

Review

SYNTHESIS OF CATALYSTS BY THE FUNCTIONALIZATION OF SILICA AND ITS APPLICATIONS

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Abstract Hybrid organic-inorganic silica materials containing organic functional groups have been prepared by the reaction of activated silica with a silane coupling reagent such as N-(2-aminoethyl)3-aminopropyltrimethoxysilane. The hybrid silica was further modified by organic compounds having a bifunctional group. These modified hybrid silicas were used as catalysts for various nucleophilic reactions. And also, these were complexed with metallic ions for use as catalysts for oxygen oxidation of hydrocarbons.

Keywords Organic-inorganic hybrid polymer, Functionalized silica, Dioxygen oxidation of hydrocarbon, Reaction with functionalized silica

INTRODUCTION

There are many natural and artificial high polymers in the world. The various subsistence commodities are made up of these polymers. When synthesis of new-type polymers is attempted, two kinds of methods are used: One is the synthesis of a new-type monomer and the other is modification of the available polymers. The latter case can be a very effective and convenient strategy in order to obtain high performance polymers^[1].

A mild reaction condition is essential for the effective utilization of energy and resources in the field of organic synthesis. Many improved methods have been published^[2]. To achieve these purposes, organic polymers are used because organic chemical reactions show many diversifications for modifying the catalysts. When polymers are used as supported catalysts or organic reagents, the reactivity and selectivity of the supported catalysts or reagents may be significantly changed. It is recognized that such changes may originate from physical (viscous ions' diffusion effects, steric effects, site separation effects, local concentration, etc.) or chemical (microenvironmental interactions, coordination unsaturation, etc.) effects. When organic polymers are used as catalyst supports in the reaction with organic solvents, they swell and render the active centers less effective by the subsequent chain entanglement, neighboring group effects and solvation.

In contrast to organic polymers, inorganic supports are also used for their outstanding mechanical stability, in spite of the difficulties usually encountered with the modification by chemical reactions.

The synthesis and the usage of organic-inorganic hybrid polymers were performed as follows: We took silica gel and montmorillonite as the inorganic polymer and the modification was carried out by reacting them with silane coupling reagents in order to obtain the immobilized organic-

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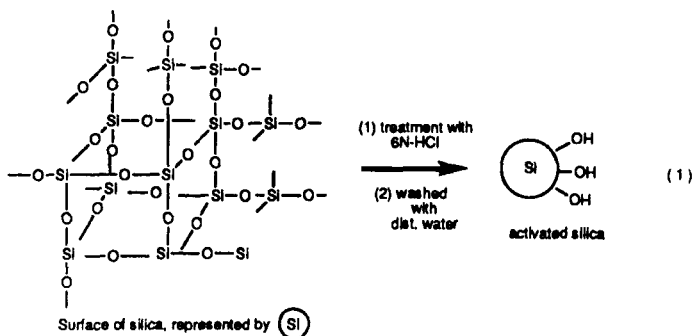
inorganic hybrid polymer. Then, organic reactions were investigated by the immobilized organic-inorganic hybrid polymer containing ammonium groups and the functionalized polymer was complexed with metal ions.

FUNCTIONALIZATION OF SILICA^[3] AND MONTMORILLONITE^[4]

Silica

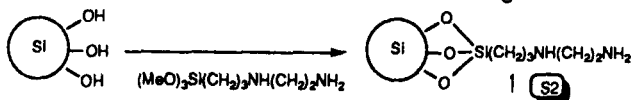
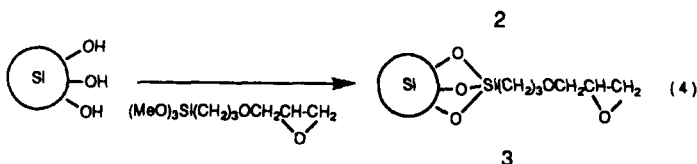
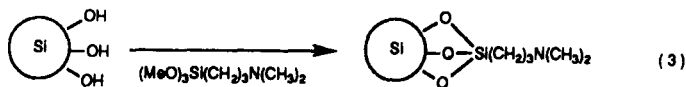
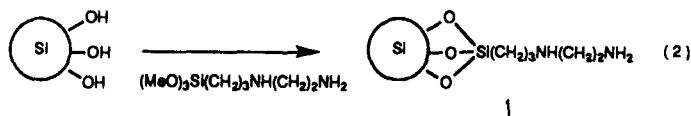
Activation of silica

