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Oxidation of Alcohols to Aldehydes and Ketones over Hydrous Zirconium(IV) Oxide Modified by Trimethylsilyl Chloride

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A modified catalyst was prepared by the reaction of trimethylsilyl chloride and hydrous zirconium(IV) oxide. It was then applied to the oxidation of alcohols by using carbonyl compounds as hydrogen acceptors. In the case of cycloalkanols, the oxidation proceeded efficiently to give the corresponding ketones. Further, primary aliphatic alcohols were converted to the corresponding aldehydes in high yields in a batch reaction system. In addition, it was investigated that the oxidation was influenced by a variety of solvents and hydrogen acceptors.

It is considered that the oxidation of alcohols by using carbonyl compounds as hydrogen acceptors, which is known as an Oppenauer-type oxidation, is an excellent method for preparing aldehydes or ketones from alcohols over a solid catalyst. Recently, it was reported that secondary alcohol is efficiently converted to the corresponding ketone over alumina.[1)] However, it has been difficult to obtain aldehyde by the Oppenauer-type oxidation, since an aldol condensation easily occurs between a produced aldehyde and a hydrogen acceptor.

In previous papers[2,3)] we reported that the Oppenauer-type oxidation of alcohols, by using ketones and quinone as hydrogen acceptors, proceeded efficiently over hydrous zirconium(IV) oxide. In a flow-reaction system, primary alcohol could be efficiently converted to the corresponding aldehyde. However, in a batch system, primary alcohols and cycloalkanols could not be converted to the corresponding carbonyl compounds in high yield.

It was reported that the organosilicon groups were combined with a solid surface by the coupling reaction of organosilyl chloride with a metal oxide to change the features of the solid surface.[4—7)] We reported that selective reactions could be achieved over a catalyst modified by organosilicon compounds.[8—10)] In this investigation, Oppenauer-type oxidations of primary alcohols and cycloalkanols were carried out over hydrous zirconium(IV) oxide modified by a trimethylsilyl compound.

Experimental

Materials. Hydrous zirconium(IV) oxide was prepared in the manner described in a previous paper.[11)] Hydrous zirconium(IV) oxide was calcined at 300 °C for 5 h in air. Commercial reagents for the reactions were used without any further purification.

Preparation of a Trimethylsilyl-Modified Catalyst. Trimethylsilyl chloride (10.0 g) was dissolved in 20 cm^3 of hexane. Hydrous zirconium(IV) oxide was immersed in this solution overnight at room temperature. The catalyst, after being modified by trimethylsilyl chloride, was filtered off, washed with hexane and acetone, and dried at room temperature under reduced pressure. The catalyst modified by trimethylsilyl chloride was named TMS-HZO. The amounts of the surface hydroxyl group on TMS-HZO and hydrous zirconium(IV) oxide were determined by the lithium aluminium hydride method.[12)] The surface of TMS-HZO was analyzed by X-ray photoelectron spectroscopy (XPS).

General Procedure for Oxidation of Alcohols. The following materials were placed in a 10 cm^3 round-bottom flask equipped with a reflux condenser: the catalyst (0.4 g), alcohol (0.1 mmol), and a xylene solution (5.0 cm^3) containing carbonyl compound (5.0 mmol) and dodecane as an internal standard. The contents were heated under reflux. The products were analyzed by GLC (a capillary column PEG 20M 25 m and DB-1 30 m) and GC-MS (Shimadzu QP1100 EX).

Results and Discussion

Characterization of Hydrous Zirconium(IV) Oxide Modified by Trimethylsilyl Chloride (TMS-HZO). It was reported that the organosilyl group easily combined with the acidic hydroxyl group on the surface of the metal oxide by a coupling reaction involving organosilyl chloride and the metal oxide.[4—7)] In this investigation, hydrous zirconium(IV) oxide modified by trimethylsilyl chloride was prepared in a similar manner to that described above. The amounts of the surface hydroxyl group on TMS-HZO and hydrous zirconium(IV) oxide were 2.78×10^{-4} and 1.53×10^{-3} $mol\,g^{-1}$, respectively. It was found that the number of surface hydroxyl groups on TMS-HZO decreased; it was estimated to be ca. 1/6 compared with that on hydrous zirconium(IV) oxide. In the case of TMS-HZO, it was suggested that the surface hydroxyl group was converted to a trimethylsiloxy group. In order to confirm the existence of trimethylsilyl group, the surface of TMS-HZO was analyzed by XPS. A peak appeared at 102.3 eV, coinciding with the value for silicon (2p). These data thus indicated that the trimethylsilyl group combined the surface hydroxyl group on hydrous zirconium(IV) oxide as a covalent bond.

