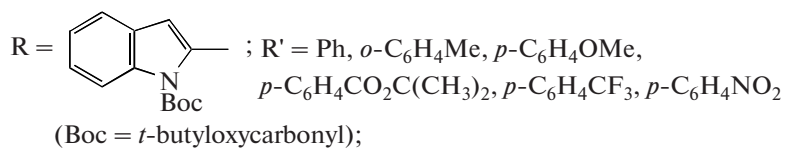
(N $\frown$ N = Me$_2$N $\frown$ NMe$_2$, $\bigcirc$; Ar = Ph, Me$_2$C$_6$H$_3$, C$_6$F$_5$, C$_6$H$_3$F$_2$).
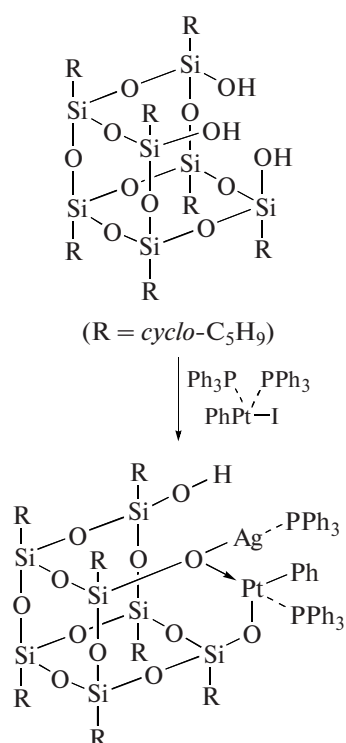
These compounds are molecular models of the silicate matrix activated by metal atoms, some of them being structurally similar to catalytically active zeolites, and have promising catalytic properties. Their additional advantage is that, although the metal atom at the vertex has a bulky environment as a siloxane cage, it is accessible to coordinating reactants. When some Si−OH groups stay in cage vertices, there can be further activation of the catalytic site owing to the enhanced polarization of the M−O fragment through the formation of hydrogen bonds between Si−OH and Si−O−M, as was demonstrated by the example of palladium MS's [45]:
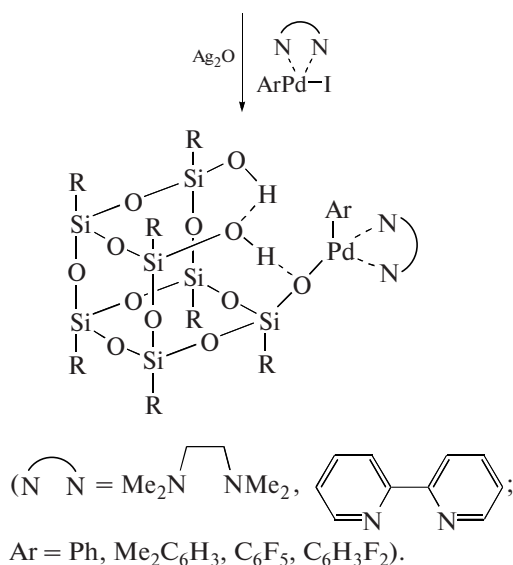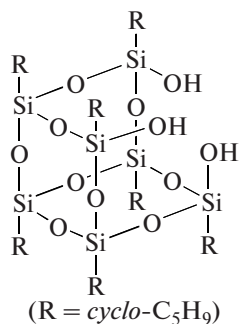
Several authors independently suggested that the organosiloxane cage could be used as a silicate matrix to replace conventional inorganic supports (primarily, silica gel) [46−50], and this idea proved fruitful, offering a number of obvious advantages. In the silsesquioxane cage (consisting of RSiO$_{1.5}$ units), catalytic sites containing atoms of various transition metals can be designed in an appropriate way and will not subsequently undergo the changes that would occur upon the conventional anchoring of the catalyst to an inorganic support. This allows the catalytic site to be structured purposefully during the synthesis.

More recent studies proved the fruitfulness of this idea. Titanium-containing MS's have been studied in detail. The polyhedral titanium(IV) silsesquioxane
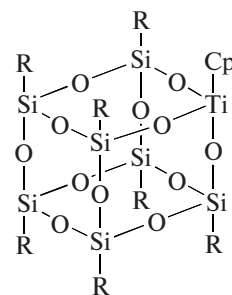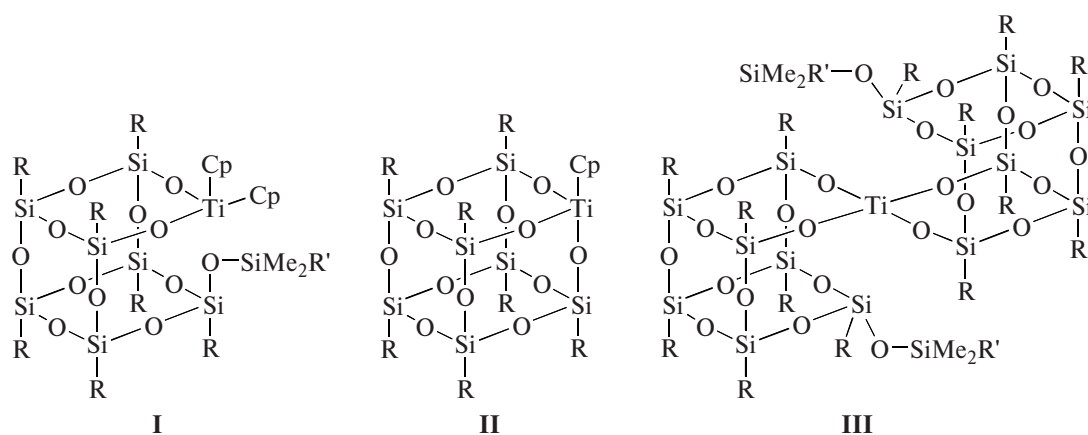
(R = *cyclo*-C$_5$H$_9$, *cyclo*-C$_6$H$_{11}$)

catalyzes olefin epoxidation with *t*-butyl peroxide [51, 52] or hydrogen peroxide [53] (both homogeneous and heterogeneous catalyses are possible).

There has been a study of compounds in which one edge of the cubic cage is open [54] (Scheme 3).

This structural feature allowed the factors in catalytic activity to be revealed. In the epoxidation of cyclohexene with *t*-butyl peroxide (50−60°C, 4 h), the product yield is 22% when the dangling branch at the silicon atom has an aliphatic group (compound **I**, R' = Me) and a higher yield of 28% is observed in the case of alkenyl groups (compound **I**, R' = Vin, All). The structure of the catalytic site itself has a still better

$(R = cyclo\text{-}C_5H_9, cyclo\text{-}C_6H_{11}; R' = Me, Vin, All)$.