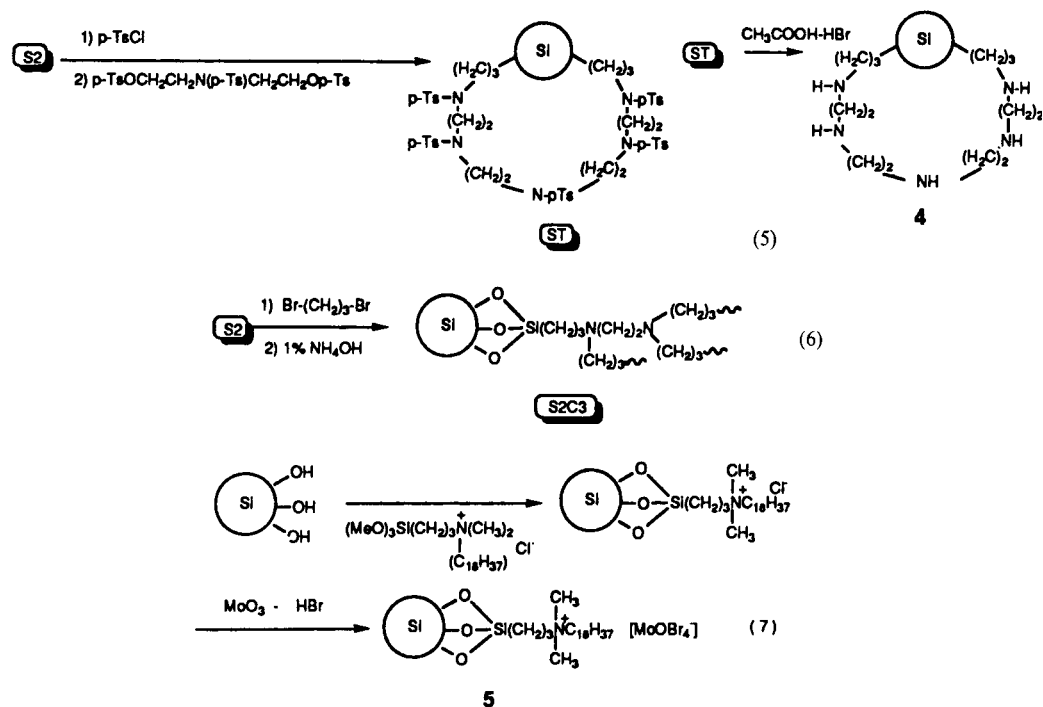
The Si—O—Si bond of the silica must be modified in order to obtain a species active enough to react with silane coupling reagents. Silica becomes more active by increasing the content of the Si—OH group. For the purpose of this conversion, reaction with dilute hydrochloric acid is the most effective method throughout this experiment. (eq. 1)



Reaction with silane coupling reagents

The activated silica reacted in alcohol with the following silane coupling reagents, such as N-(2-aminoethyl)-3-aminopropyltrimethoxy silane, N, N-dimethyl-3-aminopropyl trimethoxysilane, 3-glycidoxypropyltrimethoxysilane, octadecyldimethyl[3-(trimethoxy-silyl)propyl]ammonium chloride. The modified silica was further treated with other bi-functional compounds. Their reactions are shown in eqs. (2)~(6). These hybrid silicas reacted with silane coupling reagents in liquid phase. Metal complex was tethered on the functionalized silica, which is shown in Scheme 1 and Scheme 2.





Scheme 1

The catalytic activity of this functionalized and metal complexed silica was investigated for its use as an oxidation catalyst.

Montmorillonite

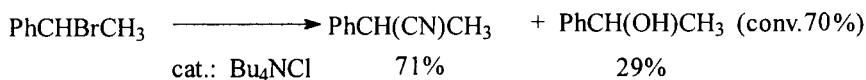
The functionalization was carried out by the same method described above. This is shown in Scheme 2.

Reaction with functionalized silica

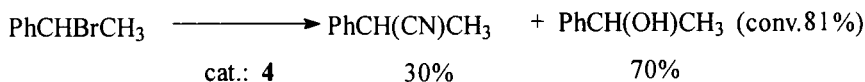
(1) The two-phase reactions between aqueous and organic solution were conducted in the presence of the modified silica obtained by the method mentioned above.

