

# Formation of Brønsted acid site on halide clusters of group 5 and 6 transition metals Catalytic methylation and demethylation of methylbenzenes with methanol

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## Abstract

Toluene was allowed to react with methanol in the presence of  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$  supported on silica gel. When the temperature was raised above 300 °C, the catalytic activity of the cluster appeared. Toluene alkylation proceeded selectively yielding xylenes with a small amount of trimethylbenzenes. Similarly, the corresponding clusters of Nb, Mo, and Ta catalyzed the reaction. Methylation of xylenes, trimethylbenzenes, and tetramethylbenzenes also proceeded; however, the main reaction of trimethyl- and tetramethylbenzenes was isomerization. Methylation of pentamethylbenzene hardly occurred, but demethylation of pentamethyl- and hexamethylbenzene proceeded. Thus, the clusters catalyzed methylation, demethylation, and isomerization of the methylbenzenes in the presence of methanol. Hydrogen gas accelerated the reactions. IR analyses of adsorbed pyridine on the catalyst showed the presence of a Brønsted acid site; however, a Lewis acid site was not observed. A hydroxo ligand that formed on the cluster complex would be the active site of the catalyst.

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## 1. Introduction

More than 100 types of halide clusters have been synthesized since the first report of molybdenum chloride, which had been synthesized as  $\text{MoCl}_2$  in 1859 [1] and fully characterized as  $[\text{Mo}_6\text{Cl}_8^i]\text{Cl}_2^a\text{Cl}_4/2^{a-a}$  in 1967 [2]. At present, 17 types of group 3–7 transition metals coordinated with four types of halogen ligands constitute the halide clusters [3–5]. They have characteristic features such as a multi-center and multi-electron system, an intermediate oxidation state of the metal atoms, and high thermal stability, and they have been candidates for catalysts for a long time [6–8], like “Sleep-

ing Beauty” [9]. In recent years, we have reported a series of reactions catalyzed by halide clusters: intramolecular ring-attachment isomerization of diethylbenzenes [10], isomerization of olefins [11], dehydrohalogenation of halogenated alkanes [12], dehydration of alcohols [13], and decomposition of phenyl acetate to phenol and ketene [14]. Although these reactions proceed over conventional acid catalysts, closer inspection showed some conspicuous features, particularly in terms of selectivity. In order to understand the scope and limitations of cluster catalysis and hence to establish the nature of the active site, they have been studied for various reactions. In this paper, we report that a Brønsted acid site emerges by heat treatment of halide clusters and that methylation with methanol of methylbenzenes, such as toluene and xylenes, proceeds over the halide clusters as catalysts.

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Alkylation of the aromatic ring has been widely studied using ether [15], olefin [16], halogenated hydrocarbon [17], or alcohol [18–21] as an alkylating reagent, and inter alia methylation of toluene with methanol has been studied extensively owing to the commercial demand for the products. When Friedel–Crafts catalysts such as  $\text{AlCl}_3$  [22],  $\text{AlCl}_3/\text{charcoal}$  or  $\text{AlBr}_3/\text{charcoal}$  [16], and  $\text{BF}_3$  [23] are employed for the reaction using alcohol, they serve as stoichiometric reagents. Solid acids such as  $\text{Al}_{13}$ -pillared montmorillonite [24],  $\text{AlPO}_4\text{-Al}_2\text{O}_3$  [25,26],  $\text{TiO}_2/\text{silica-alumina}$  and  $\text{MoO}_3/\text{silica-alumina}$  [21], and Nafion-H [27], a perfluorinated resin sulfonic acid, have been utilized for the reaction as catalysts.

Detailed research has been focused particularly on ZSM-5 with a microporous structure, since it has shape selectivity for production of commercially important *p*-xylene [28,29]. In the absence of diffusion constraints, the alkylation reaction over ZSM-5 is *o/p*-directing, similar to that of aluminum chloride and amorphous silica/alumina catalysts [30]. The selectivity for *p*-xylene over H-ZSM-5 catalyst is reported to be rather low at 200 °C, while high *p*-selectivity was observed at 300 °C, at which temperature isomerization to *p*-xylene exceeded the rate of alkylation and accumulation of the bulk products *m*- and *o*-xylene in the pore [31]. In contrast, the external surface of H-ZSM-5 is non-selective [32]. Inactivation of acid sites on the external surface without affecting its intercrystalline void space by CVD with alkoxides [33] or adsorption of quinoline [34] was achieved, and enhanced *p*-selectivity was obtained. Treatment with phosphorus or boron compounds reduced the dimensions of pore openings and channels sufficiently to permit favorable formation and outward diffusion of *p*-xylene [35]. Another method for distinguishing the inner or outer active site is to compare the catalytic activity between large and small crystals [18,30,36,37]. Halide clusters treated in this study are in the form of molecules and supported on silica gel. These supported clusters have no such micropore structures, and hence the intrinsic reactivity of all the methylbenzenes with or without methanol will be shown on the cluster catalyst.