Scheme 3.

defined influence on catalytic activity: as the number of metalasiloxane fragments at the Ti atom increases from 2 to 4 in the compound series **I–III**, the catalytic activity increases markedly. In the case of compound **III** with R' = alkenyl, the product yield under the same conditions is as high as 64% (the synergetic effect of the above two factors is observed).

The Zr- and Hf-containing MS dimers structurally similar to compounds **I–III** catalyze ethylene polymerization [55]:

$(M = Zr, Hf)$.
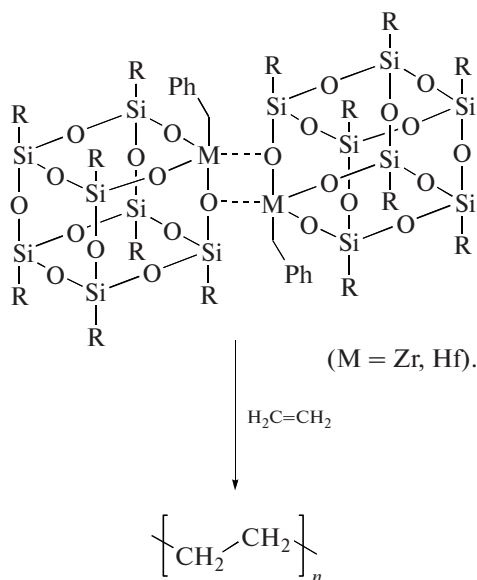
As distinct from the classical Ziegler–Natta catalysts, these systems are active without the AlR$_3$ cocatalyst. This difference is due to the fact that the metal atoms in these systems are inequivalent (according to X-ray crystallography) and the cyclic fragment M$_2$O$_2$ is polarized. The similar titanium compound is not dimerized and is inactive. The activity of the zirconium and hafnium compounds (in terms of the

amount of ethylene formed in a unit time) is comparatively low $((5-10) \times 10^3 \text{ g/h})$.

The asymmetry of the active site was enhanced by eliminating one benzyl group from the atom **M** via binding this group into the B(C$_6$F$_5$)$_3$ complex:


$(M = Zr, Hf)$
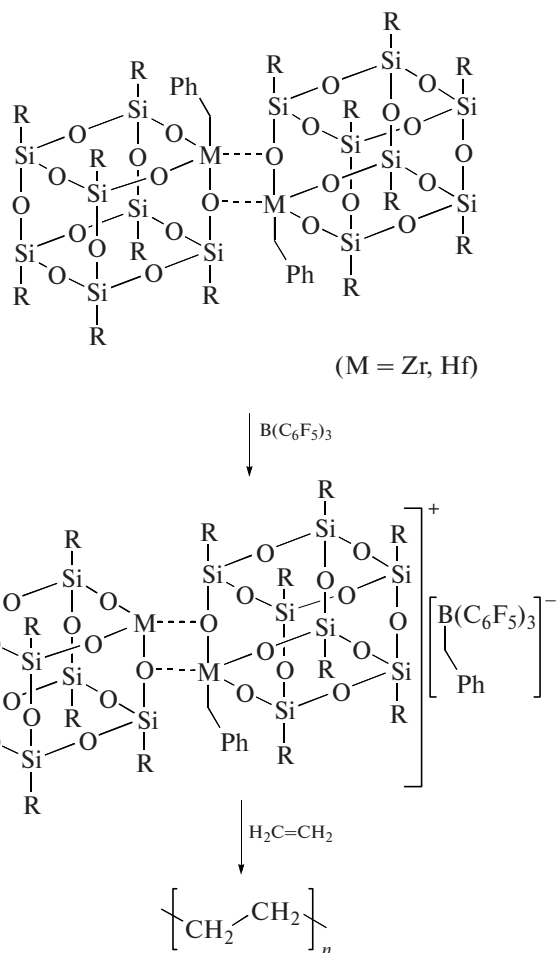
This increased the catalytic activity of the system to $(2-8) \times 10^6$ g/h.

It is noteworthy that the polydispersity index of the molecular mass distribution (M_w/M_n) of the resulting polyethylene is as low as 2.3–3.2, while the same parameter in the case of conventional catalyst is 7–11.

Other interesting catalysts are those in which the Ti atom is outside the cage and the siloxane polyhedron remains unchanged—another organization of the catalytic site. The compounds shown below are catalytically active in ethylene and hex-1-ene polymerization reactions [56, 57]:
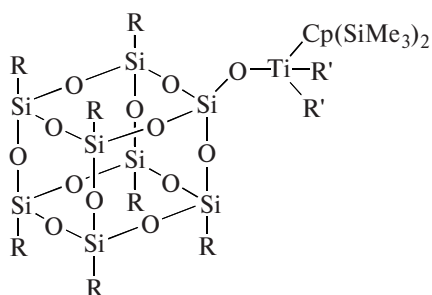
$R = cyclo\text{-}C_5H_9$
$R' = Me, CH_2Ph$

A
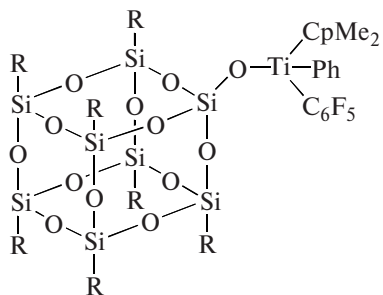
B

The compounds **A** are active in the presence of the $B(C_6F_5)_3$ cocatalyst, yielding polyethylene with $M_w = 260\,000$ and $M_w/M_n = 3.3$ (for hex-1-ene, $M_w = 29\,000$ and $M_w/M_n = 2.0$). Slight modification of compound **A** (introduction of a C_6F_5 group, compound **B**) obviates the need for the cocatalyst.

