Aldol condensation of acyclic ketones with benzaldehyde and subsequent cyclodehydration to form indenes over halide cluster catalysts

Satoshi Kamiguchi [a], Satoru Nishida [a,b], Ikuko Takahashi [a,b],
Hideki Kurokawa [c], Hiroshi Miura [b], Teiji Chihara [a,*]

[a] *The Institute of Physical and Chemical Research (RIKEN), Wako, Saitama 351-0198, Japan*
[b] *Graduate School of Science and Engineering, Saitama University, Shimo-Okubo, Sakura-Ku, Saitama City, Saitama 338-8570, Japan*
[c] *Molecular Analysis and Life Science Center, Saitama University, Shimo-Okubo, Sakura-Ku, Saitama City, Saitama 338-8570, Japan*

Abstract

When a molecular halide cluster $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**)/SiO_2 was treated in a helium stream above $200\,^{\circ}C$, it catalyzed the aldol condensation of acetone with benzaldehyde to yield *E*-4-phenyl-3-buten-2-one. The bromide cluster of Ta and chloride clusters of Nb, Mo, and W of the same octahedral metal framework also catalyzed the reaction. 3,3-Dimethyl-2-butanone combined with benzaldehyde similarly yielded the corresponding aldol condensation product over **1**/SiO_2 at $400\,^{\circ}C$. On the other hand, 3-pentanone combined with benzaldehyde provided indenes such as *E*- and *Z*-1-ethylidene-2-methylindene and 2-methyl-3-vinylindene of the same carbon skeletal structure, which would be formed by cyclodehydration of the aldol condensation product, *E*-2-methyl-1-phenyl-1-penten-3-one. One of the advantages of halide cluster catalysts is thermal stability, and high temperatures above $350\,^{\circ}C$ promoted the cyclodehydration.
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1. Introduction

We have reported a series of reactions catalyzed by halide clusters, which have an octahedral metal array structure with terminal, edge-bridging, or face-capping halogen π-donor ligands. One of the specific features of halide cluster catalysis is Brønsted acidity. Dehydration of alcohol [1], ring-attachment isomerization of diethylbenzenes [2], methylation of toluene with methanol [3], and dehydrogenation of aliphatic amines [4] have been reported. One of the approaches to characterizing the catalytic activity of halide clusters and, accordingly, to understanding the scope and limitations of halide cluster catalysis is a physicochemical investigation of activated halide clusters. Another approach is to apply clusters to many organic compounds and to discover new catalytic reactions: a comprehensive view of the catalyst can be obtained by comparison with other catalysts.

Thermal stability is characteristic of halide clusters. In contrast to carbonyl clusters, which decompose below $200\,^{\circ}C$, halide clusters are synthesized at a temperature range of 650–$1700\,^{\circ}C$. The maximum catalytic activity of a molybdenum cluster $[(Mo_6Cl_8)Cl_4(H_2O)_2]\cdot 6H_2O$, for example, appeared at around $400\,^{\circ}C$; its cluster framework began to decay above $400\,^{\circ}C$ and was partly retained as high as at $600\,^{\circ}C$ [5].

The aldol condensation is well investigated and is catalyzed by acids and bases, the latter being more frequently employed [6]. Sulfuric acid [7], Nafion-H, Amberlite IR-120 [8], and $RuCl_3$ [9] have been used as acid catalysts, and NaOH [10], $Ba(OH)_2$ [11], choline hydroxide/MgO [12], hydrotalcite [13], guanidine [14], and the basic sites of alumina [15,16] have been used as base catalysts. In near-critical water both oxonium ion and hydroxide ion catalyzed the reaction [17]. Catalytic activities of halide clusters for the aldol condensation are the subject of this report. Successive reactions to create indenes by taking advantage of the high temperatures will also be shown.

* Corresponding author. Tel.: +81 48 467 9399; fax: +81 48 462 4631.
E-mail address: chihara@riken.jp (T. Chihara).