Oxidation of Cycloalkanol. In a previous paper[2)] we reported that cyclohexanol was not converted to cyclohexanone at high yield by the catalytic oxidation of hydrous zirconium(IV) oxide, due to an aldol condensation of cyclohexanone. In this investigation, the oxidation of cyclohexanol was carried out over TMS-HZO. The time courses of the oxidation over TMS-HZO and hydrous zirconium(IV) oxide are shown in Fig. 1. When

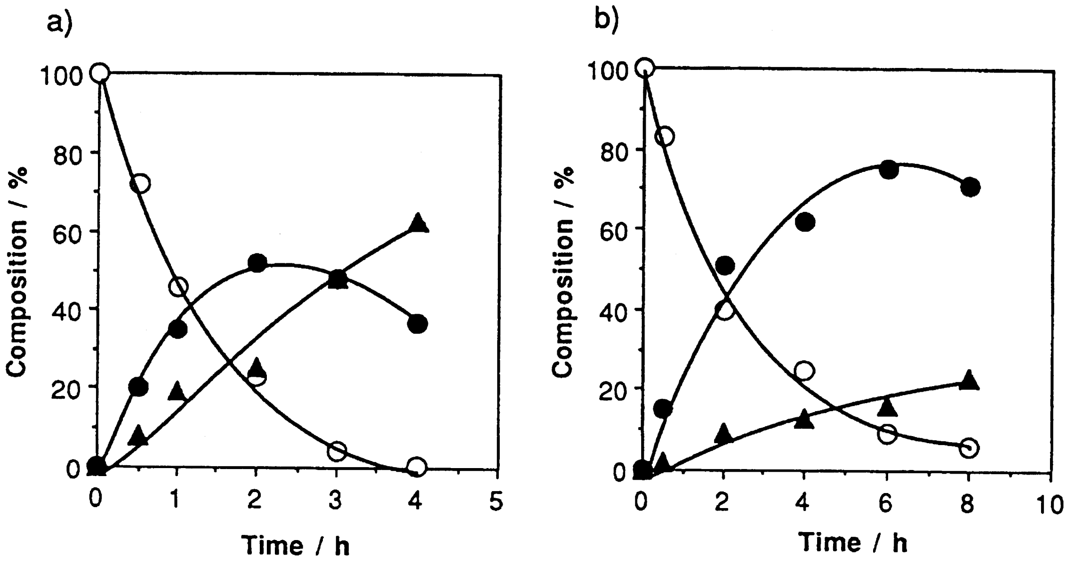


Fig. 1. Time course for the oxidation of cyclohexanol. a) Hydrous zirconium(IV) oxide, b) TMS-HZO. Conditions: catalyst, 0.4 g; cyclohexanol, 0.1 mmol; acetone, 0.5 cm^3; benzene 4.5 cm^3. ○: cyclohexanol. ●: cyclohexanone. ▲: aldol compounds.

Table 1. Oxidation of Cycloalkanols over Hydrous Zirconium(IV) Oxide Modified by Trimethylsilyl Chloride [a)]

Reactant	Product	Hydrogen acceptor	Conv./%	Sel./%	Yield%
Cyclohexanol	Cyclohexanone	Acetone	16	63	10
Cyclohexanol	Cyclohexanone	Diethyl ketone	84	85	71
Cyclohexanol	Cyclohexanone	Diisopropyl ketone	95	62	59
Cyclohexanol	Cyclohexanone	Acetone[b)]	91	83	75
Cyclooctanol	Cyclooctanone	Acetone[b)]	98	100	98

a) Catalyst, 0.4 g; cycloalkanol, 0.1 mmol; hydrogen acceptor 5.0 cm^3. b) Hydrogen acceptor, 0.5 cm^3; benzene (diluent) 4.5 cm^3.

TMS-HZO was used, it was found that cyclohexanol was converted to cyclohexanone in a high yield, compared with the case of hydrous zirconium(IV) oxide. It was found that aldol condensation is inhibited over TMS-HZO, due to a blocking of the acidic hydroxyl group on hydrous zirconium(IV) oxide by trimethylsilyl chloride. From these results, it was considered that the aldol condensation proceeds by the acidic hydroxyl group on hydrous zirconium(IV) oxide.