A distinct research area in MS chemistry is concerned with compounds in which metal atoms used in Ziegler cocatalysts (Ti, Mg, Al) are in a framework*

structure involving siloxane or metal oxide fragments [58, 59]:
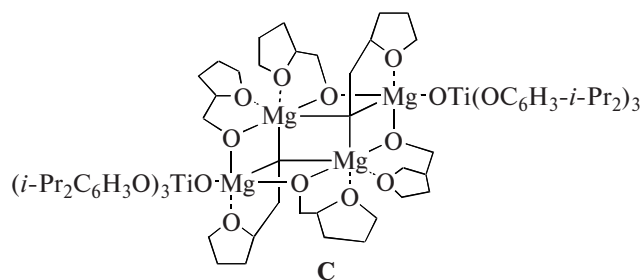
C
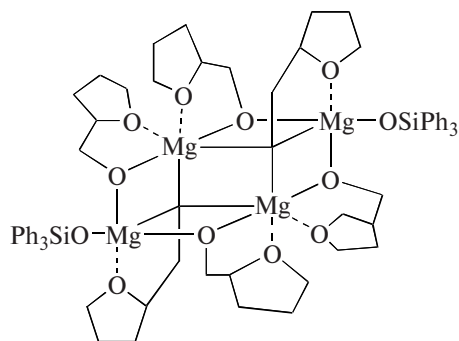
D
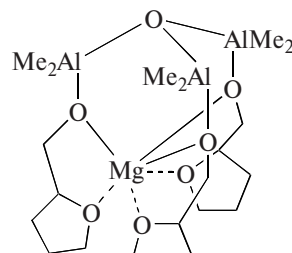
E

The catalytic system **E**–$TiCl_4$–$AlMe_3$ for ethylene polymerization is much more active that the conventional system $MgCl_2$–$TiCl_4$–$AlMe_3$ [60].

Compounds **B**, **C**, and **E** demonstrate the catalyst formation principle according to which different components of the catalytic system are combined in one molecule.

Metalasiloxanes Forming a Catalytic Surface on a Support

It was mentioned above that the siloxane matrix in polyhedral MS's with a cubic structure plays the role of an inorganic support. At the same time, the conventional technology of supporting a catalyst on an inorganic material turned out to be applicable to the MS catalysts as well.

Catalytic processes are very sensitive to the state of the surface of the catalytic system. The most efficient catalysis in oxidation processes on vanadium catalysts is observed when the VO_4 tetrahedra are isolated and are uniformly distributed on the support surface. However, the problem of surface structure control is a complicated one [61], and it is much more readily solvable by using polyhedral MS's. On being supported on silica gel and heat-treated at $250-450°C$ for 2 h, the isolated and coupled polyhedra of the V-containing MS's [41, 62]
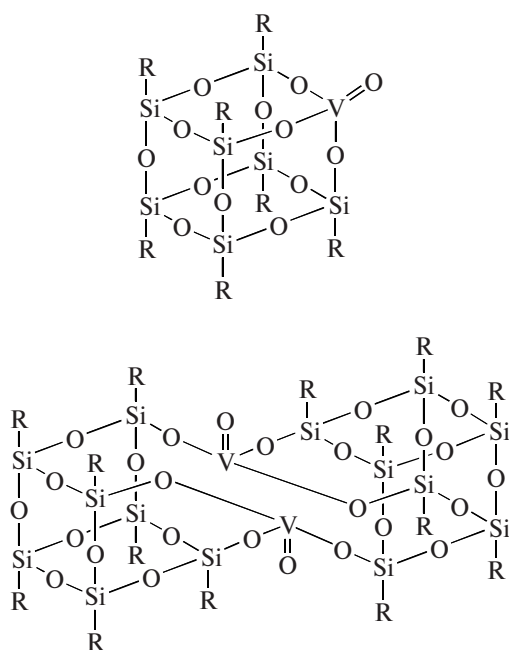
form a catalytic surface with regularly arranged catalytic sites:

Methane photooxidation over these catalysts,

$$CH_4 + O_2 \xrightarrow{h\nu,\ 200°C,\ Cat} \begin{matrix} H \\ \diagdown \\ C=O + H_2O \\ \diagup \\ H \end{matrix}$$
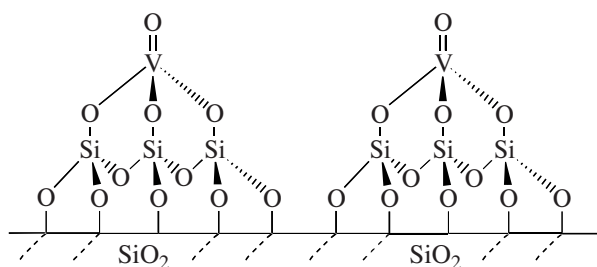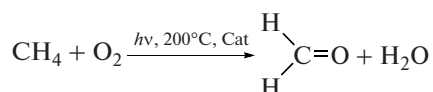
affords a two times higher conversion than the same process on the conventional V_2O_5/SiO_2 catalysts.

The V-containing MS catalyst is also used in ethylene polymerization in the presence of the Ziegler cocatalyst $AlMe_3$ [63] or $Al(CH_2SiMe_3)_3$ [64].

This process yields polyethylene with a molecular mass of 48 000 and a comparatively low polydispersity index of 2.3.

The introduction of a metal atom into the siloxane polyhedron markedly changes its catalytic properties: for example, the compound $(Ph_3SiO)_3V=O$, which is similar in composition to the above V-containing MS's, is catalytically inactive under the same conditions [63].

The Cr(VI)-containing catalyst

(R = *cyclo*-C_6H_{11})
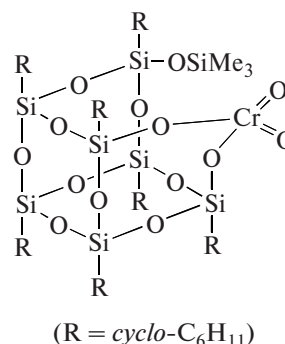
with the $AlMe_3$ cocatalyst affords polyethylene with $M_n = 61 400$, $M_w = 376 500$, and a polydispersity index of 6.13 [65]. The cagelike Cr-containing siloxane is substantially more stable and active than the compositionally similar compound $(Ph_3SiO)_2CrO_2$. Thus, the results obtained for the Cr- and V-containing catalysts indicate an enhanced activity and stability of the catalytic sites introduced into the siloxane polyhedron.

Polyethylene obtained over the Mg- and Ti-containing bimetallic MS [66]
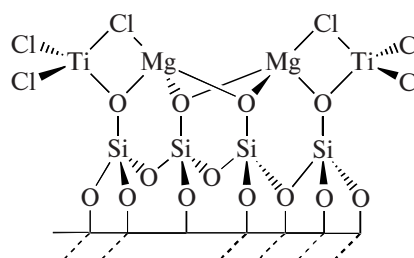
is characterized by $M_w = 140 000$ and $M_w/M_n = 5.5$.

Using siloxy derivatives of osmium, it is possible to immobilize triatomic Os cluster on the silica gel surface. These clusters efficiently catalyze the hydrogenation of unsaturated ketones $(130-170°C)$ [67] and the Fischer–Tropsch reaction [68].