## 2. Experimental

Crystals of the molecular cluster complexes of  $[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  [38],  $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  [39],  $[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$  [38], and  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (**1**) [40] were synthesized according to the published procedures followed by repeated recrystallization to give well-grown crystals. Methanol (350 mL) was added to a 1 L flask containing canary yellow **1** (0.452 g). After dissolution of the cluster, silica gel (Nippon Aerosil, Tokyo, Aerosil 380 m<sup>2</sup>/g, 8.60 g) was added 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. All of the clusters

were supported on the silica gel in 5.0 wt.% in the same way. Commercial 1,2,3,4-tetramethylbenzene (Tokyo Kasei, >90%, mp –6 °C) and 1,2,3,5-tetramethylbenzene (Tokyo Kasei, >80%, mp –24 °C) were repeatedly recrystallized from the neat liquids in a deep refrigerator until greater than 99% purity was achieved. All of the other organic compounds (>99%) were commercially available and used as received. A conventional vertical glass fixed-bed microreactor with a continuous flow system was operated at atmospheric pressure [11].

Typically, a weighed supported sample of **1** (200 mg) was packed in a borosilicate glass tube (3 mm i.d.) with the aid of quartz glass and placed in the center of an electric furnace. The catalyst sample was initially treated from room temperature to 450 °C for 1 h in a stream of hydrogen (120 mL/h). Within 10 min, the temperature reached the set point. The reaction was initiated by feeding a mixture of toluene and methanol (0.10 and 0.68 mmol/h, respectively) into the stream of hydrogen at the same temperature. The reaction was monitored every 20 min by sampling the reaction gas (1 mL) with a six-way valve kept at 100 °C followed by analysis using an on-line GLC (Benton 34 + DNP packed column). The reactor effluent was frozen in a dry-ice trap for subsequent analyses with GLC (polyethylene glycol capillary column for separation of tetramethylbenzene isomers or dimethylpolysiloxane capillary column for separation of the other products) and GC/MS (dimethylpolysiloxane capillary column). Analyses of the trapped products showed that the material balance based on toluene was around 90% and that the main products were xylenes with small amounts of benzene, ethylbenzene, and trimethylbenzenes. Analyses of the gaseous products in the gas sampler also showed the formation of methane, ethane, and ethylene. In this report, conversion and selectivity will be discussed based on the data from the on-line GLC analyses. The conversion was proportional to the amount of the catalyst and hydrogen carrier gas, and inversely proportional to the amount of the reactant mixture added. Then the reactants were in saturated adsorption. For IR measurements, the silica gel or the supported sample of **1** on silica gel (15 mg) was pressed to form a tablet (10 mm o.d.). It was treated in a stream of hydrogen at 450 °C for 1 h and adsorbed with pyridine (20 mmHg) at 100 °C for 1 h, followed by evacuation at ambient temperature for 30 min.

## 3. Results and discussion

### 3.1. Methylation of toluene over halide clusters

A typical reaction profile of toluene over supported  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (**1**) on silica gel is plotted in Fig. 1, showing the decrease in activity with time. Analyses by on-line GLC showed the formation of methane, which would be produced from methanol [30], with small amounts of ethane and ethylene as gaseous products. Deposition of coke formed by polymerization of ethylene may retard the

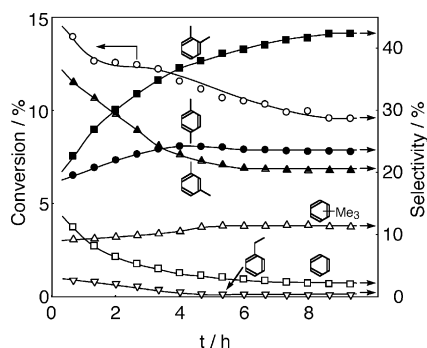


Fig. 1. Typical activity and selectivity profiles for methylation of toluene with methanol over  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (**1**)/ $\text{SiO}_2$  under an  $\text{H}_2$  stream. Following the treatment of the supported **1** on silica gel (200 mg) in a stream of  $\text{H}_2$  (120 mL/h) at  $450^\circ\text{C}$  for 1 h, reaction was started by introduction of a mixture of toluene and methanol (0.10, 0.68 mmol/h, respectively) to the  $\text{H}_2$  stream at the same temperature. Conversion = products/(products + recovered toluene)  $\times$  100 (%), selectivity = product/total amount of products  $\times$  100 (%) based on aromatic compounds. Decomposition of the aromatic ring was not detected.

reaction. In the same reaction over  $\text{AlPO}_4\text{-Al}_2\text{O}_3$  [25], Y-zeolite [41,42], and various zeolite catalysts [43], the decrease in activity is ascribed to coke deposition. Cluster **1** catalyzed methylation of toluene to yield xylenes in higher than 80% selectivity, and successively, trimethylbenzenes with 13% selectivity after 4 h of reaction, as shown in Fig. 1. On the other hand, the selectivity for side chain alkylation to produce ethylbenzene was as low as 0.8%. Demethylation proceeded to a small extent, producing benzene in 3% selectivity.

Table 1 summarizes the catalytic activity of various clusters of group 5–7 metals and related compounds. This table

shows that W metal exhibited no catalytic activity under the same reaction conditions. Mononuclear tungsten hexachloride cannot be used as a catalyst under the same reaction conditions because it boils at  $347^\circ\text{C}$ . Cluster **1** is a coordinatively saturated stable complex that has no metal–metal multiple bonds. Silica gel or no catalyst did not yield any of the reaction products. Hence, halide cluster **1** developed catalytic activity on thermal treatment by taking advantage of its thermal stability and low vapor pressure, as well as its high melting point.