The oxidation of cycloalkanols was carried out over TMS-HZO. The results are given in Table 1. When benzene was used as the diluent, cycloalkanols were efficiently converted to the corresponding ketones.

Further, in order to elucidate the dependence on ketone as a hydrogen acceptor in the oxidation of cyclohexanol, a variety of ketones, i.e. acetone, diethyl ketone and diisopropyl ketone, were used. It was found that the oxidation using diethyl ketone gave the best selectivity as well as yield of cyclohexanone (Table 1). It was also found that the diluent was not needed in the oxidation if diethyl ketone instead of acetone to achieve a high yield.

Oxidation of Primary Alcohols over TMS-HZO. TMS-HZO was applied to oxidize primary alcohols. The oxidations of 1-octanol were performed over TMS-HZO and hydrous zirconium(IV) oxide. The results are given in Fig. 2. The yield of octanal was low over hydrous zirconium(IV) oxide (Fig. 2a). However, the yield of octanal by the oxidation over TMS-HZO was increased, estimated to be 2-times compared with that over hydrous zirconium(IV) oxide (Fig. 2b). On the other hand, compared with the oxidation of 1-octanol to octanal, the rate of the aldol condensation was very slow over TMS-HZO. In other words, aldol condensation is inhibited in the case of oxidation over TMS-HZO. Table 2 shows a comparison of TMS-HZO and hydrous zirconium(IV) oxide for a variety of oxidations of primary alcohols. It was found that TMS-HZO is superior to hydrous zirconium(IV) oxide as a catalyst for the oxidation in all cases.

Effect of a Hydrogen Acceptor. In order to elucidate the dependence on the hydrogen acceptor, the oxidation of 1-decanol was performed with a variety of aldehydes over TMS-HZO. The results show that the selectivity of decanal is dependent on the substituent group. As shown in Ta-

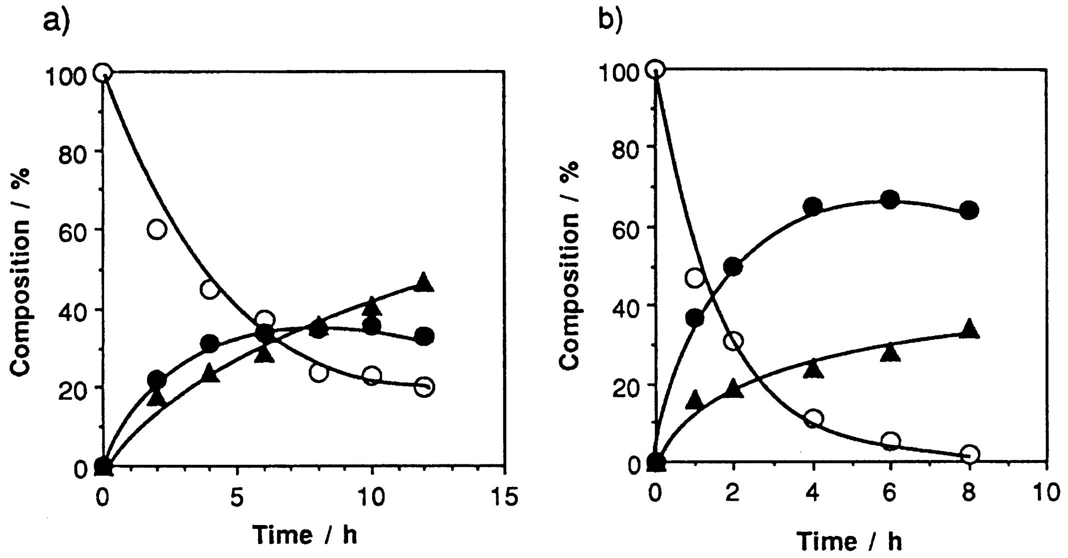


Fig. 2. Time course for the oxidation of 1-octanol. a) Hydrous zirconium(IV) oxide, b) TMS-HZO. Conditions: catalyst, 0.1 g; 1-octanol, 0.1 mmol; benzaldehyde, 5.0 mmol, xylene solution, 5.0 cm^3. ○: 1-octanol. ●: ocatnal. ▲: aldol compounds.