2. Experimental

The cluster complexes $[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ [18], $(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot6H_2O$ [19], $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot$ $4H_2O$ (**1**) [18], $[(Ta_6Br_{12})Br_2(H_2O)_4]\cdot4H_2O$ [18], and $(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O$ [20] were prepared according to published procedures. The cluster Re_3Cl_9 was a commercial product. The clusters were supported on silica gel (Nippon Aerosil, Tokyo, Aerosil 380 m^2/g) at 5.0 wt.% in the following manner. Silica gel (19.0 g) was added to a methanol solution (330 mL) of the cluster (1.0 g) and allowed to stand for 1 h with occasional shaking. Then the solvent was evaporated to dryness under vacuum at ambient temperature. Masses of the dried silica gel were crushed and screened to 150–200 mesh.

A conventional vertical glass fixed-bed micro reactor with a continuous flow system was operated at atmospheric pressure [21]. Typically, a weighed supported sample of **1**/SiO$_2$ (100 mg) was packed in a glass tube (3 mm i.d.) and located at the center of an electric furnace. The catalyst sample was initially treated at 400 °C for 1 h in a helium stream (300 mL/h). The reaction was initiated by feeding an equimolar mixture of acetone (42 μL/h, 0.57 mmol/h) and benzaldehyde (58 μL/h, 0.57 mmol/h) into the stream of helium at the treatment temperature. The reaction was monitored by sampling the reaction gas followed by analyses using an online GLC (Apiezon Grease L on Uniport B packed column). The reactor effluent was frozen in a dry-ice trap for subsequent analyses with GLC and GC/MS. Most of the reaction products, including all the indenes, were isolated by preparative GLC and subjected to NMR and mass analyses. Spectral data for 2-methyl-1-methyleneindene (**2a**): ^{1}H NMR (C_6D_6) δ 1.84 (s, 3H), 5.33 (s, 1H), 5.69 (d, 1H, J = 1.7 Hz), 6.29 (m, 1H); MS m/z (relative intensity) 142 (75) $[M^+]$, 141 (100), 115 (39). Spectral data for 2-ethyl-1-methyleneindene (**2b**): ^{1}H NMR (C_6D_6) δ 1.18 (t, 3H, J = 7.4 Hz), 1.84 (q, 2H, J = 7.4 Hz), 5.51 (s, 1H), 5.85 (d, 1H, J = 1.5 Hz), 6.48 (m, 1H); MS m/z (relative intensity) 156 (41) $[M^+]$, 141 (100), 115 (33).

3. Results and discussion

3.1. Aldol condensation of acetone

Supported Ta cluster, $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**), on silica gel in a glass reaction tube was initially heated at 400 °C for 1 h in a helium stream, and then reaction was commenced by introduction of an equimolar mixture of acetone and benzaldehyde without changing the temperature. The reaction profile is plotted in Fig. 1. The reactivity decreased with time, but the selectivity leveled off after 3 h. The cluster catalyzed the cross aldol condensation to yield *E*-4-phenyl-3-buten-2-one with around 75% selectivity (Eq. (1)), with some decomposition to benzene, toluene, and styrene. No *Z* isomer of the condensation product was detected as reported in other cases of the aldol condensation [6]. The material balance was 90%. In many reported cases, excess acetone with solvent is used to prevent self-condensation of acetone and for effective use of benzaldehyde [22]. In this study, both substrates were effi-
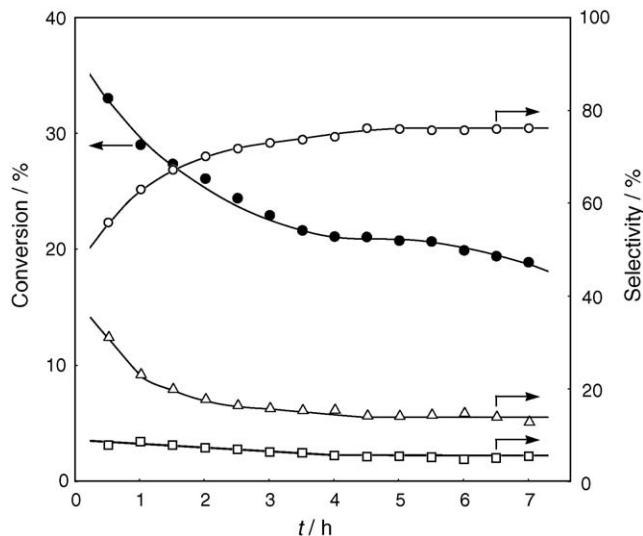