A. Cyanide displacement reaction

The nucleophilic substitution of 1-bromoethylbenzene was carried out in the presence of **4**, treated with methyl iodide or 10% hydrogen chloride. The results are shown in the following equations:

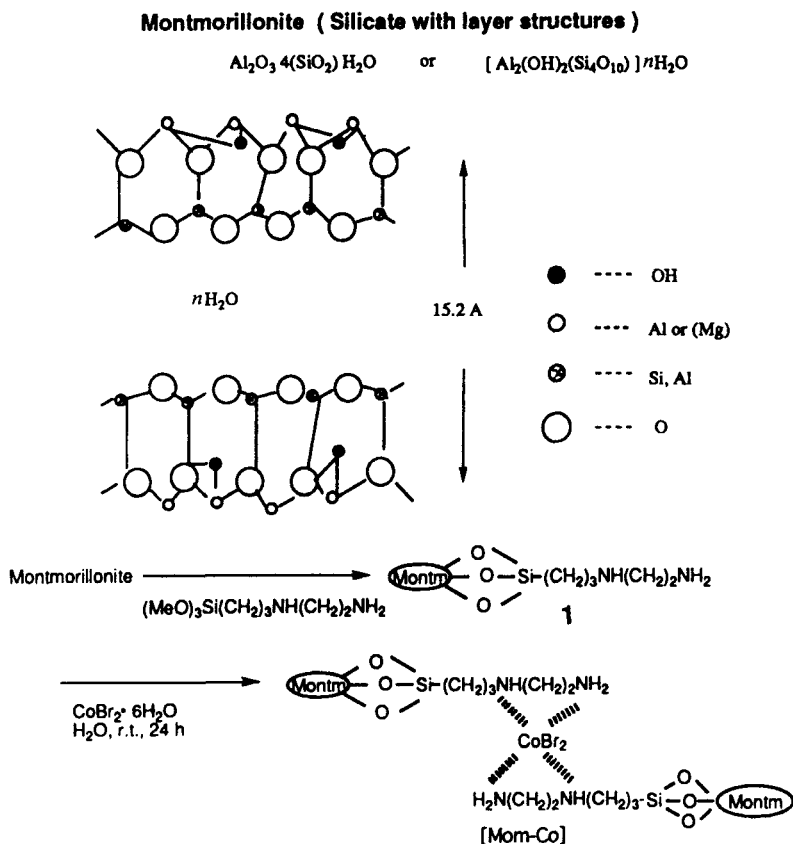


[reaction condition: benzene(2 mL) and water(2 mL), KCN(10 mL), room temp.]



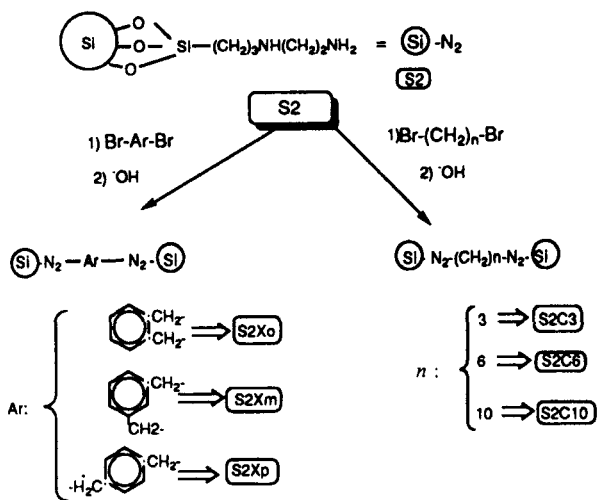
[reaction condition: benzene(2 mL) and water(2 mL), KCN(10 mL), room temp.]

In the reaction mentioned above, there was a difference between tetrabutylammonium chloride and **4**. As the ammonium group of **4** accounts for a few percent in a Si—O—Si group calculated from elemental analysis, the $(=\text{N}^+) \cdot (\text{CN}^-)$ group was not effective but the group of tetrabutylammonium chloride was active for cyanation. From these results, the further modified



Scheme 2

silica was used for the reaction. The functionalized silica (S2) was treated with phenylenedibromides or dibromoalkanes as shown in Scheme 3. The product yield of these hybrid silicas (S2Xp, S2C# S2C6, S2C10) obtained from the above treatment is showed in Table 1.



Scheme 3

B. Knoevenagel condensation

The following reaction was investigated in the presence of silica catalysts and the results are shown in Table 2.