Table 2. Comparison of TMS-HZO and Hydrous Zirconium(IV) Oxide(HZO) for Oxidation of a Variety of Primary Alcohols $^{a)}$

Catalyst	Reactant	Hydrogen acceptor	Yield/%
TMS-HZO$^{a)}$	1-Octanol	Benzaldehyde	67
HZO$^{a)}$	1-Octanol	Benzaldehyde	36
TMS-HZO$^{b)}$	1-Octanol	Pivalaldehyde	43
HZO$^{b)}$	1-Octanol	Pivalaldehyde	19
TMS-HZO$^{c)}$	1-Decanol	Benzophenone	25
HZO$^{c)}$	1-Decanol	Benzophenone	12

a) Catalyst, 0.1 g; reactant, 0.1 mmol; hydrogen acceptor, 5.0 mmol; xylene solution, 5.0 cm^3; b) Catalyst, 0.4 g;
c) Catalyst, 0.2 g.

Table 3. Effect of a Hydrogen Acceptor for the Oxidation of 1-Decanol over TMS-HZO $^{a)}$

Hydrogen acceptor	Conv./%	Sel./%	Yield/%
Benzaldehyde	86	74	64
m-Tolualdehyde	88	80	70
p-Tolualdehyde	66	48	32
m-Chlorobenzaldehyde	68	60	41
p-Chlorobenzaldehyde	87	74	64

a) Catalyst, 0.2 g; 1-decanol, 0.1 mmol; hydrogen acceptor, 5.0 mmol, xylene solution, 5 cm^3.

ble 3, it was found that *m*-tolualdehyde and *p*-chlorobenzaldehyde were superior to *p*-tolualdehyde and *m*-chlorobenzaldehyde regarding selectivity.

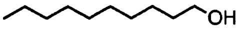
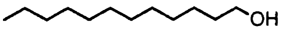
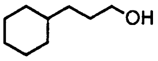
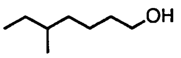
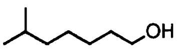
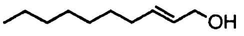
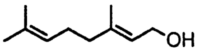
Effect of Solvent. It was also investigated whether or not the oxidation is influenced by the solvent as a diluent. These results are given in Table 4. It was found that toluene and xylene were superior to others in both the yield and selectivity of aldehyde.

Table 4. Effect of a Solvent over THS-HZO $^{a)}$

Solvent	Conv./%	Sel./%	Yield/%
Benzene	58	31	18
Toluene	82	76	62
Xylene	86	74	64
1,4-Dioxane		No reaction	
Dodecane	74	35	26

a) Catalyst, 0.2 g; 1-decanol, 0.1 mmol; benzaldehyde, 5.0 mmol; mixture solution, 5 cm^3.

Table 5. Oxidation of a Variety of Primary Alcohols over TMS-HZO $^{a)}$

Reactant	Hydrogen acceptor	Yield/%
	Benzaldehyde	67
	*m*-Tolualdehyde	70
	Benzaldehyde	42
	Benzaldehyde	57
	*m*-Tolualdehyde	69$^{b)}$
	*m*-Tolualdehyde	67$^{b)}$
	*m*-Tolualdehyde	54$^{c)}$
	*m*-Tolualdehyde	16$^{c)}$

a) Catalyst, 0.2 g; reactant, 0.1 mmol, hydrogen acceptor, 5.0 mmol; xylene solution, 5 cm^3; b) Catalyst, 0.4 g;
c) Catalyst, 0.1 g; toluene solution, 5 cm^3.

Oxidation of a Variety of Primary Alcohols. The oxidation of a variety of primary alcohols was carried out over the TMS-HZO catalyst. As shown in Table 5, most of the alcohols were efficiently converted to the corresponding aldehydes. For instance, 5- and 6-methylheptanol were converted to 5- and 6-methylheptanal, which are known as being the main flavor components in *Nicotiana Umbratica*,13) in about 70% yields. In the case of allylic alcohols, the oxidation of 2-decenol proceeded efficiently; on the other hand, geraniol could not be oxidized in high yield.

Conclusions

Hydrous zirconium(IV) oxide has a variety of catalytic-active sites on its surface. Accordingly, it is difficult to avoid side reactions in some cases. In this investigation, the active site of the side reaction was blocked by the alkylsilylation of hydrous zirconium(IV) oxide. As a result, the selectivity was increased in the oxidation of alcohol to aldehyde. It is expected that this strategy can be applied to other reactions of hydrous zirconium(IV) oxide.

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