Fig. 1. Typical reaction profile of acetone with benzaldehyde over $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)/SiO$_2$ in a He stream. Following treatment of **1**/SiO$_2$ (150–200 mesh, 100 mg) in a He stream (300 mL/h) at 400 °C for 1 h, reaction was started by introduction of a mixture of acetone (42 μL/h, 0.57 mmol/h) and benzaldehyde (58 μL/h, 0.57 mmol/h) to the He stream at 400 °C. Conversion = products/(products + recovered benzaldehyde) × 100 (%), selectivity = product/(total amount of products) × 100 (%) based on aromatic compounds. Conversion of benzaldehyde (●), selectivity for aldol condensation to *E*-4-phenyl-3-buten-2-one (○), selectivity for decomposition to benzene, toluene, and styrene (△), and selectivity for indenes (□).

ciently converted to the corresponding product. Higher adducts such as *E,E*-dibenzylideneacetone and oligomers were not formed.

$$C_6H_5CHO + CH_3COCH_3$$
$$\rightarrow C_6H_5-CH=CH-CO-CH_3 + H_2O \quad (1)$$

Neither the cross aldol condensation of acetophenone with benzaldehyde nor self-condensation of benzaldehyde proceeded under the same reaction conditions. Reactions of acetone with butyraldehyde proceeded non-selectively, affording a wide variety of disproportionation products with trace amounts of the cross aldol condensation product, *E*-3-hepten-2-one. Thus, activation of acetone is a key step of the reaction with benzaldehyde.

The reaction profiles of acetone with benzaldehyde at different temperatures catalyzed by **1**/SiO$_2$ are plotted in Fig. 2. The activity developed slightly when the reaction was performed at 200 °C, and increased with increasing temperature. The activity decreased with time, probably because of coke deposition in the gas–solid reaction [8]. Higher reaction temperatures resulted in sharper decreases in activity.

The effect of the reaction temperature on the activity and selectivity over **1**/SiO$_2$ is presented in Fig. 3. The catalytic activity had a maximum at around 425 °C. The selectivity for the aldol condensation remained as high as 80% up to 375 °C. Above this temperature, the selectivity for decomposition to principally benzene increased with increasing temperature. In general, a reaction that increases the number of product molecules is thermodynamically favorable at higher temperatures.
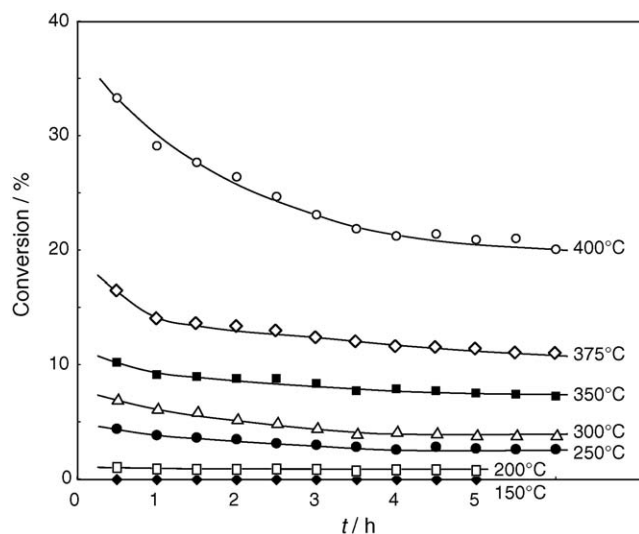
Fig. 2. Reaction profile of acetone with benzaldehyde over $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)/SiO$_2$ at different temperatures. Following treatment of **1**/SiO$_2$ at various temperatures for 1 h in a He stream, reaction was started by introduction of an equimolar mixture of acetone and benzaldehyde to the He stream without changing the temperature. Other conditions are the same as in Fig. 1. Conversion = products/(products + recovered benzaldehyde) × 100 (%) based on aromatic compounds.