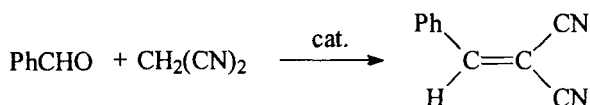


Table 1. Results of the substitution reaction by cyanide in the presence of the modified silica

Entry	Cat.	Product yield (%)
1	S2	78
2	S2Xp	93
3	S2C3	87
4	S2C6	93
5	S2C10	92

Reaction cond.: NaCN(10 mmol), $\text{C}_6\text{H}_5\text{CHBrCH}_3$ (2 mmol), H_2O (2 mL), toluene(1 mL), cat.(0.15g); Reaction temp.: 45 °C; Time: 24 h

Table 2. Knoevenagel condensation with silica catalysts

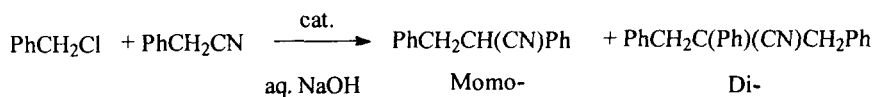
Catalyst	Yield (%)
SiO_2	0
S2	80
S2C3	97
S2C6	78
S2Xp	87

Conditions: cat. 0.10 g, PhCHO 1.5 mmol, $\text{H}_2\text{C}(\text{CN})_2$ 1.5 mmol, toluene 1 mL; Temp.: 40 °C; Time: 23 h

The formation of carbanion from malononitrile is the rate-determining step and the modification of the silica surface activates this reaction. Unmodified silica does not activate the reaction, but there is no difference in reactivity between (S2) and other modified silica. The reaction was generally carried out under the refluxing condition, so hydrolysis of nitrile groups followed by decarboxylation was observed. However, when this reaction proceeded under mild conditions, these phenomena would not be observed. Normally, after the hydrolysis, cinnamic acid is obtained, but in this case benzylidenemalononitrile will be obtained in good yield.

C. Alkylation of phenylacetonitrile (PAN) with benzyl chloride

In the presence of the modified silica catalysts, the following reaction was investigated in detail.



The results of the reaction catalyzed by the modified silicas are summarized in Table 3.

This reaction requires an alkali in high concentration. 70% aqueous sodium hydroxide solution was needed without the modified silica. With the use of modified silica the concentration of NaOH solution can be lowered to 50%. The relation between yield and reaction time is shown in Fig.1.

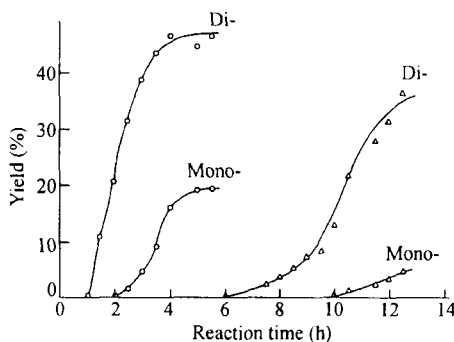
Induction periods were observed in each case. This period indicates the time necessary for the dissolution of catalysts in the reaction mixture. After the catalyst dissolved, the reaction proceeded. In the case of 33% NaOH, the yield of di-benzylated compound was about 65%. But 50% NaOH showed optimal results, as shown in Table 4.

Table 3. Benzylation of PAN with benzyl chloride

Entry	Cat.	Reaction time (h)	T (°C)	Yield (%)		
				PAN	Mono-	Di-
1	S2C3	7	50			95
2	S2C6	7	50			95
3	S2C10	7	50	100	0	0
4	S2C10	19	55			96
5	S2Xo	7	50	50		50
6	S2Xm	7	50	23.5		76.5
7	S2Xp	7	50	92.5		7.5
8	S2Xp	19	55			95

Reaction condition: benzyl chloride (6 mmol), PAN (3 mmol), toluene (1 mL) in the presence of 50% NaOH

After the completion of reaction, toluene (10 mL) was added, followed by GC analysis.

