Alkane oxidation with mixed addenda heteropoly catalysts containing Ru(III) and Rh(III) [1]

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Abstract

Oxidation of alkanes, mainly of cyclohexane, with t-butyl hydroperoxide (TBHP) catalyzed by alkylammonium salts of mixed addenda heteropoly compounds having Keggin-type polyanions were studied in benzene solutions, with regard to the relative catalytic activity, reaction orders and the stability of catalysts. Tetra-n-hexylammonium salts of $SiRu(H_2O)W_{11}O_{39}^{5-}$ and $SiRh(H_2O)W_{11}O_{39}^{5-}$ showed higher catalytic activities than the corresponding Fe- and Co-substituted catalysts for the selective oxidation of cyclohexane to cyclohexanol and cyclohexanone. Although the Ru catalyst was possibly a mixture, it consisted mainly of $SiRu(H_2O)W_{11}O_{39}^{5-}$ and gave reproducible catalytic performance for repeated preparations. The initial rates were approximately proportional to the concentrations of cyclohexane, TBHP and the catalyst. Although the rate decreased with the consumption of TBHP, the initial rate was resumed by the addition of TBHP, indicating the absence of the deterioration of catalytic activity. Similarly alcohols and ketones were selectively formed from n-decane and ethylbenzene.

Keywords: Alkane oxidation; Heteropoly catalysts; Rhodium; Ruthenium

1. Introduction

Heteropoly compounds are well-known as efficient catalysts for acid and oxidation catalyses (see, e.g., Ref. [1]). It is possible to control their catalytic properties by changing their addenda atoms, heteroatoms, counter cations, and polyanion structures.

Among different kinds of heteropoly compounds, those having so-called 'Keggin-type'

polyanions' have mostly been used for catalysts due to their thermal and chemical stability, and the high capability for the modification of the constituting elements. In this study, the Keggin-type heteropoly catalysts substituted at the addenda atoms were used for alkane oxidation in homogeneous system. When transition metals are added to the solution of lacunary Keggin compounds under appropriate conditions, the metal ions are 'trapped' at the hole in the polyanion, and 'substituted Keggin-type' compounds are formed (Fig. 1) [2].

There have been several reports on oxidation reactions of alkanes catalyzed by mono- or tri-substituted heteropoly compounds with tungsten as addenda atoms, $[XM(H_2O)W_{12-x}O_{40-x}]^{n-}$
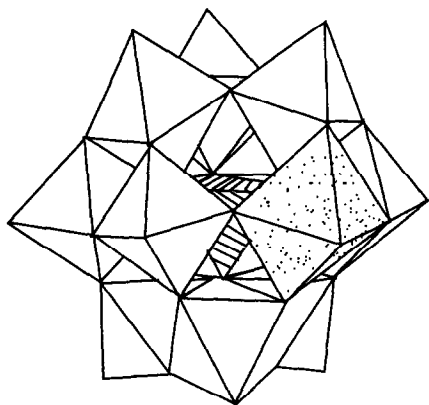

Fig. 1. Structure of $XM'M_{11}O_{39}^{n-}$ (mono-substituted Keggin structure; M' is located in the shaded octahedron) in a polyhedra model.

2.2. Preparation of catalysts

Heteropoly catalysts were prepared as in the literature [5,6] with a slight modification. The general methods adopted are as follows: $K_8SiW_{11}O_{39} \cdot xH_2O$ was prepared according to the method in Ref. [7], and recrystallized twice or three times from water. The amount of water of crystallization, x, was estimated to be 13 as in the literature [8]. Aqueous solutions of a slightly excess amount of chlorides of the above transition metals were added to an aqueous $K_8SiW_{11}O_{39} \cdot xH_2O$ solution at 50–90°C. In the case of cobalt, the solution was buffered at about pH 6 by adding potassium hydrogencarbonate. After stirring the solution at the same temperature for 30–60 min and cooling to room temperature, the solution was filtrated. An excess amount of KCl and then methanol were added to it, and the solution was kept in a refrigerator. Potassium salt was collected by using a suction filter. For Ru and Rh compounds a cation (K^+) exchange-resin (Amberlite IR-120B) was used (repeatedly in most cases) before the addition of methanol in order to remove the cationic Ru or Rh species. The potassium salts obtained were dissolved into water, and catalysts were extracted by benzene or 1,2-dichloroethane solution containing slightly excess amount of tetra-n-butyl- or tetra-n-hexylammonium. Beilstein's method of the products was negative, so that Cl^- is not present [9]. L is most probably H_2O.