For cubane-type organosiloxanes, there is an original method of catalytic surface formation in which the metal is not incorporated in the polyhedral struc-

ture. Combining methanolic solutions of $Pd(OAc)_2$ and the cagelike

$(R = (CH_2)_3NH_3^+Cl^-)$
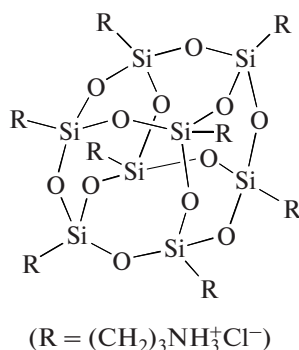
siloxane yields spherical aggregates of metallic palladium 70 nm in diameter with an exceptionally narrow size distribution [69]. The metal clusters result from the coordination of amino groups of the siloxane to palladium ions followed by the reduction of the latter to palladium metal. Here, the cagelike siloxane plays the role of a matrix organizing the Pd ions.

### Polyhedral MS's As Precursors of Inorganic Catalytic Systems with a Regular Structure

Another distinct area of MS chemistry is concerned with MS's that, upon heat treatment, yield catalytically active materials characterized by an ordered arrangement of a metal oxide in the silicate matrix.

The titanasiloxane [70]

$(R = i\text{-}Pr,$
$R' = 2,6\text{-}i\text{-}Pr_2C_6H_3NSiMe_3)$
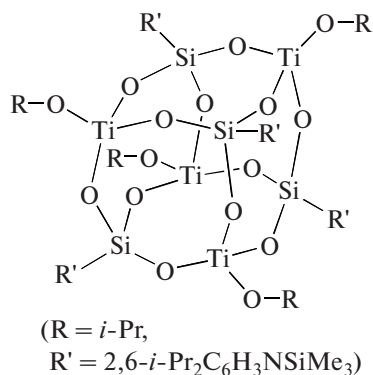
which contains four Ti atoms in its cubelike structure, is a homogeneous catalyst for cyclohexene oxidation with cumyl hydroperoxide (room temperature, 24 h, 15% conversion). A still more interesting result was obtained after thermal treatment of this compound at 600–800°C without an inorganic support. The resulting product has the same composition as the inorganic titanium silicate $TiO_2 \cdot 2SiO_2$, which has a highly ordered structure (according to X-ray diffraction data). Its catalytic activity (room temperature, 24 h, 11% conversion) is only slightly below the activity of the corresponding homogeneous catalyst.

A similar idea was effected by calcination of a 2 : 1 mixture of a polyhedral organosiloxane and a polyhedral iron-containing organosiloxane at 500°C for 4 h (the metal-free organosiloxane component was introduced to facilitate the formation of the SiO_2 matrix) [71]:
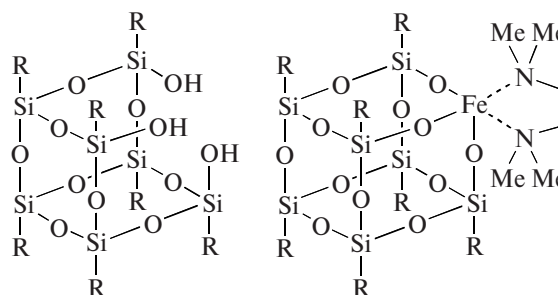
This yielded microporous materials with a highly developed surface (mean pore diameter of 6–7 Å) and a uniform distribution of iron oxide particles in the silicate matrix.

These catalysts afford 76% conversion and 95% selectivity in NH_3 oxidation into N_2 and H_2O (400°C). Their activity and selectivity can be raised to 84 and 97%, respectively, by pretreatment of the catalyst with hydrogen. These catalysts are also active in N_2O decomposition into N_2 and O_2 (500°C).

The formation of inorganic catalytic systems upon heating was also studied in the oxidative pyrolysis of Mg- and Al-containing cagelike MS's (500°C, 16 h, O_2 flow) [72]:

$(R = cyclo\text{-}C_5H_9)$
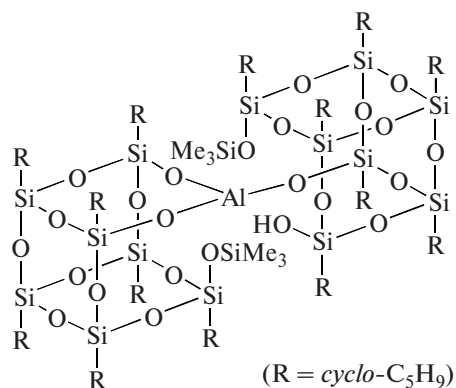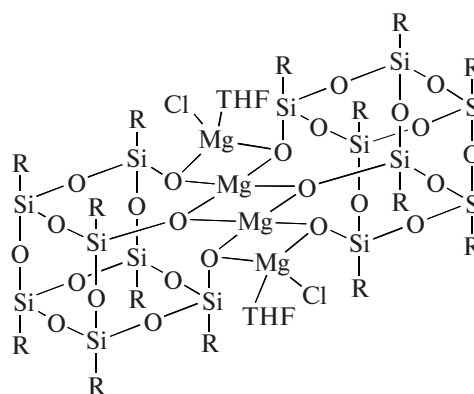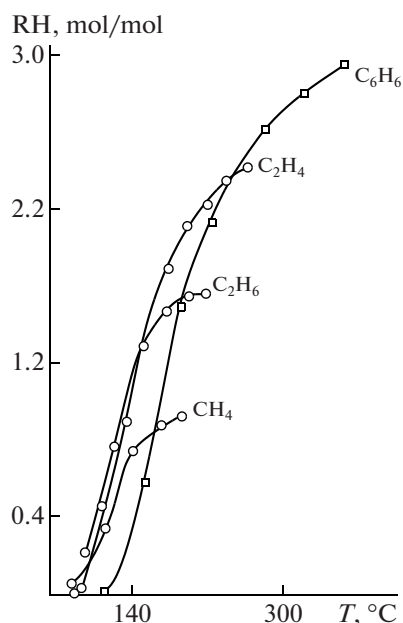
Fig. 1. Release of hydrocarbons from Al-MS upon heating (temperature rise rate of 2−3 K/min).

This process yields microporous metal silicates containing Mg−O−Si−O and Al−O−Si−O fragments with a pore diameter of 6 Å and a very narrow pore size distribution. By varying the calcination conditions, it is possible to regulate the pore diameter, but the pore diameter spread will remain very narrow.

The selective action of the Mg-containing catalyst is governed by the process temperature. At 200°C, the catalytic process converts butanol into butyraldehyde; at 300°C, the dominant process is butanol dehydration into but-1-ene. With the Al-containing catalyst, only dehydration was observed in this temperature range.