The chloride clusters of Nb, Mo, and Ta with an octahedrally arranged  $\text{M}_6$  metal core also catalyzed the reaction, as shown in Table 1. The selectivity over **1** was not similar to that over supported **1** but rather similar to that over supported  $(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  of the same group 6 metals. Selectivity may be affected by supporting. The selectivities over supported Nb, Ta, and W cluster catalysts were similar: xylenes as main products in around 90% selectivity with an *o*-, *m*-, and *p*-isomer ratio of 2:1:1; trimethylbenzenes resulted from successive methylation in 4–13% selectivity; and benzene caused by demethylation in 3% selectivity. The comparable ratio for *o*-, *m*-, and *p*-xylene of 2:1:1 is reported over ordinary acid catalysts [43] such as  $\text{AlPO}_4\text{-Al}_2\text{O}_3$  [25] and Nafion-H [27]. The preferential formation of *o*-xylene is also reported over large-pore zeolite Y [41,42] and mesoporous aluminosilicate MCM-41 [44]. Moreover, *o*-xylene is the first product in the cavity of medium-pore ZSM-5 [43]. This selectivity is explained theoretically on acidic catalysts [45,46] by electrophilic attack on the aromatic ring [47] under kinetic control [25]. On the other hand, almost no methylation of the side chain to produce ethylbenzene proceeded except for over Mo cluster. This side chain alkylation is generally accepted over base catalysts such as

Table 1  
Methylation of toluene with methanol<sup>a</sup>

Supported cluster	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>							
		Benzene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene	1,2,3-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	Ethylbenzene
$[(\text{Nb}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$	3.0	3.9	45.7	20.5	23.7	1.9	2.7	0.0	1.7
$(\text{H}_3\text{O})_2[(\text{Mo}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$	1.8	33.8	16.7	19.1	17.4	0.0	0.0	0.0	12.9
$[(\text{Ta}_6\text{Cl}_{12})\text{Cl}_2(\text{H}_2\text{O})_4]\cdot 4\text{H}_2\text{O}$	2.2	2.8	44.5	20.5	26.5	1.3	2.4	0.0	2.1
$(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$	10.5	3.2	37.7	21.4	24.2	5.0	7.3	0.4	0.8
$(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}^d$	1.0	50.9	14.9	13.4	10.6	3.6	1.4	2.1	3.2
$(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}^e$	4.2	6.9	41.1	21.0	23.5	2.3	3.6	0.0	1.6
$(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}^f$	7.2	0.0	43.5	20.9	24.2	3.9	6.5	0.0	1.0
$\text{Re}_3\text{Cl}_9$	0.0								
$\text{Re}_3\text{Cl}_9^e$	1.7	79.5	2.2	6.0	4.0	0.0	0.0	0.0	8.3
$\text{SiO}_2$	0.0								
W metal	0.0								
$\text{Na}_2\text{WO}_4\cdot 2\text{H}_2\text{O}^g$	0.0								

<sup>a</sup> After treatment of supported cluster (5 wt.% on silica gel, 200 mg) in a stream of  $\text{H}_2$  (120 mL/h) at  $450^\circ\text{C}$  for 1 h. Reaction was started by introduction of a toluene–methanol mixture (0.10 mL/h, 0.68 mmol/h each) at the same temperature.

<sup>b</sup> Conversion = products/(products + recovered ethylbenzene)  $\times$  100 (%) after 4 h of reaction.

<sup>c</sup> Selectivity = product/total amount of products  $\times$  100 (%) after 4 h of reaction.

<sup>d</sup> Unsupported crushed crystalline cluster (150–200 mesh, 200 mg).

<sup>e</sup> Under He.

<sup>f</sup> Under  $\text{N}_2$ .

<sup>g</sup> 5 wt.% on silica gel, 200 mg.

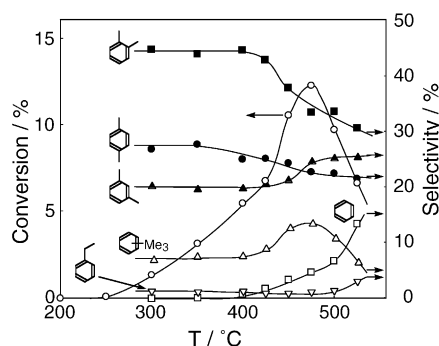


Fig. 2. Effect of temperature on the reaction of toluene with methanol over  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (**1**)/ $\text{SiO}_2$  under an  $\text{H}_2$  stream. Both pre-treatment and reaction temperatures were altered concomitantly. Other reaction conditions are the same as in Fig. 1. Conversion = products/(products + recovered toluene)  $\times$  100 (%), selectivity = product/total amount of products  $\times$  100 (%) based on aromatic compounds 4 h after the reaction started.

basic Y-zeolite [48], potassium-cation-exchanged zeolite [49], Cs-exchanged zeolite, alkali-impregnated carbon [50], and magnesia [51]. Thus, clusters of Nb, Ta, and W exhibited acidic character in the catalysis.

When supported **1** was treated in the same way in a helium or nitrogen stream, its selectivity remained virtually the same as listed in Table 1. However, its catalytic activity became rather low, indicating the participation of hydrogen molecules. Metallic rhenium that resulted from rhenium chloride,  $\text{Re}_3\text{Cl}_9$ , by hydrogen reduction under the reaction conditions [12] had no catalytic activity. However, the rhenium cluster catalyzed demethylation under helium.

The effects of temperature on reactivity and product selectivity over **1** are presented in Fig. 2. There are two obvious aspects in the reaction. Catalytic activity appeared above  $250^\circ\text{C}$  and increased with increasing temperature up to  $400^\circ\text{C}$  with constant selectivity. At temperatures above  $475^\circ\text{C}$ , the activity decreased with increasing temperature and the selectivity changed with temperature: the selectivity for trimethylbenzenes as well as for *o*- and *p*-xylenes decreased, but those for benzene and *m*-xylene increased with increasing temperature. Thus, an apparent isomerization proceeded by the reversible methylation and the isomeric distribution of xylenes approached the thermodynamic equilibrium distribution [52].