Catalysts obtained were characterized by IR with KBr pellets or on silicon wafers (Fig. 2 and see also Fig. 6). Since intense IR bands due to the Keggin structure were observed, the compounds used for catalysts are mainly $(R_4N)_{8-n}[SiM(L)W_{11}O_{39}]$ where R is C_6H_{11}, L is H_2O and M^{n+} is Fe^{3+}, Co^{2+}, Ru^{3+} or Rh^{3+}. The possibility of impurity as pointed out in the literature [10] cannot be excluded, as the IR data for the Ru catalyst agreed with that in the literature [6]. However, the ion-exchange performed additionally in the present preparation would have improved the purity, because we
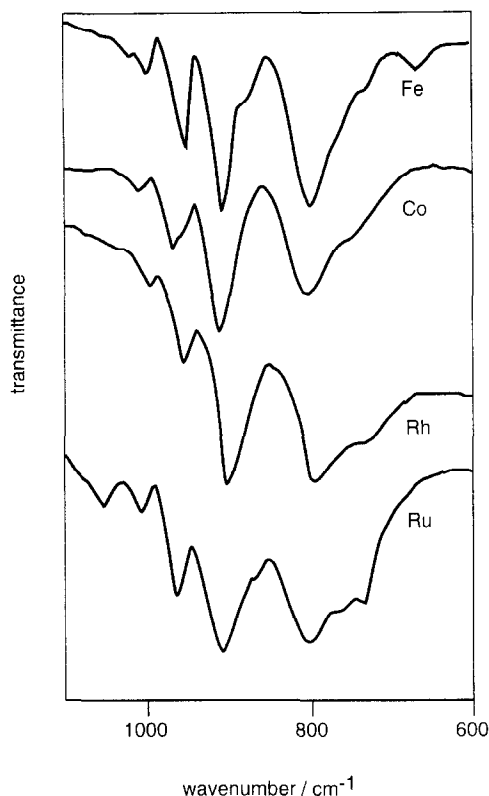
($X = Si^{4+}$, P^{5+}; $M^{n+} = Co^{2+}$, Fe^{3+}, Cr^{3+}, etc.) (see, for example, Refs. [3,4]). Here is reported the performance and kinetic behavior of oxidation of cyclohexane, n-decane and ethylbenzene with t-butyl hydroperoxide (TBHP) catalyzed by tetra-n-butyl- or tetra-n-hexylammonium salts of $[SiM(L)W_{11}O_{39}]^{(8-n)-}$ ($M^{n+} = Ru^{3+}$ and Rh^{3+}, $L = H_2O$) and compared with those with Co^{2+} and Fe^{3+} for M^{n+}.

2. Experimental

2.1. Reagents

The following commercially available reagents were used for the experiments without further purification: Sodium silicate solution (Nacalai, EP grade), sodium tungstate (Nacalai, GR), cobalt acetate (Wako, GR), ferric chloride (Kanto, GR), ruthenium chloride (hydrate) (Tanaka Kikinzoku, 99.9%), rhodium chloride (Tanaka Kikinzoku, 99.9%), cyclohexane (TCI, GR), t-butylhydroperoxide (Nacalai, 30% aqueous solution), tetra-n-butylammonium bromide (TCI, EP), tetra-n-hexylammonium bromide (Nacalai, EP), and 2,4-di-t-butyl-4-methl-phenol (TCI, GR). The other reagents were also commercially obtained.

Fig. 2. IR spectra of $SiMW_{11}O_{39}$ ($M^{n+} = Fe^{3+}$, Co^{2+}, Rh^{3+} and Ru^{3+}).

assumed that cationic Rh or Ru species are the impurities to be carefully avoided for the present study. Furthermore, it was confirmed that the Rh and Ru catalysts prepared repeatedly gave reproducible catalytic performance. These catalysts are denoted by $SiMW_{11}O_{39}$ hereafter. The yield of the Ru compound was 20–25%.