Actually, we have a new approach to the preparation of heterogeneous catalysts: polyhedral MS's are employed as precursors for regularly structured inorganic catalytic systems. Thus, in addition to being usable as synthetic organoelement catalysts, the MS's

can be heat-treated to obtain inorganic catalysts with an ordered arrangement of metal oxide particles in the silicate matrix [73].

To conclude this section, we will note that many of the studies address the use of the organosiloxane moiety as a kind of ligand. The nature of the metal incorporated in the siloxane chain determines the anticipated set of catalyzed reaction, and the organosiloxane environment enhances the stability and, in some cases, the activity of the catalyst since it allows low-coordination-number complexes to be obtained.

Extra opportunities in the design of catalytic systems have been opened up by cubelike MS nanostructures. Over 40 metals (including lanthanides) have been incorporated into the silsesquioxane framework to date, so there will likely be extensive studies of the properties of these catalysts.

Very interesting results have been obtained on the catalytic properties of oligomeric MS's (see the next section).

II. CATALYTIC PROPERTIES OF OLIGOMERIC METALASILOXANES

The studies of the catalytic properties of oligomeric MS's were inspired by the idea that MS's can be used as organics-surrounded analogues of inorganic metal silicates, and this idea initially determined the choice of catalytic reactions to be examined. These were primarily petrochemical processes (cracking and alkylation), which had conventionally been carried out using catalytic systems based on inorganic silicates.

Between 110 and 450°C, the oligomeric MS's gradually lose organic groups, approaching the composition of the corresponding inorganic metal silicates [74−79]. The elimination of organic groups takes place via the condensation of silanol and organic groups at silicon atoms (Scheme 4).

The highest conversion was observed for compounds having vinyl and phenyl groups (Fig. 1). The condensation products retain the specific features of

(M = Mg, Al, Ti, Mn, Cr;
R = Me, Et, Vin, Ph).
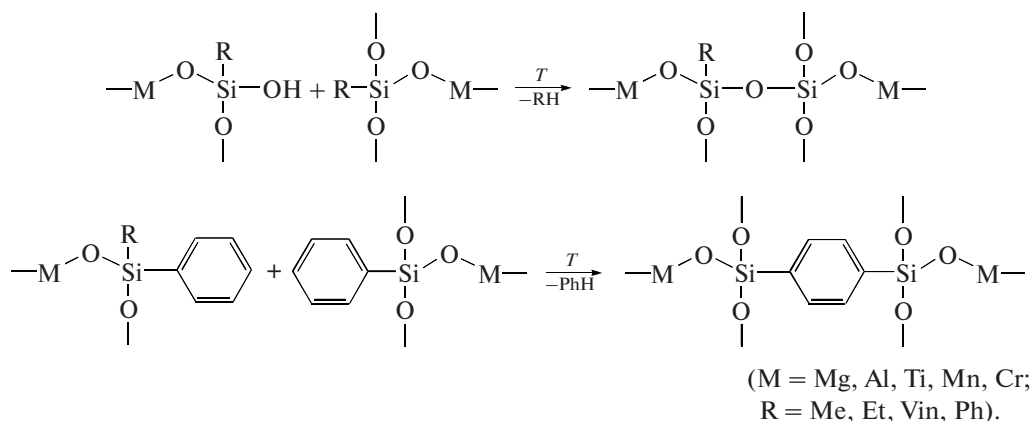
Scheme 4.

the cyclocondensed structure of the initial MS [80]. A similar catalyst formation conception applied to cage-like MS's was considered in the previous section of this review (see [70–73]); however, historically, this conception was initially suggested for, and tested on, oligomeric MS's.

The condensation products as catalysts defy competition with compositionally similar disordered metal silicates synthesized by conventional methods of inorganic chemistry. In some processes, MS's are more active and more selective than inorganic silicate catalysts, including in cracking [81–85], dehydration [86], and halogenation [87]:

$$C_2H_5OH \xrightarrow{T,\ Cat} H_2C{=}CH_2 + H_2O,$$

$$C_6H_6 + Cl_2 \xrightarrow{T,\ Cat} C_6H_{6-x}Cl_x \ (x = 1{-}3).$$

In cumene cracking on Ti-, Cr-, Zr-, and Al-containing MS's (410°C, pulsed feeding) under identical conditions, the cumene conversion is 17, 27, 48, and 68%, respectively.
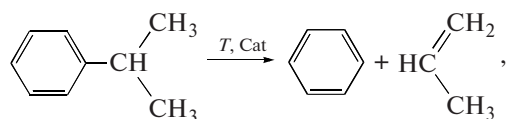
The compounds that have lost a small proportion of organic groups retain their solubility in organic solvents and are usable as homogeneous catalysts.

More recent studies have demonstrated that oligomeric MS's can catalyze reactions in which inorganic metal silicates are practically inactive. These reactions include the stereoselective oxidation of hydrocarbons (e.g., 1,4-dimethylcyclohexane) with hydrogen peroxide or perchloric acid in the presence of an oligoferrophenylsiloxane [88, 89]:
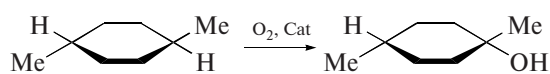

In these processes, the Fe-MS's show noticeable activity and high stability.

The high activity of the oligomeric MS's was utilized in industrially important processes of halohydrocarbon conversion. A specific feature of halohydrocarbons is that they have only a low capacity for coordination to most metal complexes. This sets limitations on the catalysts to be used in halohydrocarbon conversions under mild conditions. In addition, the high reactivity of halohydrocarbons at comparatively low temperatures (80–180°C) imposes heightened requirements upon the stability of the catalyst.

Most halohydrocarbon conversion processes proceed via a radical chain mechanism. In some cases, redox reactions involving variable-valence metals are efficient sources of radicals and play a significant role in the initiation of radical chains. This makes oligomeric MS's promising catalysts because the transition metal ions incorporated in the organosiloxane matrix can change their oxidation state (which is the key point in catalysis for this class of reactions) without leaving the siloxane backbone. We studied the catalytic properties of Cu-, Ni-, Co-, and Fe-containing MS's synthesized using a trifunctional organosilicon monomer with a phenyl group at the silicon atom [90] (Scheme 5).

These MS's have cyclocondensed fragments in their chains and are structurally rigid systems.