**Fig.1** Benzylation of PAN in the following silica catalyst

○ S2C3, △ S2

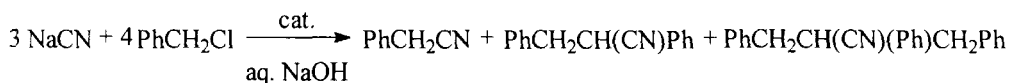
Table 4. Effect of alkali concentration (S2C10)

Entry	NaOH (%)	Reaction time (h)	T (°C)	Yield (%)		
				PAN	Mono-	Di-
1	11	23	60	98	2	0
2	20	23	60	84	4.8	31
3	33	12	68	25.6	8.3	65.3
4	50	19	56			96

S2C3 and S2C6 were effective for the reaction. In the case of S2C10, S2Xo, S2Xm and S2Xp, the reaction was very slow. This difference came from the solubility of the functionalized silica in the alkali medium.

D. One-pot synthesis of benzylated PAN in the presence of sodium cyanide

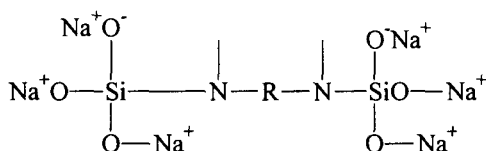
In the presence of the modified silica catalyst, the following nucleophilic reaction was also carried out:



In the reaction mentioned above, PhCH_2Cl is changed to PhCH_2CN at first by the reaction with CN^- , and then PAN was alkylated by benzyl chloride. In 50% NaOH solution, only di-alkylated compound, α, α -dibenzylphenylacetone nitrile, was obtained at 68% yield with 48 h reaction time period. Also, in this case, after the catalyst dissolved in alkali solution, the benzylation started. From these observations, the catalysts were effective for the reaction after they

were dissolved in alkali solution in this system.

Therefore, the catalysts must have the structure depicted in Scheme 4. Such a structure is analogous to that of a surface active reagent, and therefore it behaves like a surface active reagent. When the functionalized silicas were dissolved in an alkaline medium, the difference of the bi-functional compound was observed. The solubility depends on the R group in Scheme 4. The phenylene group and the long methylene group showed such strong hydrophobicity that it was relatively difficult to dissolve the silica in the alkaline medium.



Scheme 4

E. Recycling of catalyst in the alkylation of PAN with α -phenylethyl bromide

The reaction also proceeded well in this case. For this reaction, recycling of the functionalized silica was investigated, and the results for catalyst S2C3 are shown in Table 5. Repeated runs gave relatively good yields. The catalyst behaves actively in the dissolved state.

Table 5. Recycling of catalyst in the alkylation of PAN

Reaction	Cycle no.	Yield (%)
PhCH ₂ CN+PhCHBrCH ₃	1	85
→ PhCHCH ₃ CHCNPh	2	80
	3	78

(2) Oxidation by *t*-BuOOH in the presence of Br₄MoO⁻ immobilized on the modified silica^[6]

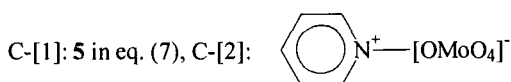
The selective oxidation of borneol, isoborneol and menthols by *t*-BuOOH in the presence of Br₄MoO⁻ was studied and the difference in reactivity between the inorganic polymer and the organic polymer was compared. We observed that the selective oxidation proceeded in the less hindered side. The results of the oxidation of a mixture of borneol and isoboreol (1:1 mol ratio) are summarized in Table 6.

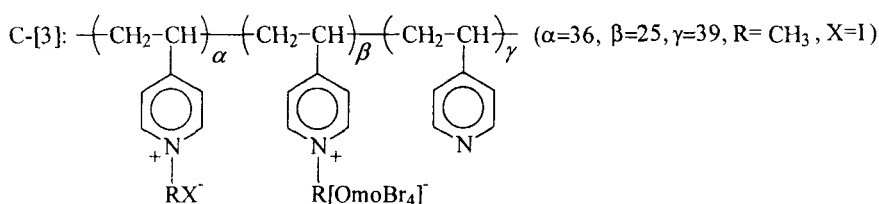
Table 6. Oxidation of isoborneol and borneol (1:1) mixture

Catalyst ^{a)}	Yield of camphor (%)	Reactive ratio
		Camphor from isoborneol (%) Camphor from borneol (%)
C-[1]	90	83/17
C-[2]	91	73/27
C-[3]	83	57/43

Substrate 3 mmol, *t*-BuOOH 1 mmol, catalyst Mo eq. 0.02 mmol, benzene 7 mL, *T* 60 °C

a) C-[1], [2] and [3] in Tables 6~8, are shown as follows:





The reactivities of pyridinium tetrabromooxomolybdate and the functionalized silica immobilized tetrabromooxomolybdate are similar, but they are somewhat different from that of poly-*p*-vinylpyridine. The active sites of the silica-immobilized catalyst are isolated on the silica surface, whereas there can be mutual interactions of active sites on the organic polymer. This is the reason why the organic polymer is more flexible in organic solvent than the silica polymer. Moreover, the swelling capacity of the polymer is larger than that of the functionalized silica polymer. This difference may be responsible for the selective oxidation.