2.3. Catalytic reaction and analysis

The benzene solutions of catalysts were dried by anhydrous magnesium sulfate and used for reaction. To the catalyst solution (catalyst 1–5 μmol in 20 ml solvent), 0.4–2 mmol of TBHP (4.1 M, 0.488 ml) and then 18.5 mmol of alkanes were added. A tetra-n-butylammonium salt was used for Co(II) catalyst because no reliable tetra-n-hexylammonium salt was obtained. As the tetra-n-butylammonium salt was not soluble in benzene, 1,2-dichloroethane was

used for solvent. All reactions were carried out at 333 K in an Ar-purged vial with shaking. Under these conditions, the oxidation of alkyl chains in the ammonium counterion may be possible. A small amount of white precipitates due to carboxylic acids were observed in some cases, but nothing was detected by GC analysis except for those compounds described in the text.

Products were analyzed by an FID gas chromatograph (capillary column; Carbowax 20-M, 30 m) with increasing temperature (333–503 K). Before the GC analysis the remaining TBHP was decomposed by triphenylphosphine. The amount of TBHP remaining after the reaction was determined by the conventional iodometry. To 20 ml of acetic acid, 1 ml of saturated KI aqueous solution and then 0.5 ml of reaction solution were added. After the solution was left in the dark at room temperature for 30 min, 20 ml of degassed water was added and the solution was titrated with 0.004 N of $Na_2S_2O_3$ solution.

3. Results and discussion

Typical results obtained for the oxidation of cyclohexane catalyzed by mixed addenda 12-heteropolyanions, $[SiMW_{11}O_{39}]^{(8-n)-}$ ($M^{n+} = Fe^{3+}$, Co^{2+}, Ru^{3+} and Rh^{3+}), at 333 K are listed in Table 1. Products were cyclohexanol and cyclohexanone, and no other products were detected by GC analysis. Among the four catalysts, Rh and Ru catalysts showed higher conversions of TBHP and turnovers for the oxidation of cyclohexane than Fe and Co catalysts. In spite of the possibility that the Ru catalyst was a mixture [10], the Ru and Rh catalysts prepared repeatedly gave satisfactorily reproducible results to enable kinetic analysis. The turnover was highest for the Ru catalyst. The yield of cyclohexanone, a product oxidized to a deeper extent, was greatest for the Ru catalyst, the yield being in the order of Ru > Rh > Co ~ Fe. The turnovers for Fe and Co catalysts after 6 h

are similar to those reported in the literature for the same catalysts [3].

Time courses of the reaction are shown in Fig. 3 for two different concentrations of the Ru catalyst. With the consumption of TBHP, both cyclohexanol and cyclohexanone were formed, where cyclohexanone tended to appear at the later stage of the reaction. The delayed production of cyclohexanone was more clearly observed when the reaction was slower, that is, for the lower concentrations of catalyst and for less active Fe and Co catalysts. The conversion of cyclohexanol to cyclohexanone was also noted in the later stage of the cyclohexane oxidation (see, for example, the reaction after 2 h in Fig. 3B). These results indicate that cyclohexanone was formed mainly as a product of secondary reaction of cyclohexanol.

$$\text{(1)}$$
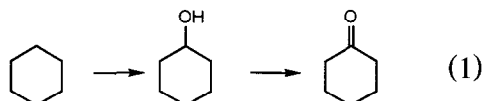
To confirm this, the oxidation of cyclohexanol was carried out in a separate experiment, where the reaction conditions were the same as those for the runs shown in Fig. 3, except that the cyclohexanol was used in place of cyclohexane. The oxidation of cyclohexanol to cyclohexanone took place rapidly by the Ru catalyst. The rate was about 10 times greater than the oxidation of cyclohexane. In this experiment about
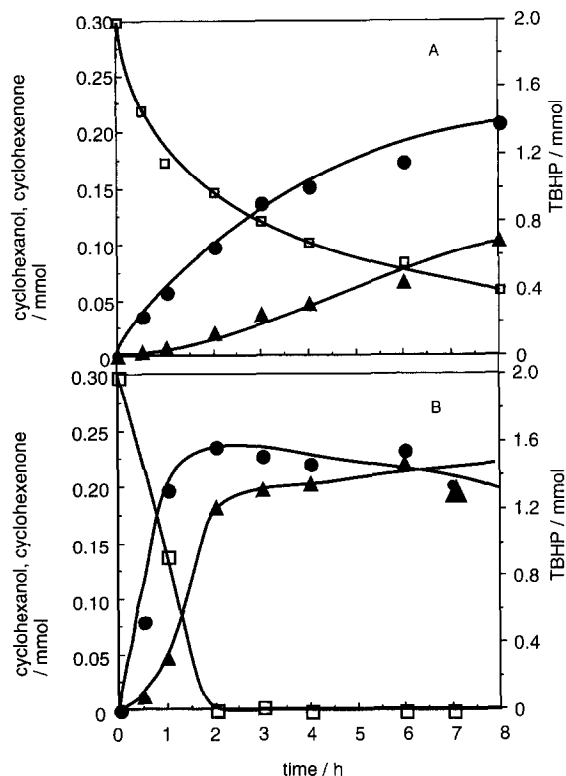