Fig. 3. Effect of temperature on the reaction of acetone with benzaldehyde over $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)/SiO$_2$ in a He stream at 3 h after the reaction started. Both initial treatment and reaction temperatures were altered concomitantly. Other conditions are the same as in Fig. 1. Conversion = products/(products + recovered benzaldehyde) × 100 (%), selectivity = product/(total amount of products) × 100 (%) based on aromatic compounds. Conversion of benzaldehyde (●), selectivity for aldol condensation to E-4-phenyl-3-buten-2-one (○), selectivity for hydrogenolysis to benzene, toluene, and styrene (△), and selectivity for indenes (□).

Table 1 lists the catalytic activity of various clusters of group 5–7 metals and related compounds. Supported Ta bromide cluster exhibited considerably higher activity and selectivity for the aldol condensation. Under both helium and nitrogen streams, supported **1** exhibited moderate selectivities for the reaction. Supported Nb and W chloride clusters also demonstrated moderate selectivities; however, the Re chloride cluster, which has a triangular metal core, catalyzed hydrogenolysis to yield benzene preferentially.

3.2. Aldol condensation of acyclic ketones

Some acyclic ketones were subjected to reaction with benzaldehyde in the presence of **1**/SiO$_2$, and the results are summarized in Table 2. 3,3-Dimethyl-2-butanone, which has no α-hydrogen at the site opposite to the methyl group, was effectively converted to the cross aldol condensation product, E-4,4-dimethyl-1-phenyl-1-penten-3-one.

Table 1
Aldol condensation of acetone with benzaldehyde[a]

Catalyst	Conversion (%)[b]	Selectivity (%)[c]			
		E-C$_6$H$_5$CHCHCOCH$_3$	Indenes[d]	C$_6$H$_5$R (R = H, CH$_3$, CHCH$_2$)	Others
$[(Nb_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O/SiO_2$	17.3	48.2	6.4	42.0	3.4
$(H_3O)_2[(Mo_6Cl_8)Cl_6]\cdot6H_2O/SiO_2$	7.7	33.5	3.5	59.9	3.1
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)/SiO$_2$	23.3	72.3	6.4	16.3	5.0
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)/SiO$_2$[e]	6.5	59.2	6.5	29.6	4.7
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)/SiO$_2$[f]	12.1	51.4	8.9	36.4	3.3
$[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot4H_2O$ (**1**)[g]	5.0	24.2	0.2	71.7	3.9
$[(Ta_6Br_{12})Br_2(H_2O)_4]\cdot4H_2O/SiO_2$	12.2	61.7	2.6	33.0	2.7
$(H_3O)_2[(W_6Cl_8)Cl_6]\cdot6H_2O/SiO_2$	7.8	47.0	6.8	44.2	2.0
Re$_3$Cl$_9$/SiO$_2$	5.4	20.3	1.6	73.8	4.3
Ta metal[h]	0.0				
SiO$_2$	0.0				

[a] After treatment of catalyst (150–200 mesh, 100 mg) in a helium stream (300 mL/h) at 400 °C for 1 h, reaction was started by introduction of acetone (42 μL/h, 0.57 mmol/h) and benzaldehyde (58 μL/h, 0.57 mmol/h) to the helium stream at the same temperature.

[b] Conversion = products/(products + recovered benzaldehyde) × 100 (%) based on aromatic compounds at 3 h after the reaction started.

[c] Selectivity = product/(combined products) × 100 (%) based on aromatic compounds at 3 h after the reaction started.

[d] 1-Methyleneindene [23] and 3-methylindene [24].

[e] In a hydrogen stream (300 mL/h).

[f] In a nitrogen stream (300 mL/h).

[g] Unsupported crushed crystalline cluster (150–200 mesh, 100 mg).