The results of oxidation of a mixture of menthols are shown in Table 7.

Table 7. Selective oxidation of menthols

Catalyst	Yield of menthone (%)	Reactivity ratio		
		Isomenthone	Menthone	Neomenthone
C-[1]	54	21	35	44(%)
C-[2]	98	16	27	57(%)

Substrate 3 mmol (isomenthol : menthol : neomenthol = 1:1:1), *t*-BuOOH 3 mmol, *n*-decane 1 mmol, catalyst 0.16 g, benzene 7 mL, *T* 60 °C, time 24 h

This also shows similar reactivities for pyridinium tetrabromooxomolybdate and the silica-immobilized catalyst. However, we have observed that the oxidation by poly-*p*-vinylpyridinium tetrabromooxomolybdate showed low conversion and no selectivity (The yield of menthone was 28%, and the yield of isomenthone was 23%)^[6]. This result comes from the same reason suggested above for the oxidation of borneol and isoborneol. From the facts described above, we may conclude that silica is a suitable carrier for the immobilization of Br₄MoO⁻. The recycling reaction by the silica-immobilized Br₄MoO⁻ are shown in Table 8.

Table 8. Repeated use of immobilized catalyst for the oxidation of borneol

Catalyst	1st Run		2nd Run	
	Yield of camphor (%)	Oxid. ^{a)} Select. (%)	Yield of camphor (%)	Oxid. ^{a)} Select. (%)
C-[1]	89	89	33	85
C-[2] ^{b)}	24	92	17	85

Substrate 3 mmol, *t*-BuOOH 3 mmol, benzene 7 mmol, reaction temp. 60 °C, reaction time 24 h, yield were determined by GC

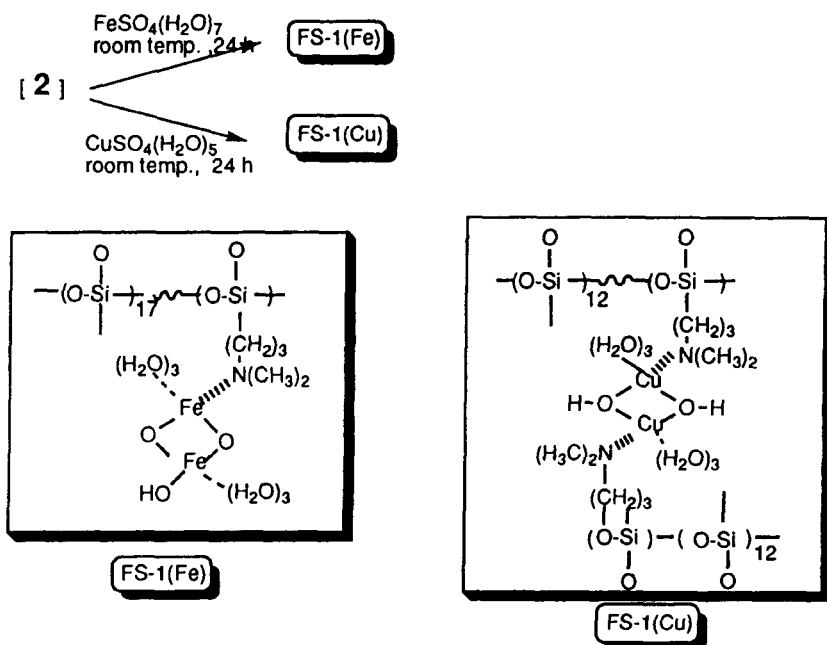
a) The mols of *t*-BuOOH for alcohol oxidation divided by the mols of *t*-BuOOH decomposed, expressed as a percent; b) R = H, X = TsO

The activity of the catalyst decreased on reuse but its selectivity was not changed. The reduction of the activity was due to the scission of the Mo-Br and the formation of Mo-OH bond, which was proved by IR spectrum. The reused catalyst was reactivated through treatment with hydrogen bromide solution. This modified silica was an effective catalyst for the oxidation, because the behavior of catalyst C-[1] was different from the case of the organic polymer (e.g. polystyrene and polyvinylpyridine). This difference is due to the following reason: The silica as the main chain was stable for oxidation in this condition, and the appropriate balance between the

hydrophilic and hydrophobic characters of organic groups in the functionalized silica treated with a silane coupling reagent resulted in effectiveness in the two phase reaction.