Fig. 3. Time courses of the oxidation of cyclohexane with TBHP catalyzed by $SiRuW_{11}O_{39}$. (A) $SiRuW_{11}O_{39}$: 1 μmol, and (B) $SiRuW_{11}O_{39}$: 5 μmol. TBHP: 2 mmol, cyclohexane: 18.5 mmol, benzene: 20 ml, and reaction temperature: 333 K. (●) Cyclohexanol, (▲) cyclohexanone and (□) TBHP.

80% of the TBHP added were utilized for the oxidation of cyclohexanol.

The results after 2–3 h of the oxidation of cyclohexane with different catalyst concentrations are summarized in Table 2. The dependen-

Table 1

Oxidation of cyclohexane by *t*-butyl hydroperoxide catalyzed by mixed addenda heteropolyanions

Catalyst	Reaction time (h)	Yield (%) [a]		Conversion of TBHP (%)	Turnovers [b]
		⬡-OH	⬡=O		
$SiFeW_{11}O_{39}$	2	13	1	32	20
	6	15	5	70	67
$SiCoW_{11}O_{39}$	2	23	2	21	22
$SiRuW_{11}O_{39}$	2	11	6	75	72
$SiRhW_{11}O_{39}$	3	11	3	78	53

Catalyst: 5 μmol, cyclohexane: 18.5 mmol, benzene (1,2-dichloroethane for Co): 20 ml, TBHP: 2 mmol, and reaction temperature: 333 K.
[a] Based on TBHP converted; (moles of cyclohexanol or cyclohexanone)/(moles of TBHP converted).
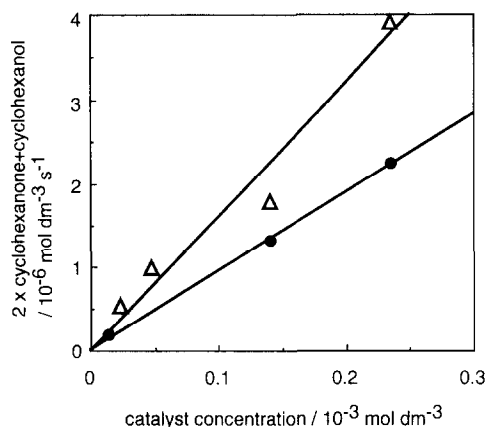[b] Turnovers = {(moles of cyclohexanol) + 2(moles of cyclohexanone)}/(moles of catalyst).

Fig. 4. Plots of the initial rate of the oxidation of cyclohexane versus the catalyst concentration. ($\bullet$) $SiRhW_{11}O_{39}$, ($\triangle$) $SiRuW_{11}O_{39}$. Catalyst: 5 μmol, TBHP: 2 mmol, cyclohexane: 18.5 mmol, benzene: 20 ml, and reaction temperature: 333 K.

Fig. 5. Effect of the addition of TBHP during the oxidation of cyclohexane. TBHP was added at A. ($\bullet$) Cyclohexanol, ($\blacktriangle$) cyclohexanone and ($\blacksquare$) 2 × [cyclohexanone] + [cyclohexanol]. Catalyst ($SiRuW_{11}O_{39}$): 5 μmol, TBHP: 2 mmol, cyclohexane: 18.5 mmol, benzene: 20 ml, and reaction temperature: 333 K. The amounts of TBHP added initially and at A were both 2 mmol.

cies of the initial rates of oxidation on the catalyst concentration are shown in Fig. 4 for Ru and Rh catalysts. Here, the extent of oxidation is expressed by [cyclohexanol] + 2[cyclohexanone], assuming that the oxidation of cyclohexane to cyclohexanone consumes two moles of TBHP. This figure indicates that the initial rates are proportional to the catalyst concentration for both catalysts.