We studied the homogeneous catalytic allyl isomerization of dichlorobutenes in solution in the presence of Cu-containing MS's [91]:
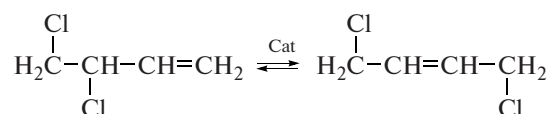
This process is not describable in terms of a simple kinetic equation: the kinetic curve clearly indicates an induction period, and a slowdown is observed at large extents of the reaction. This is due to the structural changes in the siloxane framework occurring at elevated temperatures. These changes eventually result in the formation of cross-linked structures and in the precipitation of the catalyst as a solid phase. These results suggest that it is necessary to pass to more stable
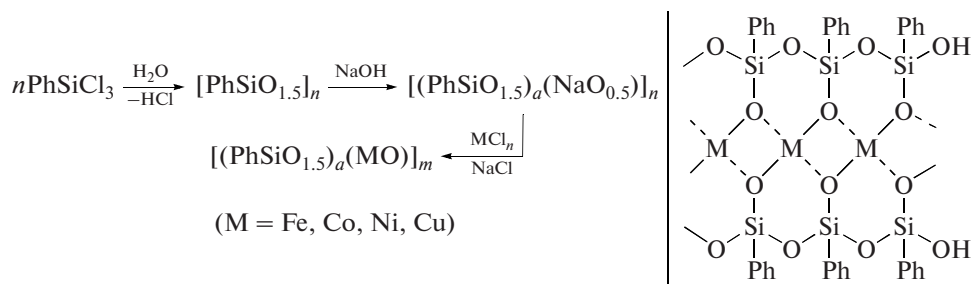
Scheme 5.

catalysts. Such catalysts can be obtained, for example, by MS immobilization on mineral supports [92, 93].

The anchoring of the catalyst to the surface of silica gel is due to the interaction of the residual hydroxyl groups of the oligo-MS with surface OH groups of the mineral support at elevated temperatures (100–180°C). The existence of this interaction was demonstrated by IR spectroscopy, which indicated a multifold decrease in the intensity of the absorption band of the free hydroxyls of silica. According to EXAFS data, the nearest neighbors of the metal ion remain the same as in the initial oligomer. A Cu ion is in the environment of four oxygen atoms, and the mean Cu–O distance is 1.96 Å, which is equal to the Cu–O distance in the crystalline copper-containing cagelike MS [94]. In the $d-d$ electron transition region of the diffuse reflectance spectra of the supported catalysts, there are bands at 710–730 nm, which are similar to the bands observed for the initial oligomers [90].

The catalytic properties of the immobilized MS's in dichlorobutene isomerization are very stable: after an MS is used six to ten times with fresh portions of reactants, its catalytic activity will be only slightly lower (by at most 10%) and 10^2–10^4 mol of the product will form per mole of the metal. Varying the nature of the metal (Cu, Ni, co, Fe) in oligo-MS's demonstrated that the Cu-containing catalysts are the most active. The apparent rate constant for Cu-MS exceeds the same parameter for an MS containing any other metal by a factor of 8 or more [93]. No synergism was revealed for the Cu,Co-MS and Cu,Al-MS bimetallic systems [91]. In all cases, the activity of the catalyst was almost entirely determined by its copper content. The substantially higher activity of Cu-MS (as compared to the oligo-MS's containing the other metals) provided additional support to the view that the copper ions undergo partial reduction during the catalytic reaction because copper is the most readily reducible among the metals examined. Although the Co- and Fe-containing MS's show a lower activity, they are of interest owing to their high selectivity. In the presence of these catalysts, 3,4-dichlorobut-1-ene isomerization does not yield *cis*-1,4-dichlorobut-2-ene [93, 95].
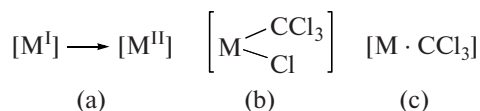
The catalytic properties of Cu-MS's are manifested in a variety of processes involving halohydrocarbons. For example, these MS's are effective catalysts for the exchange reactions between CCl_4 and alkanes:

$$CCl_4 + RH \xrightarrow{\text{Cat } 160-180°C} CHCl_3 + RCl.$$
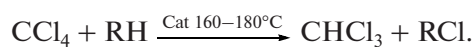
Cu-MS is inferior in catalytic activity to some other copper complexes. However, it has obvious advantages from the standpoint of stability: its activity in this process, like its activity in dichlorobutene isomerization, remains almost unchanged after the catalyst is used five times [96].

A comparison between the $CuCl_2 \cdot (DMF)_n$ and Cu-MS catalysts elucidated some mechanistic details of the exchange reaction owing to the fact that the copper ions in these catalysts have significantly different coordination spheres. The following three mechanisms could be suggested for the process a priori:

(a) classical radical chain mechanism involving variable-valence copper ions,

(b) mechanism involving the intermediate oxidative addition of CCl_4 to the metal site, and

(c) mechanism involving the stabilization of the $^{\bullet}CCl_3$ radical and the occurrence of subsequent reactions in the coordination sphere of copper:

$$[M^I] \longrightarrow [M^{II}] \qquad \left[M \begin{matrix} CCl_3 \\ Cl \end{matrix} \right] \qquad [M \cdot CCl_3]$$

$$\text{(a)} \qquad\qquad\qquad \text{(b)} \qquad\qquad \text{(c)}$$

It was possible to decide between these schemes by analyzing the results obtained for the simultaneous chlorination, on the above catalysts [96], of the following three pairs of hydrocarbons:

$$C_{10}H_{22}/cyclo\text{-}C_6H_{12}, \quad C_{10}H_{22}/C_6H_5CH_3,$$
$$cyclo\text{-}C_6H_{12}/C_6H_5CH_3$$
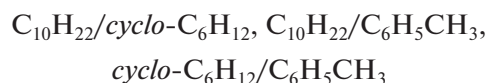
The product ratio in the competitive chlorination of two hydrocarbons was compared with data available from the literature on the relative activity of hydrogen atoms in the attack of the $^{\bullet}CCl_3$ radical on C–H bonds. it turned out that the ratio of the reactivities of two hydrocarbons is precisely equal to the ratio of the rates of hydrogen abstraction from the same substrates under the action of $^{\bullet}CCl_3$. Threfore, the process in the presence of the MS proceeds via the radical chain mechanism.

The above results suggest the following general scheme for the radical chain process [97, 98] (Scheme 6).
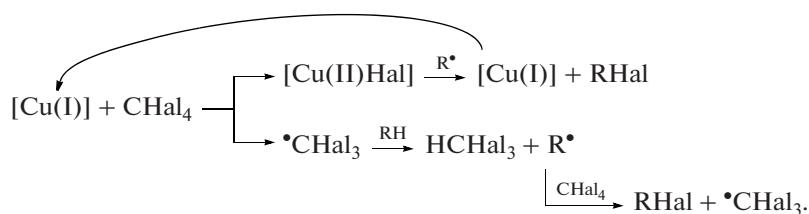
Scheme 6.