We have reported, based on XRD analyses, that unsupported molecular crystals of **1** began to lose their water of crystallization and protonated water, converting to an aquated cluster complex  $[(\text{W}_6\text{Cl}_8)\text{Cl}_4(\text{H}_2\text{O})_2]$  above  $100^\circ\text{C}$  (Eq. (1)), and that they changed to a chlorine-bridged three-dimensional solid state cluster  $[(\text{W}_6\text{Cl}_8)\text{Cl}_2\text{Cl}_4/2]$  (**2**) with low crystallinity above  $300^\circ\text{C}$  (Eq. (2)). The eliminated hydrogen chloride as well as water was removed in the stream of hydrogen:

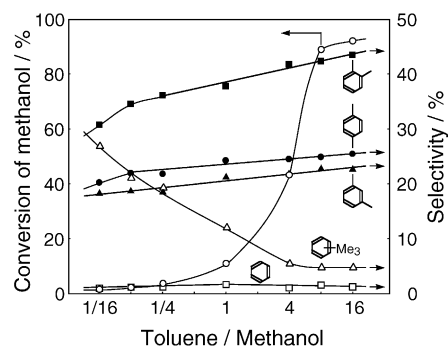
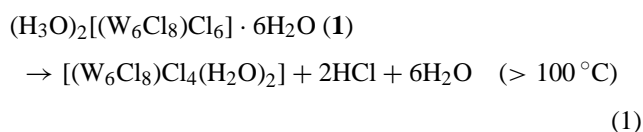
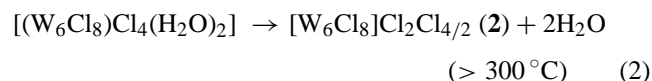


Fig. 3. Effect of the amount of toluene on the reaction with methanol over  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (**1**)/ $\text{SiO}_2$  under an  $\text{H}_2$  stream. Methanol,  $28\ \mu\text{L}/\text{h}$  ( $0.68\ \text{mmol}/\text{h}$ ). Other reaction conditions were the same as in Fig. 1. Selectivity for ethylbenzene was less than 1% and omitted for clarity. Conversion = products/(products + recovered methanol)  $\times$  100 (%), selectivity = product/total amount of products  $\times$  100 (%) based on aromatic compounds 4 h after the reaction started.



The octahedral cluster framework of  $\text{W}_6$  in **2** was definitely retained up to  $400^\circ\text{C}$  in a hydrogen stream [11]. Although the present catalyst employed was in the form of a supported cluster on  $\text{SiO}_2$ , this supported cluster would retain the cluster framework since the selectivity was sustained up to  $400^\circ\text{C}$ , as shown in Fig. 2. Treatment of **1** above  $450^\circ\text{C}$  exhibited neither obvious Raman peaks attributable to the  $\text{W}_6$  metal framework nor XRD patterns assignable to **2** [11]. However, when the  $450^\circ\text{C}$ -treated dark brown sample was washed with methanol followed by filtration and acidification with hydrochloric acid, **1** was recovered in 69% yield. Cluster **1** was partly disrupted but a large portion should be strongly deformed to change its vibrational modes as well as its crystal structure, and hence the selectivity changed.

### 3.2. Effect of the amount of toluene and methanol

The effect of the amount of toluene on the methylation over supported **1** is presented in Fig. 3. The conversion of methanol increased with increasing amount of toluene, and about 90% of the methanol was efficiently utilized for the methylation in the presence of toluene more than eight times the molar amount of methanol, suggesting the stronger adsorption of methanol. When 1/16 equivalent of toluene was employed, the apparent conversion of methanol was only 1.7%. This conversion may be small; however, it corresponds to 27% conversion of toluene used under an ample supply of methanol, implying weaker adsorption of toluene than methanol. The increase in xylene selectivity and the decrease in trimethylbenzene selectivity with increasing amount of toluene can be elucidated by the relative abundance of toluene. The relative selectiv-

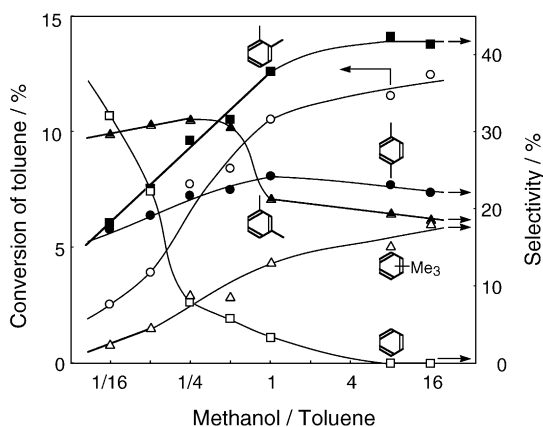


Fig. 4. Effect of the amount of methanol on the reaction with toluene over  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (**1**)/ $\text{SiO}_2$  under an  $\text{H}_2$  stream. Toluene,  $72 \mu\text{L/h}$  ( $0.68 \text{ mmol/h}$ ). Other reaction conditions were the same as in Fig. 1. Selectivity for ethylbenzene was less than 1% and omitted for clarity. Conversion = products/(products + recovered toluene)  $\times$  100 (%), selectivity = product/total amount of products  $\times$  100 (%) based on aromatic compounds 4 h after the reaction started.

ities for xylenes were not affected by the amount of toluene added, and *o*-xylene was obtained predominantly throughout. In the toluene methylation with methanol over acidic zeolite catalysts, methanol is strongly adsorbed in competitive adsorption with toluene [43]. The relative selectivities for xylenes were practically constant under kinetic control with an *o*-, *m*-, and *p*-xylene selectivity of 2:1:1 [25,26]. On the whole, the selectivity profiles illustrated in Fig. 3 are reasonable.