In the oxidation of cyclohexane shown in Fig. 3B, TBHP expired within the first 2 h and then the oxidation almost stopped. In a separate run, the same amount of TBHP as initially
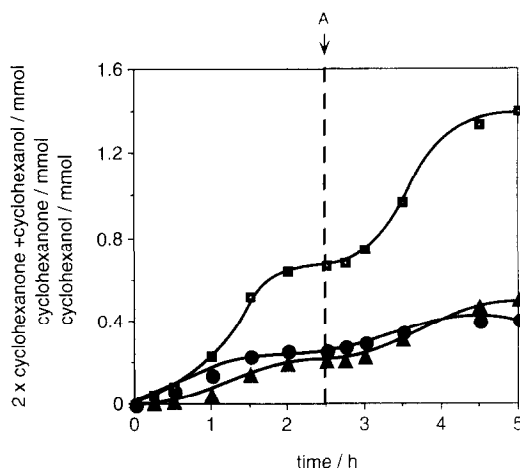
added was added again to the reaction system after 2 h. Fig. 5 shows the time course of the reaction. TBHP initially added (2 mmol) expired in about 2 h, and when 2 mmol of TBHP was added after 2.5 h (at A), the reaction started again at a rate similar to the initial rate. This result demonstrates that the catalyst was intact during the reaction and maintained its initial activity.

Possible decomposition of Ru and Rh cata-

Table 2
Oxidation of cyclohexane by TBHP catalyzed by $SiRuW_{11}O_{39}$ and $SiRhW_{11}O_{39}$

Amount of catalyst (μmol)	Reaction time (h)	Yield (%) [a]		Conversion of TBHP (%)	Turnovers [b]
		⬡-OH			
Catalyst: $SiRuW_{11}O_{39}$					
5	2	12	9	100	120
3	2	12	5	70	102
1	2	7	1	76	141
0.5	2	9	1	38	178
Catalyst: $SiRhW_{11}O_{39}$					
5	3	11	6	78	53
1	2	18	6	21	85

Cyclohexane: 18.5 mmol, benzene: 20 ml, TBHP: 2 mmol, and reaction temperature: 333 K.
[a] Based on TBHP converted; (moles of cyclohexanol or cyclohexanone)/(moles of TBHP converted).
[b] Turnovers = {(moles of cyclohexanol) + 2(moles of cyclohexanone)}/(moles of catalyst).
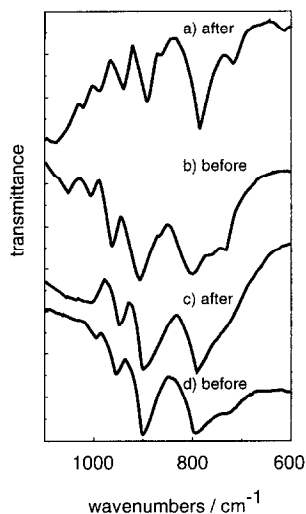
Fig. 6. IR spectra of $SiRuW_{11}O_{39}$ and $SiRhW_{11}O_{39}$, after (a) and before (b) the oxidation of cyclohexane for $SiRuW_{11}O_{39}$ and after (c) and before (d) the reaction for $SiRhW_{11}O_{39}$.

lysts during the reaction was also examined by IR spectroscopy. Fig. 6 shows the IR spectra of the Rh and Ru catalysts before and after the reaction. They are essentially identical in the range of 600–1100 cm^{-1}, where the typical bands of Keggin-type polyanions are observed. The small differences observed in this range are probably due to the different concentrations of the products. Little change in IR is in accordance with the fact that the catalytic activity

was resumed by the addition of TBHP after the reaction stopped as shown in Fig. 5. The IR spectra for the other two catalysts before and after the reactions were similar.