(3) Dioxygen-oxidation of hydrocarbons by metal complexed modified silica^[7]

Recently, the study of the oxygen oxidation of hydrocarbons has become of interest. Barton reported the oxidation of hydrocarbons in pyridine with some acetic acid in the presence of iron powder, hydrogen sulfide or zinc powder and oxygen. He named this reaction the Gif system. In this reaction, iron, pyridine and acetic acid formed a complex which was active for the oxidation^[8]. We have synthesized the metal complex from the functionalized silica by the following synthetic route (Scheme 5).



Scheme 5 Reactions of the functionalized silica with CuSO_4 and FeSO_4 and plausible structure of the products

The structures of iron complex (FS-1(Fe)) and copper complex (FS-1(Cu)) were deduced from elemental analysis^[9]. The results of the oxygen oxidation of cyclohexane are summarized in Table 9. Other metal complexes (Co, Mn, Ni) were not as effective as Fe and Cu and the yield of cyclohexanone was lower than those of Fe, Cu. The stability of the complex may be an important factor.

Their reactivity is in the order of: $\text{Cu} > \text{Fe} > \text{Mn} \sim \text{Ni} \sim \text{Co}$ ^[7]. The stability constants for complex formation of metal ions with ethylenediamine diacetate as a ligand are known^[10]. By using these constants and by using an ion with a mean value of Fe^{2+} and Fe^{3+} , Cu(II) might form the most stable complex with FS-1 as compared with other metals. When a stable metal complex reacts with dioxygen, a new reactive metal-oxygen complex is produced and acts as an oxidizing catalyst. The main product obtained from the oxidation of cyclohexane by the present method is cyclohexanol. In contrast, Barton and coworkers obtained cyclohexanone as the main product. This suggests that the mechanisms of the oxidations by the two reactions are different, because our reaction was carried out in the presence of the modified silica.

Oxidation of the methylcyclohexane was carried out using the method described previously^[4]. The reaction products were analyzed by HPGC. The results showed that abstraction of hydrogen

from methenyl and methylene groups as well as from the methyl group by the hydroxyl radical does occur. However, open chain compounds were not observed. The results are summarized in Table 10.

Table 9. Oxidation of cyclohexane and dioxygen in the presence of metal-complexed functionalized silica (FS-1(Fe) and FS-1(Cu))

Run	Cyclo-hexane (g; mol)	Metal inFS-1 ^{a)} metal atom $\times 10^3$	Zn Powder (g; mmol)	AcOH (g; mmol)	React. time (h)	Yield(%) from cyclo-hexane	Ratio anol/anone	Turnover number
1	19.2	0	0.892	1.05	20.5	0.01		
	0.228		13.7	16.6				
2	13.4	FeSO ₄ 7H ₂ O	1.07	1.98	16	0.19	8/1	6.04
	0.159	0.014; 0.050	16.4	28.0				
3	19.5	Fe	0.93	1.05	161.6	0.1	5/1	7.25
	0.232	23.6; 0.032	14.3	16.6				
4	19.2	CuSO ₄ 5H ₂ O	0.998	2.30	24	0.6	8.8/1	2.28
	0.228	14.9; 0.6	15.1	38.3				
5	19.3	Cu	7.035	1.92	24	1.3	5.8/1	96.0
	0.229	29.8; 0.031	75.8	32.0				
6	19.4	Cu	1.223	1.97	67	4.3	3.3/1	134.2
	0.231	70.5; 0.074	18.8	32.8				

a) Metal contents in FS-1(Fe) or (Cu): Fe 7.60%, Cu 6.71%

Table 10. Oxidation of methylcyclohexane in the presence of FS-1(Fe) and FS-1(Cu)