The effect of the amount of methanol is presented in Fig. 4. The conversion of toluene increased with increasing amount of methanol. However, the maximum conversion of toluene was not more than 15%, even when a 16-fold excess amount of methanol was employed, which also demonstrates that the adsorption of toluene was weaker than that of methanol. It is generally accepted that the alkylation of toluene with methanol proceeds via electrophilic substitution [28], and that a Brønsted acid site on zeolite catalysts is the active center and is covered with methanol [47]. The strongly adsorbed methanol [43] is activated to a carbenium ion, which reacts with weakly adsorbed toluene [31] or toluene in the cavity of zeolites through the Eley–Rideal mechanism [26,43].

One of the remarkable features of the selectivities shown in Fig. 4 is that demethylation of toluene increased significantly with decreasing amounts of methanol. The selectivity ratio for *o*-, *m*-, and *p*-xylenes is the same as that shown in Fig. 3, as long as the methanol/toluene ratio is greater than 1. In contrast, the selectivity for *m*-xylene, which is thermodynamically the most stable isomer among the three [52], increased with decreasing methanol fraction. Apparent isomerization was also shown under conditions of insufficient alkylating reagent.

### 3.3. Methylation and demethylation of methylbenzenes

Methylation of methylbenzenes over supported **1** is summarized in Table 2. Unsubstituted benzene did not react under the conditions; however, methylation of methylbenzenes other than hexamethylbenzene proceeded. The increasing reactivity order of toluene, xylenes, and trimethylbenzenes accords with the increasing proton affinity order of polymethyl-substituted benzenes [53]. The same reactivity order is reported on the Nafion-H catalyst [27]. Hence, the acid site on **1** would catalyze this electrophilic substitution. Side chain methylation of toluene occurred in 0.8% selectivity. However, no other side chain methylations of the other methylbenzenes were observed at all, which precludes base catalysis.

Successive methylation of toluene proceeded, as Table 1 shows. The same feature was observed for xylenes, which yielded trimethylbenzenes as the main product and tetramethylbenzenes as a by-product. Generally, this type of low substrate selectivity in which the initial product successively reacts is observed over some other catalysts: Nafion-H [27],  $\text{AlPO}_4\text{-Al}_2\text{O}_3$  [25,26],  $\text{Al}_{13}$ -pillared montmorillonite [24], and mesoporous MCM-41 [44]. A highly energetic methylation species is assumed to participate in the reaction [27].

Xylene methylation afforded 1,2,4-trimethylbenzene preferentially, irrespective of the equilibrium distribution, which contains a maximum amount of the 1,3,5-isomer [54], as shown in Table 2. Essentially the same consequence was observed for  $\text{AlPO}_4\text{-Al}_2\text{O}_3$  [25] and Nafion-H catalysts [27]. The 2-position of *p*-xylene is unique, the 4-position of *o*-xylene is sterically not crowded, and the 4-position of *m*-xylene is electron-rich with less steric hindrance. In all cases, 1,2,4-trimethylbenzene is expected as the main product in the electrophilic substitution of the aromatic rings. On the other hand, the formation of 1,3,5-trimethylbenzene was minor in all cases, since it can be formed only from *m*-xylene, as long as the methyl migration can be ignored and the electron density of the 5-position of *m*-xylene is low.

In methylation of xylenes, isomerization and demethylation were observed in 10–20% and 4–9% selectivity, respectively. Superimposition of these reactions complicated the methylation. These side reactions were pronounced in the absence of methanol. When *o*- and *p*-xylenes were allowed to react in the absence of methanol, the main reaction changed to isomerization, yielding thermodynamically stable *m*-xylene, as shown in Table 2. Demethylation, as well as methylation, proceeded in around 10% selectivity.

When the three isomers of trimethylbenzene were allowed to react with methanol, isomerization proceeded mainly. A predominant side reaction was methylation yielding 1,2,3,5-tetramethylbenzene, which can be formed by direct methylation of each trimethylbenzene. The distribution of the tetramethylbenzene isomers is roughly proportional to that in equilibrium at  $450^\circ\text{C}$  [54]. Demethylation of trimethylbenzenes was also observed in around 10% selectivity. Similarly, tetramethylbenzenes underwent those three reactions. Thus,

Table 2  
Methylation of methylbenzenes with methanol over  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6] \cdot 6\text{H}_2\text{O}$  (**1**)/ $\text{SiO}_2$  catalyst<sup>a</sup>