The reaction orders of the oxidation of cyclohexane catalyzed by $SiRuW_{11}O_{39}$ with respect to cyclohexane and TBHP are shown in Fig. 7. Here, the initial slopes of the plots as in Fig. 3 are plotted in the logarithmic scale against the concentration of cyclohexane and TBHP. The orders are 1.1th in cyclohexane and 0.7th in TBHP, respectively. If the possible errors in determining the initial slopes are taken into account, these results indicate that the orders are approximately first-order with respect to cyclohexane and TBHP. Thus, the rate is expressed by

$$- d[cyclohexane]/dt$$

$$= k[cyclohexane][TBHP][SiRuW_{11}O_{39}] \quad (2)$$

In Fig. 8 the amounts of products are plotted against the amounts of TBHP consumed, for the case of the oxidation of cyclohexane with several concentrations of Ru catalyst. The slopes, that is, the amount of products divided by TBHP consumed, are the selectivities of TBHP utilization for cyclohexane oxidation. The slopes increased as the reaction proceeded. This indi-
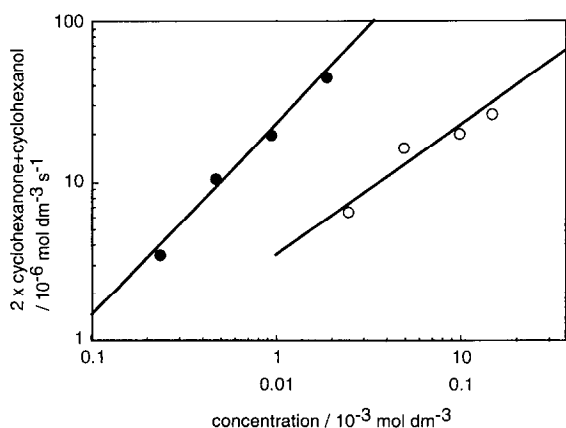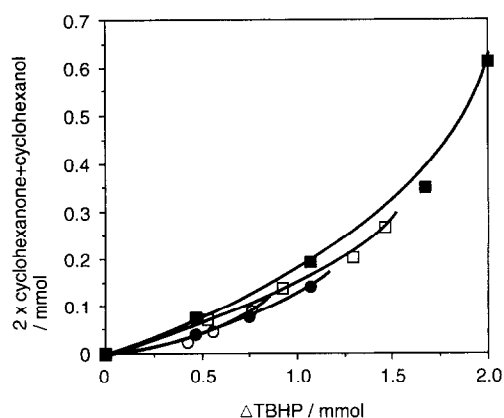

Fig. 7. Log–log plots of the initial rate of the oxidation of cyclohexane versus the concentrations of cyclohexane and TBHP. (●) Cyclohexane, (○) TBHP. $SiRuW_{11}O_{39}$: 5 μmol, benzene: 20 ml, and reaction temperature: 333 K.

Fig. 8. The amount of oxidized product as a function of TBHP consumed (ΔTBHP). Catalyst: $SiRuW_{11}O_{39}$ ((○) 0.025, (●) 0.050, (□) 0.150 and (■) 0.250 mmol dm^{-3}), cyclohexane: 18.5 mmol, TBHP: 2 mmol, benzene: 20 ml, and reaction temperature: 333 K.

cates that the TBHP decomposition during oxidation exhibits a reaction order higher than first-order in TBHP. A similar trend was observed for the Rh catalyst, while the slope tended to increase slightly with the catalyst concentration. The dependency shown in Fig. 8 is probably due to the decomposition reaction of TBHP, $2BuOOH \rightarrow O_2 + 2BuOH$, which becomes faster at higher concentrations.