Run	Catalyst FS μ mol. metal	React. cond. temp. (°C) Time (h)	Yield (%) turn over number	Distribution of products				
1	Fe	r.t./24	0.45/16.7	56	21	8	12	3
					(2.5:1)	(8:1)	(5:1)	
	54	60/24	11.2/415	3	59	36	1	1
					(----)	(----)	(1:1)	
2	Cu	r.t./24	0.51/21.7	68	10	10	34	8
					(3.6:1)	(----)	(----)	
	47	60/24	2.4/10.2	15	13	48	2	2
					(----)	(----)	(----)	

Substrate 0.2 mol, CH₃COOH 30 mmol, Zn 15 mmol, (:), ol: none mol ratio, (----), not determined methylcyclohexane, yield (%) was determined by GC

FS-1(Fe) and FS-1(Cu) also show greater reactivity than FS-1(Ni). The tertiary hydrogen at 1-position is most easily oxidized at room temperature, but at higher temperature hydrogen at 2-position and 3-position becomes more reactive. Alcohols were produced instead of ketones. In the oxidation of cyclohexane, FS-1(Fe) and FS-1(Cu) showed high activity at higher temperature. But the oxidation of methylcyclohexane was different from that of cyclohexane, because of the difference in their solubilities. The solvation energy of methylcyclohexane is larger than that of cyclohexane^[11]. Therefore the coagulation or association of active site and molecular chain with methylcyclohexane was larger, and the complex was more stable in the reaction of methylcyclohexane with FS-1(Fe). Consequently, the oxidation of methylcyclohexane was activated under these conditions at a higher reaction temperature. On the other hand, FS-1(Cu) showed lower activity at high reaction temperature, because of the low stability of the complex

structure. This suggests that the active dinuclear structure of copper is more easily decomposed by the solvation of substrate methylcyclohexane than that of cyclohexane.

(4) Dioxygen-oxidation of ethylbenzene in the presence of CoBr_2 immobilized montmorillonite^[4]
The comparison of the oxidation reaction was carried out either in the presence or in the absence of hydrogen peroxide. The results are summarized in Table 11.

Table 11. Oxidation of ethylbenzene in the presence of montmorillonite- CoBr_2 complex ([Mom-Co])

Run	Catalyst	React time (h)	Conversion (%)	Selectivity (%)		
				PhCOMe	PhCH(OH)Me	PhCH ₂ CHO
1 ^b	CoBr_2	1	0.5	100	0	0
		3	3.8	50	50	0
		44	41.3	57	24	19
2 ^a	[Mom-Co] +NaBr	24	15.0	65	35	0
		48	73	67	31.5	2
		20	55	55	25	14
3 ^b	[Mom-Co]	1	2.8	61	39	0
		3	8.3	60	40	0
		20	38.5	63	19	18
	+NaBr	1	7.0	55	45	0
		3	20.2	55	33	19
		20	52.1	54	18	28
	+LiBr	1	5.4	38	52	10
		20	7.4	23	33	34
	Without Co-cat (blank)					
		20	0	0	0	0

Reaction condition: temp. 90°C; O_2 1 atm; catalyst(Co) 0.17 mmol; acetic acid 40 mmol; ethylbenzene 32 mmol; hydrogen peroxide, 2 mmol; salt content 1 mmol

a: Reaction without H_2O_2 , b: reaction with H_2O_2

The yield with hydrogen peroxide is about 2.5 times higher than that without hydrogen peroxide. This effect is the same as with the addition of salts. This means that both chemicals may be available for radical chain transfer reagents. Also, the activity of the oxidation is two times higher in the metal ion immobilized by the modified montmorillonite than in the unimmobilized metal ion case. The immobilized catalyst and this catalyst shows the same activity with recycle usage. As for the addition of salt, the kind of cation used for the activation was critical. In our case, Na^+ and K^+ were effective for the activity but Li^+ lowered the activity. However the selectivity of the oxidation was observed, that is, a large degree of oxidation of β -position of ethylbenzene was observed.

CONCLUSION

In order to synthesize supported catalysts which are applicable in the organic reaction, silica and montmorillonite composed from Al_2O_3 and SiO_2 were modified by the reaction of silane coupling reagents. These new kinds of the supported catalysts composed of inorganic and organic group were useful and highly active for a nucleophilic reaction and dioxygen oxidation of hydrocarbons under mild conditions. These inorganic and organic hybrid-type catalysts exhibited new characteristics, which are due to the balance of the hydrophobic and hydrophilic characters introduced by the reaction of silane coupling agents.

The experimental section was omitted and may be referred to in the papers cited in the references.

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