Substrate	Conversion (%) <sup>b</sup>	Selectivity (%) <sup>c</sup>												
		Benzene	Toluene	<i>o</i> -Xylene	<i>m</i> -Xylene	<i>p</i> -Xylene	1,2,3- Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,4- Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,3,5- Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	1,2,3,4- Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	1,2,3,5- Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	1,2,4,5- Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	Me <sub>5</sub> C <sub>6</sub> H	Me <sub>6</sub> C <sub>6</sub>
Benzene	0.0													
Toluene <sup>d</sup>	10.5	3.2	–	37.7	21.4	24.2	4.9	7.3	0.5	0.0	0.0	0.0	0.0	0.0
<i>o</i> -Xylene	29.4	0.0	3.7	–	3.0	8.9	20.8	35.8	2.1	10.8	8.7	6.4	0.0	0.0
<i>o</i> -Xylene <sup>e</sup>	24.6	0.9	11.2	–	67.3	9.6	1.3	7.5	1.6	0.1	0.4	0.1	0.1	0.0
<i>m</i> -Xylene	18.4	0.0	1.4	1.7	–	17.9	17.2	40.9	4.6	5.0	6.2	4.9	0.0	0.0
<i>p</i> -Xylene	18.8	0.0	8.7	3.1	18.0	–	2.4	52.8	2.4	1.9	6.0	4.6	0.0	0.0
<i>p</i> -Xylene <sup>e</sup>	78.5	1.4	14.4	21.1	52.7	–	0.8	6.7	2.4	0.0	0.4	0.1	0.0	0.0
1,2,3-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	24.4	0.0	2.6	8.0	6.1	0.2	–	37.5	1.7	1.5	33.0	6.0	3.4	0.0
1,2,4-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	22.4	1.1	0.5	4.4	5.7	2.6	24.3	–	29.9	4.0	14.4	11.7	1.5	0.0
1,3,5-Me <sub>3</sub> C <sub>6</sub> H <sub>3</sub>	94.7	1.1	0.8	2.5	4.7	1.8	15.6	35.9	–	4.2	16.3	12.2	4.7	0.2
1,2,3,4-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub>	81.7	0.1	0.1	0.1	0.1	0.0	2.0	3.2	0.5	–	37.1	25.9	30.4	0.5
1,2,3,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub> <sup>f</sup>	28.5	1.9	0.8	0.1	0.2	0.1	1.1	3.5	2.4	8.5	–	33.6	47.2	0.4
1,2,4,5-Me <sub>4</sub> C <sub>6</sub> H <sub>2</sub> <sup>g</sup>	57.3	0.0	1.6	0.9	1.4	0.7	2.6	12.4	5.4	19.4	11.2	–	44.5	0.0
Me <sub>5</sub> C <sub>6</sub> H <sup>h</sup>	62.7	–	5.6	0.3	1.2	0.8	2.0	8.7	1.4	9.2	33.2	35.1	–	2.3
Me <sub>6</sub> C <sub>6</sub> <sup>i</sup>	87.2	–	7.0	–	0.9	0.5	0.2	0.9	3.1	0.4	3.3	10.0	6.8	66.8
Me <sub>6</sub> C <sub>6</sub> <sup>j</sup>	96.4	–	9.4	1.2	0.8	0.2	1.1	4.0	0.9	4.4	14.8	10.4	52.9	–
Me <sub>6</sub> C <sub>6</sub> <sup>k</sup>	21.5	–	12.0	0.1	0.2	0.1	0.0	0.5	0.4	1.9	4.1	2.3	78.5	–
Me <sub>6</sub> C <sub>6</sub> <sup>l</sup>	8.5	–	14.2	0.1	0.1	0.1	0.0	0.7	0.3	1.3	3.0	4.8	75.5	–
Equilibrium distribution <sup>m</sup>				25	52	23	16	32	52	18	38	44		
Relative basicity <sup>n</sup>			0.01	3	9	1	18	18	1400	85	2800	60	4350	44500

<sup>a</sup> After treatment of supported cluster (200 mg) in a stream of H<sub>2</sub> (120 mL/h) at 450 °C for 1 h, reaction was started by the introduction of a mixture of substituted benzene and methanol (0.68 mmol/h each) at the same temperature.

<sup>b</sup> Conversion = products/(products + recovered ethylbenzene) × 100 (%) after 4 h of reaction.

<sup>c</sup> Selectivity = product/total amount of products × 100 (%) after 4 h of reaction.

<sup>d</sup> Ethylbenzene was produced in 0.8% selectivity.

<sup>e</sup> In the absence of methanol.

<sup>f</sup> 1,2,3,5-Me<sub>4</sub>C<sub>6</sub>H<sub>2</sub>:MeOH:ether = 1:1:5 (mole ratio, 1,2,3,5-Me<sub>4</sub>C<sub>6</sub>H<sub>2</sub> and MeOH 0.68 mmol/h each).

<sup>g</sup> 1,2,4,5-Me<sub>4</sub>C<sub>6</sub>H<sub>2</sub>:MeOH:ether = 1:1:1 (mole ratio, 0.68 mmol/h each).

<sup>h</sup> Me<sub>5</sub>C<sub>6</sub>H:MeOH:C<sub>6</sub>H<sub>6</sub> = 1:1:1 (mole ratio, 0.068 mmol/h each).

<sup>i</sup> Me<sub>6</sub>C<sub>6</sub>:MeOH:C<sub>6</sub>H<sub>6</sub> = 1:1:20 (mole ratio, Me<sub>6</sub>C<sub>6</sub> and MeOH 0.068 mmol/h each).

<sup>j</sup> Me<sub>6</sub>C<sub>6</sub>:C<sub>6</sub>H<sub>6</sub> = 1:20 (mole ratio, Me<sub>6</sub>C<sub>6</sub> 0.068 mmol/h), in the absence of MeOH.