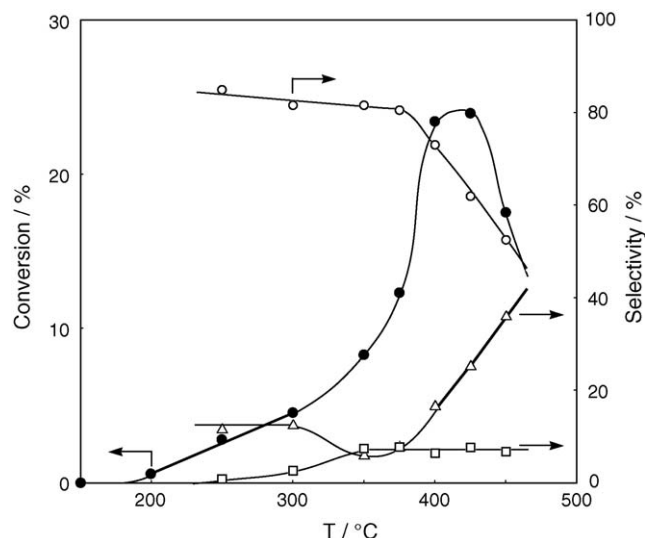[h] Ta metal (150–200 mesh, 100 mg).

Table 2

Reaction of ketones with benzaldehyde over $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**)/SiO$_2$[a]

Ketone	Conversion (%)[b]	Selectivity (%)[c]			
		E-C$_6$H$_5$CHCR$_1$COR$_2$	Indenes	C$_6$H$_5$R (R = H, CH$_3$, CHCH$_2$)	Others
Acetone	23.3	72.3 (R$_1$ = H, R$_2$ = CH$_3$)	6.4[d]	16.3	5.0
Butanone	8.4	9.6 (R$_1$ = H, R$_2$ = C$_2$H$_5$)	23.4[e]	47.9	19.1
2-Pentanone	13.8	17.9 (R$_1$ = H, R$_2$ = C$_3$H$_7$)	31.4[f]	15.7	16.0
3-Pentanone	29.7	0.0 (R$_1$ = CH$_3$, R$_2$ = C$_2$H$_5$)	78.4[g]	10.2	11.4
3,3-Dimethyl-2-butanone	20.0	81.1 (R$_1$ = H, R$_2$ = t-Bu)	0.0	8.1	10.8
E-4-Phenyl-3-buten-2-one[h]	21.6	–	35.8[i]	13.9	50.3[j]

[a] $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**)/SiO$_2$ (150–200 mesh, 100 mg) was used as catalyst, and equimolar amount of ketone and benzaldehyde (0.57 μmol/h, each) was used. Other conditions are the same as in Table 1.

[b] Conversion = products/(products + recovered benzaldehyde) × 100 (%) based on aromatic compounds at 3 h after the reaction started.

[c] Selectivity = product/(total amount of products) × 100 (%) based on aromatic compounds at 3 h after the reaction started.

[d] 1-Methyleneindene [23] (2.2%) and 3-methylindene [24] (4.2%).

[e] 2-Methyl-1-methyleneindene (**2a**, 4.5%) and 2,3-dimethylindene [25] (18.9%).

[f] 2-Ethyl-1-methyleneindene (**2b**, 13.6%) and 2-ethyl-3-methylindene [26] (17.8%).

[g] Z-1-Ethylidene-2-methylindene [27] (45.9%), E-1-ethylidene-2-methylindene [27] (14.7%), 2-methyl-3-vinylindene [27] (6.1%), and 3-ethyl-2-methylindene [28] (11.7%).

[h] Butyl ether solution (15%) in the absence of benzaldehyde.

[i] 1-Methyleneindene (3.5%) and 3-methylindene (32.3%).

[j] 4-Phenyl-2-butanone, 1-phenyl-1-butene, naphthalene, etc.