This mechanism is peculiar in that it combines the features of typical radical chain reactions with the features of a catalytic process. The products of this process result from reactions of radicals with valence-unsaturated molecules. At the same tome, the copper(I) complex participating in chain initiation is regenerated during the reaction and can, therefore, be viewed as a catalyst.

This scheme might to be self-contradictory: the copper atom in the initial Cu-MS catalyst is in the Cu(II) state, while the generation of radicals needs Cu(I). In order to clarify this point, the initial copper-containing organosiloxanes and the same compounds held at 180°C (last preparation step before using the catalyst) were treated with *ortho*-phenanthroline and the UV spectra of the resulting phenanthroline complexes [99] were compared. The spectral properties of the Cu(I) and Cu(II) complexes are radically different, making it possible to determine the oxidation state of the metal. The spectra of the heat-treated catalysts show an absorption band at 450 nm, which is characteristic of Cu(I) complexes. For the complexes that were not subjected to heat treatment, we observed only a band at 600 nm, which is characteristic of Cu(II) complexes. Therefore, part of the metal undergoes reduction upon heat treatment, ensuring the initiation of the radical chain process.

Obviously, the introduction of ligands stabilizing Cu(I) and, therefore, facilitating the Cu(II) $\longrightarrow$ Cu(I) transition in the catalytic system would be expected to enhance the catalytic activity. The introduction of a γ-aminopropyl group into the organic environment of silicon [90],

indeed favors the Cu(II) $\longrightarrow$ Cu(I) transition:
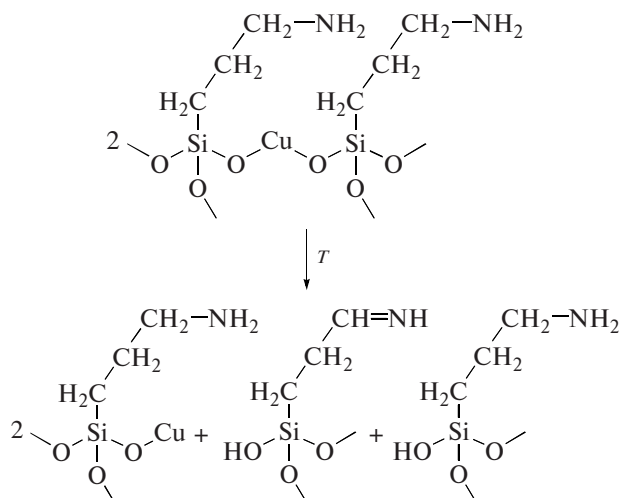
This makes the catalyst more active than the phenyl-containing Cu-MS's [97].

Another approach to the design of more active catalytic systems is based on the formation of catalytic sites containing a coordinatively unsaturated metal atom. Rigid-chain oligo-MS's obtained from trifunctional organosilicon monomers contain cyclocondensed fragments in which the metal atom is in a distorted tetrahedral environment of four oxygen atoms. This makes the metal atom difficult to access for reactants. Passing to oligo-MS's based on bifunctional monomers eliminates this obstacle. The following linear Cu-MS's were synthesized [100] (Scheme 7).

The MS's rearrange during their synthesis to yield compounds with a higher and lower metal contents. This provides a convenient opportunity to study compounds in which the Si/Cu ratio varies in a wide range.

The structures of the monophenyl- and diphenyl-containing Cu-MS's differ markedly in many parameters. As the metal content of a diphenyl-containing Cu-MS is decreased, unstable Cu sites with a coordination number of 2 appear in the system (according to EXAFS data), and this is not observed for the monophenyl derivatives. Therefore, the catalytic sites in these systems are readily accessible. This inference is in agreement with kinetic data: the specific activity of the linear Cu-MS's is almost 1.5 times higher than that of the cyclocondensed Cu-MS's [97].

(M = Cu, Ni)

Scheme 7.

Specific activity, mol RH/(mol Cu h)
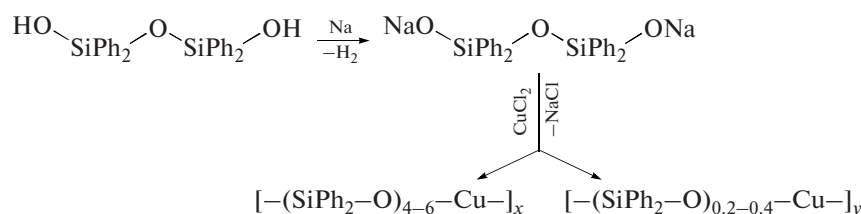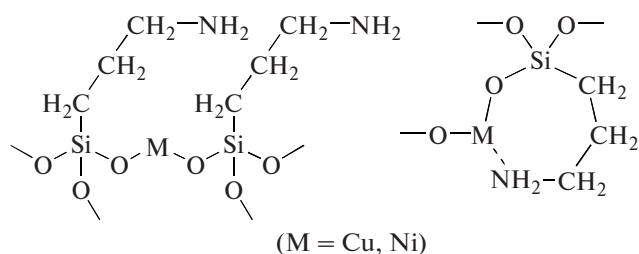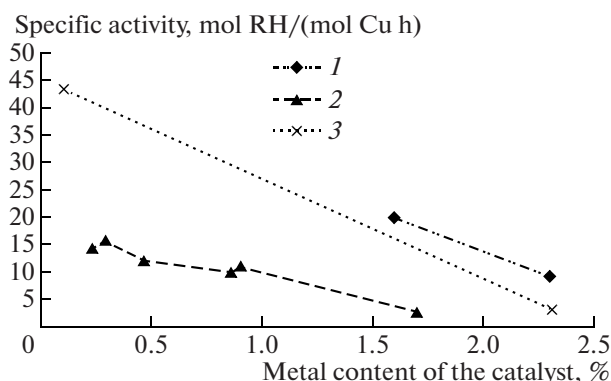
Fig. 2. Specific catalytic activity of Cu-MS as a function of its metal content for (*1*) dichloroolefin isomerization, (*2*) CCl_4 addition to olefins, and (*3*) exchange halogenation.

These results were compared with the results of quantum chemical calculations [101]. The coordination capacity of Cu was evaluated in terms of the energy of the bond between the metalasiloxane fragment and the H_2CO molecule as the model ligand. The bond energy for the linear copper siloxane turned out to be 3 times higher than the bond energy for the cagelike model. Thus, the results of quantum chemical modeling are fully consistent with the above explanation of the higher activity of the linear oligomeric catalysts.