<sup>k</sup> In He stream, Me<sub>6</sub>C<sub>6</sub>:MeOH:C<sub>6</sub>H<sub>6</sub> = 1:1:20 (mole ratio, Me<sub>6</sub>C<sub>6</sub> and MeOH 0.068 mmol/h each).

<sup>l</sup> In He stream, Me<sub>6</sub>C<sub>6</sub>:C<sub>6</sub>H<sub>6</sub> = 1:20 (mole ratio, Me<sub>6</sub>C<sub>6</sub> 0.068 mmol/h), in the absence of MeOH.

<sup>m</sup> Equilibrium distribution among three isomers of each di-, tri- and tetramethylbenzene at 450 °C [49,51].

<sup>n</sup> Relative basicity of benzene ring [50].

cluster **1** catalyzed methylation, demethylation, and isomerization of the polymethyl-substituted benzenes, and their ratio depended largely on the number of methyl substituents.

As Table 2 shows, methylation of pentamethylbenzene was difficult and demethylation proceeded almost exclusively, even in the presence of methanol. Demethylation of hexamethylbenzene also proceeded under hydrogen, both in the presence and absence of methanol. The same catalytic activities, methylation and demethylation, have been reported on an acidic large-pore zeolite, into which hexamethylbenzene can penetrate. H-beta catalyzed methylation of toluene with methanol [55,56] and demethylation of hexamethylbenzene under nitrogen [57] or polymethylbenzenes under helium [58].

In the reaction of pentamethylbenzene, toluene was formed in about 6% selectivity, regardless of the slight formation of xylenes. Table 2 also shows that toluene was produced from hexamethylbenzene in 7–14% selectivity in spite of the slight formation of xylenes and trimethylbenzenes under both hydrogen and helium streams. Benzene was used as a solvent in these experiments, as it is a good solvent for the reactants. Consequently, cluster **1** catalyzed intermolecular transfer of the methyl groups.

Table 2 shows that the conversion of hexamethylbenzene increased when the helium stream was replaced with a hydrogen stream. Similarly, an obvious accelerating effect of the hydrogen stream was observed in toluene methylation, as shown in Table 1. In contrast, W metal scarcely showed catalytic activity with hydrogen: when evaporated porous films of W metal were used for hydrogenation of ethylene, the catalytic activity was only 1/10,000 of that of Rh metal [59]. Group 6 metal atoms of the halide cluster complexes should be isoelectronic with the platinum metals by taking two or more electrons from the halogen ligands, as discussed previously [9,10]. The participation of hydrogen could be ascribed to this effect.

### 3.4. Adsorption of pyridine on the activated cluster

The IR spectrum of **1**/SiO<sub>2</sub> treated at 450 °C in a hydrogen stream followed by adsorption of pyridine is illustrated in Fig. 5 with related spectra. A band at 1445 cm<sup>-1</sup> attributable to hydrogen-bonded pyridine to the surface silanol group is common in each spectrum [60,61]. The two bands at 1540 and 1489 cm<sup>-1</sup> assignable to pyridinium ion in the spectrum of **1**/SiO<sub>2</sub>, both before and after the reaction, show the presence of a Brønsted acid site on **1**. However, there is no band that is characteristic of coordinatively bonded pyridine in the 1449–1460 cm<sup>-1</sup> region, and hence there is no Lewis acid site.

A previously proposed mechanism for the appearance of active sites on the cluster can be summarized as follows [11–14]. When **1** was heated under hydrogen gas above 100 °C, evolution of HCl gas commenced as expressed in Eq. (1) and it continued above 300 °C, implying an additional route other than Eq. (2). The retention of the octahedral

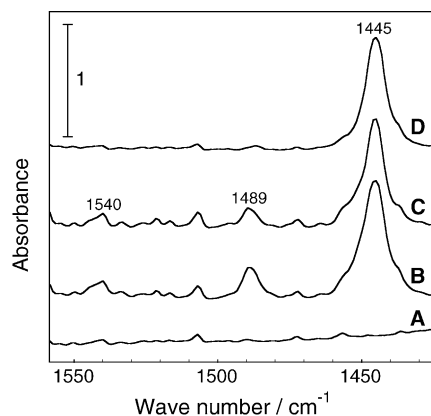


Fig. 5. IR spectra of pyridine adsorbed on (H<sub>3</sub>O)<sub>2</sub>[(W<sub>6</sub>Cl<sub>8</sub>)Cl<sub>6</sub>]·6H<sub>2</sub>O (**1**)/SiO<sub>2</sub>. Sample powder (15 mg) was pressed into a disk (10 mm diameter) and treated in a hydrogen stream at 450 °C for 1 h (A), followed by introduction of pyridine (B). Catalyst sample after 4 h of reaction (C) and unsupported silica gel (D) were treated in the same way.

cluster framework has been confirmed at least up to 400 °C by Raman spectrometry and XRD analysis, the latter also revealing the formation of a poorly crystallized solid state cluster of **2**. Elemental analyses showed that the total amount of W (72.4%) and Cl (26.7%) in the 400 °C-treated sample of **1** was 99.1%, and therefore some components, presumably originating from the water in **1**, were left in the treated sample. Very weak broad peaks attributable to W<sub>3</sub>O were observed by XRD analysis of the 450 °C-treated sample of **1**, which also supported some oxygen atoms being retained in the treated samples. Consequently, the halogen ligands would have reacted with the coordinated water, eliminating HCl to produce hydroxo or oxo species as expressed in Eqs. (3) and (4) in imperfect crystals of **2**, when the cluster was treated at above 300 °C.