Scheme 1.
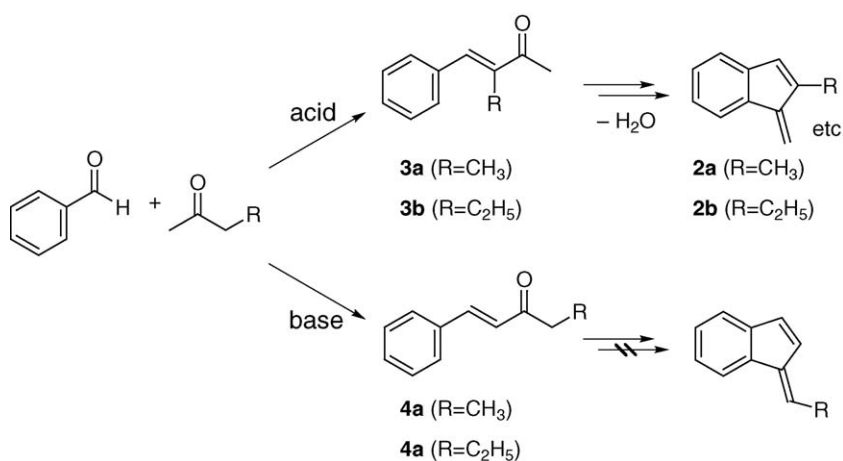
3-Pentanone afforded no aldol condensation products seemingly, but selectively provided substituted indenes of the same skeletal structure of the carbon. Different regioselectivities for the aldol condensation of unsymmetrical aliphatic ketones such as butanone and 2-pentanone have been well established: the acid-catalyzed reaction of butanone with benzaldehyde affords E-3-methyl-4-phenyl-3-buten-2-one (**3a**) by activation of the methylene group of butanone, while the base-catalyzed reaction yields E-1-phenyl-1-penten-3-one (**4a**) by activation of the methyl group [6,29,30] (Scheme 1). The methylene group of acyclic non-methyl ketones is hardly activated by base catalysts [6,31]. Formation of Brønsted acid sites on the activated

Scheme 2.
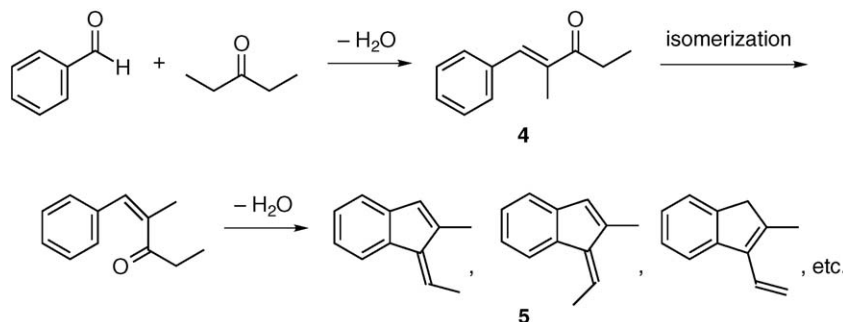
W halide cluster has been confirmed by pyridine adsorption [3], and no basic sites were detected by CO_2 adsorption on the activated Ta halide cluster. If those sites were present, the cluster catalyst would provide the acid-catalyzed product, *E*-2-methyl-1-phenyl-1-penten-3-one (**5**) (Scheme 2). When *E-Z* isomerization of this initial product proceeds, the carbonyl group is accessible to the *ortho* hydrogen, leading to cyclodehydration to yield 1,2-disubstituted indenes (**6**); this is the case for 3-pentanone. Halide clusters catalyzed *E-Z* isomerization of olefins [21] and dehydration of alcohols to olefins [1]. Thus, isomerization followed by dehydration is feasible over halide clusters. In the case of 3,3-dimethyl-2-butanone, there is no α-hydrogen in the *t*-butyl group for dehydration, and hence indene was not formed.

The aldol condensation product of acetone with benzaldehyde, *E*-4-phenyl-3-buten-2-one, was subjected to the reaction under identical conditions, and the result is listed in Table 2. The selectivity for the indenes is much higher than that starting from acetone with benzaldehyde, which shows that the aldol condensation product is an intermediate species to indene.