Therefore, the trends that the turnovers were higher for lower catalyst concentrations (Table 2) and that the yield was greater for lower concentrations of TBHP are probably due to the difference in the extent of TBHP consumption which was higher for higher catalyst concentrations. If the decomposition of TBHP produces O_2, there is a possibility that the autoxidation utilizing O_2 proceeds as reported by Arends et al. [11]. So we carried out the oxidation of cyclohexane with Ru catalyst in a stream of Ar gas. The data obtained under the Ar sweep conditions gave the identical results with those in the stationary Ar atmosphere. Therefore, the possibility of the autoxidation is excluded. However, a significant effect of a radical inhibitor, 2,6-di-t-butyl-4-methyl phenol, observed in the case of the oxidation of cyclohex-
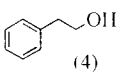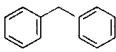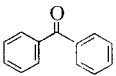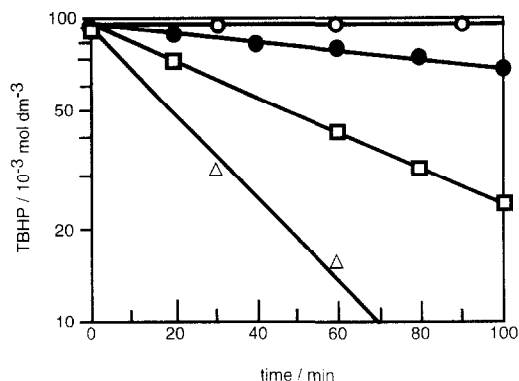

Fig. 9. First-order plots of the decomposition of TBHP. Catalyst: $SiRhW_{11}O_{39}$ ((O) 0, (●) 0.047, (□) 0.141 and (△) 0.251 mmol dm^{-3}). TBHP: 2 mmol, benzene: 20 ml, and reaction temperature: 333 K.

ane with $SiRuW_{11}O_{39}$, in contrast to the case of Co catalyst [3], indicates that the contribution of the radical reaction (not autoxidation) is significant.

The catalytic decomposition of TBHP in the absence of cyclohexane was also examined. The rate of the TBHP decomposition was greater in the absence of cyclohexane than in its presence. Cyclohexane suppresses the undesirable decomposition of TBHP to some extent. As shown in

Table 3
Oxidation of various alkanes by TBHP catalyzed by $SiRuW_{11}O_{39}$

Substrate	Yield (%) [a]		Conv. of TBHP (%)	Turnovers [b]
n-heptane	heptanols (trace)	heptanones (2)	98	13
n-decane	decanols (trace)	dacanones (5)	98	36
(structure)	OH (6)	OH (4)	O (3)	95	77
(structure)		O (12)	46	45

Catalyst: 5 μmol, TBHP: 2 mmol, alkane: 18.5 mmol, solvent: benzene 20 ml and reaction temperature: 333 K. Reaction time, 2 h.
[a] Figures in parentheses are based on TBHP consumed.
[b] Turnovers = {(moles of alcohol) + 2(moles of ketone)}/(moles of catalyst).

Fig. 9, the time courses for $SiRhW_{11}O_{39}$ are expressed by a first-order rate equation with respect to TBHP and the rate constants obtained from the slopes in Fig. 9 are proportional to the catalyst concentration. Thus, the following rate equation is derived for the decomposition of TBHP catalyzed by $SiRhW_{11}O_{39}$ in the absence of cyclohexane, where k' is the rate constant:

$$-d[\text{TBHP}]/dt = k'[\text{TBHP}][\text{SiRhW}_{11}O_{39}]$$
$$(3)$$

On the other hand, in the case of the Ru catalyst the initial rate of the TBHP decomposition in the absence of cyclohexane was 1.2th with respect to the catalyst concentration, while the time courses better fitted the second-order kinetics than first-order kinetics, and the rate constants obtained by the second-order kinetics showed 1.7th order dependency on the catalyst concentration. Thus, the reaction orders of TBHP decomposition with Ru catalyst in the absence of cyclohexane are not certain, while they are probably greater than one. The reason for the higher orders in the case of the Ru catalyst is not clear, but the high orders have been reported for the hydroperoxide decomposition catalyzed by cobalt and ruthenium compounds [12].

Table 3 shows the results obtained when the $SiRuW_{11}O_{39}$ catalyst was applied to the oxidations of n-decane, ethylbenzene, and diphenylmethane. This catalyst exhibited significant activity also in these cases, particularly, in the selective oxidation at the benzyl position. The turnovers are in general similar to those of Ru phosphine complexes reported in the literature [13], although the present Ru catalyst tended to be more active for less bulky substrates. There are known reagents for the oxidation of C–H bond at the benzyl position [14,15]. However, in these cases a large amount of acetic acid or KOH and a high temperature are often required.

With Ru catalysts the oxidation at benzyl position proceeds selectively under mild conditions.

Acknowledgements

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