The oligo-MS's provided solutions to some problems associated with bromoolefin conversion. It is a challenging preparative problem to develop convenient and efficient methods for direct bromination of alkanes. Solving this problem involves the following difficulties: bromination with molecular bromine results only in a low yield of the desired product, and is low-selective, and the other bromide synthesis methods include several steps and usually employ toxic chemicals.

Earlier, methods using polybromoalkanes (e.g., CBr_4) as brominating agents were suggested; however, they turned out to have low efficiency. For example, in the interaction of CBr_4 with alkanes and cycloalkanes in the presence of sodium hydroxide [102], the reaction time is up to 90 h and the product yield does not exceed 30−70%. The bromination of the same compounds using the catalytic complex $CBr_4 \cdot 2AlBr_3$ [103, 104] involves the following problems: the catalyst is very hygroscopic and, besides, should be added in large excess to the reaction mixture.

The bromination of alkanes (decane and dodecane), cycloalkanes (cyclohexane), and arylalkanes (toluene, xylene, and trimethylbenzene) with CBr_4 in the presence of Cu- and Ni-MS catalysts proceeds at a noticeable rate even at 100°C, and complete conversion takes place at higher temperatures of 130−150°C. The reaction is highly selective: the yield of monobromoalkanes is 98−100%, and the yield of arylalkanes

monobrominated in their side chain is above 90°C. It is interesting that, as distinct from the similar processes involving CCl_4, in which the resulting chloroform is practically inactive, the processes using carbon tetrabromide yield bromoform, which can act as a brominating agent. Because of this, the monobromide yield with respect to CBr_4 on MS catalysts formally exceeds 100% in some cases. Under optimum conditions, the process comes to completion in 0.5−1 h and the catalyst can easily be separated from the reaction mixture and can be reused [105].

The oligomeric MS's are efficient catalysts of the addition of polyhalomethanes to olefins:

$$CCl_4 + C_6H_{13}CH{=}CH_2 \xrightarrow{\text{Cat, 130°C}} C_6H_{13}CHClCH_2CCl_3.$$
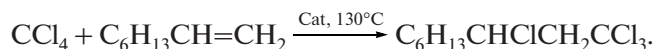
Monophenyl- and diphenyl-containing Cu-MS's are among the catalysts tested in this reaction. In the presence of these catalysts, the reaction takes place via a radical chain mechanism [99].

An analysis of the totality of data obtained for three processes (isomerization, exchange halogenation, and CCl_4 addition to olefins) revealed the following well-defined unconventional relationship: the specific activity of a catalyst increases as the metal content of the catalyst is decreased, irrespective of the type of catalyzed reaction (Fig. 2).

These results are in agreement with the results considered in the previous section of this review (see [61, 62, 65, 67]), where it was noted that the distributed arrangement of catalytic sites on the support surface raises the catalytic activity.

The fact that an appreciable part of the metal becomes excluded from the catalytic process as the metal content is increased was explained in terms of the structural features of the oligo-MS's. Magnetic measurements and spectroscopic studies of the initial MS's demonstrated that a considerable part of the metal is bound into interchain coordination clusters [106]. The metal ion seeks to fill its coordination sphere by involving the oxygen atoms of the nearest −Si−O−M− fragments:
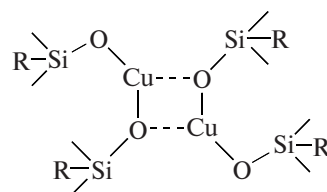
As a result, the metal ion is coordinatively saturated and unreadily accessible and its interaction with reactants is hampered. This problem was solved by replacing the phenyl group at the silicon atom by the nonyl group. Polycoppernonylsiloxanes were synthesized according to the following scheme [107]:

$$n C_9H_{19}SiO_{1.5} \xrightarrow[\text{H}_2\text{O}]{\text{NaOH}} [(C_9H_{19}SiO_{1.5})_a(NaO_{0.5})]_n$$

$$\xrightarrow[\text{NaCl}]{\text{CuCl}_2} [(C_9H_{19}SiO_{1.5})_a(CuO_{0.5})]_m.$$
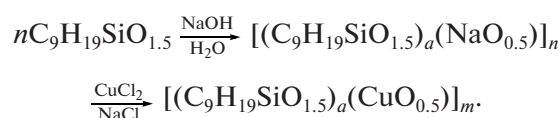
In the presence of bulky substituents, the formation of metal oxide coordination clusters is suppressed. The coordinative unsaturation of the metal atoms in the Cu-MS's with nonyl groups was confirmed by UV spectroscopy [107]. These results are in agreement with catalytic activity data: the activity of the nonyl-containing Cu-MS's in CCl$_4$ addition to oct-1-ene is two times higher than the activity of the copperphenylsiloxanes [108].

CONCLUSIONS

This brief review of the data available now on the catalytic properties of MS's demonstrates that these compounds are very promising for catalytic systems in chemical technology, petrochemistry, and preparative organic chemistry. The main advantages they offer are as follows:

—possibility of targeted design of catalytic sites with various structures, including sites with composition and properties gradually varying in fairly wide ranges;

—great prospects in the synthesis of bimetallic systems;

—possibility of combining the advantages of homogeneous and heterogeneous catalyses;

—possibility of preparation of promising catalytic systems with coordinatively unsaturated metal ions;

—availability of derivatives of a wide variety of metals.

There is a single, though serious, obstacle on the way of commercialization of MS catalysts. The individual monomeric and even oligomeric MS's are insufficiently stable under the severe conditions required by many reactions in industry. The destruction and cross-linking processes occurring at elevated temperatures can cause a progressive decline in catalytic activity (and this is indeed observed in some processes). This trouble can be eliminated by employing MS's chemically anchored to the surface of a mineral oxide support. In this case, the absence of molecular mobility prevents the interaction between MS fragments and stabilizes the system as a whole.

Another way of solving this problem is by creating heterogeneous catalytic systems with a reduced quantity of organic groups that is intermediate between the quantities of organic groups in MS's and metal silicates. These catalysts are far more stable than the initial MS's. Another, still only conceptual, approach to raising the catalytic potential of MS's is to pass to nanostructures. The immobilization of individual and oligomeric MS's on the surface of nanosized (10-nm and smaller) particles of oxide supports can afford catalysts having a very high active site concentration as compared to the conventional immobilized MS's. The presence of organic groups can favor the solubilization of the catalyst as a colloid, and the tight anchoring of the catalyst to the oxide surface is expected to make the catalyst stable for a long time. Obviously, these methods do not cover all the possible ways of developing efficient MS-based catalysts.

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