As Table 2 shows, butanone and 2-pentanone afforded 2-methyl-1-methyleneindene (**2a**) and 2-ethyl-1-methyleneindene (**2b**) with their hydrogenation products, which would be formed by way of acid-catalyzed-type products **3** (Scheme 1). In each case, the carbon frameworks of the produced indenes are the same, and hence they afford the same indane derivative when the olefinic bonds are hydrogenated [32]. Small amounts of base-catalyzed-type products **4** were formed at the same time. The regioselectivity of the aldol condensation is established as mentioned above. However, detailed studies of the reaction revealed that the product selectivity is not decisive: a small amount of the counterpart was formed concomitantly over both acid [33] and base [10,34] catalysts. In the reaction of butanone with benzaldehyde, for example, basic alumina catalyst afforded acid-catalyzed-type products with 16–35% selectivity [16], and Co(II)-2,2′-dipyridine complex catalyst yielded acid- and base-catalyzed-type products with 6:94 regioselectivity [35]. Therefore, the formation of base-catalyzed-type products **4** from butanone and 2-pentanone with 10–18% selectivity is acceptable. Indenes attributable to **4** were not detected (Scheme 1).

Acetone combined with benzaldehyde yielded the corresponding indenes with 3–9% selectivity over various clusters at 400 °C, as shown in Table 1. Fig. 3 shows that the selectivity for indenes increased above 350 °C. In general, a reaction that increases the number of product molecules is thermodynamically favorable at elevated temperatures. Increasing selectivity for decomposition of aldol condensation product to indene and water with increasing temperature accords with this principle.

There have been only a few reports of the aldol condensation performed under harsh conditions, since the rates are sufficiently rapid at room temperature and the maximum yields are usually reached within 12–24 h [6]. Ruthenium chloride, which served as an acid catalyst, did not yield the secondary product at 120 °C in the reaction of methyl ketones with benzaldehyde [9]. No secondary condensation products have been reported in the reaction of benzaldehyde with excess acetone and butanone at 160 °C over basic alumina [16]. On the other hand, under microwave

irradiation, acetone reacted with two moles of benzaldehyde yielding *E,E*-dibenzylideneacetone [36]. Three moles of benzaldehyde added to butanone afforded 5-benzylidene-2-methyl-3,4-diphenyl-2-cyclopenten-1-one in the presence of $TiCl_4$ at 120 °C [37]. In near-critical water at 250–350 °C, oligomers of butanone and benzaldehyde were obtained [17]. Thus, there are no precedents for the catalytic one-step synthesis of indenes from acyclic ketones and benzaldehyde. Application of high temperatures, which is one of the advantages of halide cluster catalyses, presumably caused the cyclodehydration of the aldol condensation products, as the equilibrium shifts to the cyclodehydration with increased temperature.

4. Conclusion

The cross aldol condensation of acyclic ketones with benzaldehyde was studied over halide clusters as catalyst. A supported tantalum chloride cluster, $[(Ta_6Cl_{12})Cl_2(H_2O)_4]\cdot 4H_2O$ (**1**), on silica gel catalyzed the condensation of acetone to yield *E*-4-phenyl-3-buten-2-one selectively above 200 °C, with the maximum activity at around 425 °C. Similarly, 3,3-dimethyl-2-butanone, which has no α-hydrogen at the site opposite the methyl group, was effectively converted to the corresponding cross aldol condensation product.

On the other hand, 3-pentanone afforded 1,2-disubstituted indenes (**6**) of the same carbon framework instead of the expected aldol condensation product, *E*-2-methyl-1-phenyl-1-penten-3-one (**5**). The initial product **5** would undergo *E–Z* isomerization followed by cyclodehydration to yield **6**. There have been no precedents for the one-step synthesis of indenes from an acyclic ketone and benzaldehyde, although more than 2300 reports on the aldol condensation were published prior to 1968 [6]. The aldol condensation is usually accomplished at room temperature, and excessively high temperatures are generally unnecessary. Application of high temperatures, which is one of the advantages of halide cluster catalyses, probably caused the cyclodehydration to indenes, as the equilibrium shifts to cyclodehydration with increased temperature.

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