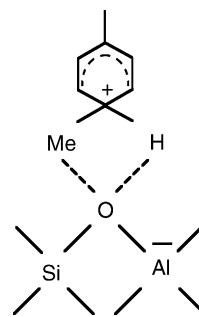
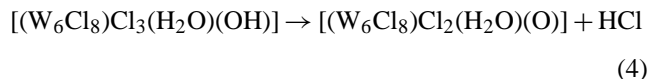
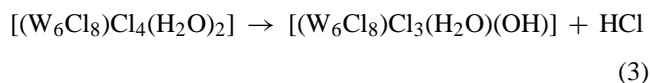


Fig. 6. Suggested intermediate in toluene alkylation with methanol over zeolite.

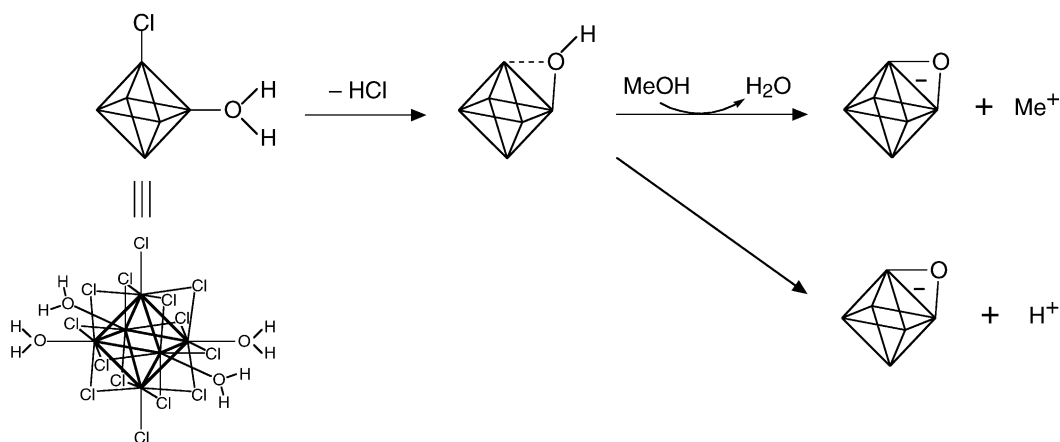


Fig. 7. Activation of halide cluster complex.

From the IR analyses of the adsorbed pyridine, the formation of a Brønsted acid site, presumably ascribed to the hydroxo species expressed in Eq. (3), was ascertained, which would be the catalytically active site of the reactions. In this case, Lewis acid sites cannot be generated. Similar examples of catalysis by Brønsted acid site originating from aqua ligands have been reported in heteropoly acids [62,63].

A possibility existed that the catalytic reaction proceeded on the oxygen atoms simply bridging Si and W atoms, and then a supported sample of  $\text{Na}_2\text{WO}_4$  on silica gel was prepared and applied to catalysis. As shown in Table 1, it had no catalytic activities for the methylation of toluene.

For toluene methylation with methanol over zeolite, the commonly accepted reaction scheme suggests that an activated form of methanol, the methyl cation, reacts with weakly adsorbed toluene, as illustrated in Fig. 6 [36,64]. In the cluster catalysis, this intermediate would be adopted by replacing the silica-alumina catalyst with the cluster moiety. Consequently, the activation of halide cluster complex and the mechanism for the methylation, demethylation, iso-

merization, and methyl transfer can be depicted as shown in Figs. 7 and 8.

#### 4. Conclusions

When the tungsten halide cluster  $(\text{H}_3\text{O})_2[(\text{W}_6\text{Cl}_8)\text{Cl}_6]\cdot 6\text{H}_2\text{O}$  (1) was treated in a stream of hydrogen above  $100^\circ\text{C}$ , it changed to an aqua complex  $[(\text{W}_6\text{Cl}_8)\text{Cl}_4(\text{H}_2\text{O})_2]$ . Above  $300^\circ\text{C}$  this complex successively turned to a poorly crystallized solid state complex  $[\text{W}_6\text{Cl}_8]\text{Cl}_2\text{Cl}_{4/2}$  (2) that contained a hydroxo complex such as  $[(\text{W}_6\text{Cl}_8)\text{Cl}_3(\text{H}_2\text{O})(\text{OH})]$ . This hydroxo group would exhibit a new type of Brønsted acid site, which catalyzed methylation with methanol, demethylation, isomerization, and intermolecular methyl transfer of methylbenzenes. Niobium, tantalum, and molybdenum halide clusters of the same metal framework also displayed the catalytic activity. A similar example of the appearance of a Brønsted acid site has been reported: heteropoly acid has several types of protons, one of which originates from its coordinated water.

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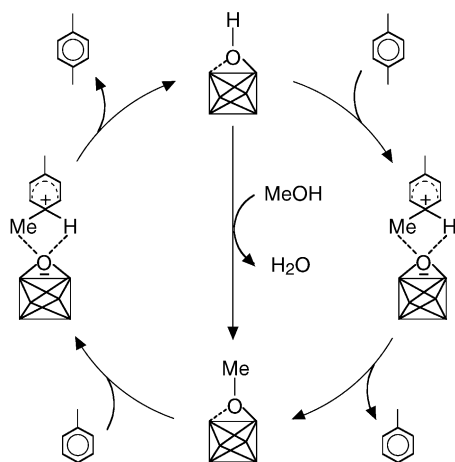


Fig. 8. Methylation and demethylation mechanism over halide cluster catalyst.



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