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Acid Strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ Heteropolyacid Catalysts as a Probe of Acid Catalysis for 2-Propanol Conversion Reaction

**Dong Ryul Park · Sang Hee Lee · Joohyung Lee ·
Sun Ho Song · Heesoo Kim · Ji Hwan Song ·
In Kyu Song**

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Abstract Acid strength of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0, 3, 6, 9$, and 12) Keggin heteropolyacid (HPA) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0, 3, 9, 15$, and 18) Wells-Dawson HPA catalysts was determined by NH_3-TPD measurements. Desorption peak temperature (acid strength) of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts showed the same trend with respect to tungsten substitution, and increased with increasing tungsten substitution in both families of HPA catalysts. In order to correlate the acid strength with the acid catalysis of HPAs, vapor-phase 2-propanol conversion reaction was carried out as a model reaction. Yield for propylene (a product formed by acid catalysis of HPA) increased with increasing tungsten substitution and with increasing desorption peak temperature (acid strength) across both HPA families, regardless of the identity of HPA catalyst (without HPA structural sensitivity). The acid strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts could be utilized as a probe of acid catalysis for 2-propanol conversion reaction.

Keywords Heteropolyacid catalyst · Keggin · Wells-Dawson · Acid catalysis · 2-Propanol conversion reaction

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D. R. Park · S. H. Lee · J. Lee · S. H. Song · H. Kim ·
I. K. Song (✉)
School of Chemical and Biological Engineering, Research
Center for Energy Conversion and Storage, Seoul National
University, Shinlim-dong, Kwanak-ku, Seoul 151-744,
South Korea
e-mail: inksong@snu.ac.kr

J. H. Song
Whimoon High School, Daechi-dong, Kangnam-ku,
Seoul 135-847, South Korea

1 Introduction

Heteropolyacids (HPAs) are early transition metal oxygen-anion clusters that exhibit a wide range of molecular sizes, compositions, and architectures [1–3]. One of the great advantages of HPA catalysts is that their catalytic properties can be tuned in a systematic way by replacing protons or by substituting framework transition metal atoms with different metals [4–7]. Their excellent thermal and chemical stability also makes HPAs good candidates for catalytic applications that may require harsh environments [8].

HPAs have been widely investigated as homogeneous and heterogeneous catalysts for acid–base and oxidation reactions [1–4]. HPAs are Brönsted acids, and retain stronger acid strength than the conventional solid acid catalysts such as acidic oxides and zeolites [9]. In addition, acid sites of HPA catalysts are more uniform and easier to control than those of other solid acid catalysts. The acid strength of HPA catalysts can be controlled by changing the molecular structure and composition of heteropolyanions [9].

Among various HPA structural classes, the Keggin HPAs have been used as catalysts in commercial processes [10–16]. However, the Wells-Dawson HPAs have attracted considerable attention as promising catalysts for several reactions such as MTBE (methyl *tert*-butyl ether) and ETBE (ethyl *tert*-butyl ether) syntheses [17–20]. Nonetheless, much progress has not been made on the catalytic performance of Wells-Dawson HPAs, and only limited information on the catalytic properties of Wells-Dawson HPAs is currently available.

In this work, acid strength of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) Keggin HPA and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0, 3, 9, 15$, and 18) Wells-Dawson HPA catalysts was examined and compared, with an aim of finding any similarity in acid catalysis between both families of HPA catalysts. The acid strength of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) Keggin HPA and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) Wells-Dawson HPA catalysts was measured by NH_3-TPD experiments. Vapor-phase 2-propanol conversion reaction was carried out as a model reaction to investigate the acid catalysis of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts. The measured acid strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts was then correlated with the acid catalysis of the HPA catalysts.

2 Experimental

2.1 $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) Keggin HPAs and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) Wells-Dawson HPAs

$H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) Keggin HPAs were purchased from Sigma-Aldrich and Nippon Inorganic Colors & Chem. $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) Wells-Dawson HPAs were prepared according to the similar method reported in the literature [8, 21–25]. Successful formation of Wells-Dawson structure of $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) HPA catalysts was confirmed by FT-IR (Nicolet, Magna 750) and ICP-AES (Shimadzu, ICPS-1000IV) analyses, as reported in our previous work [24]. $H_3PW_xMo_{12-x}O_{40}$ Keggin HPAs with $x = 0$, 3, 6, 9, and 12 were denoted as PMo_{12}, PW_3Mo_9, PW_6Mo_6, PW_9Mo_3, and PW_{12}, respectively. $H_6P_2W_xMo_{18-x}O_{62}$ Wells-Dawson HPAs with $x = 0$, 3, 9, 15, and 18 were denoted as P_2Mo_{18}, $P_2W_3Mo_{15}$, $P_2W_9Mo_9$, $P_2W_{15}Mo_3$, and P_2W_{18}, respectively.

2.2 NH_3-TPD Measurement

Acid strength of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts was determined by NH_3-TPD (temperature-programmed desorption) measurements. Each HPA catalyst (50 mg) was charged into a tubular quartz reactor of the conventional TPD apparatus. The catalyst was pretreated at 200 °C for 1 h under a flow of He (20 mL/min) to remove any physisorbed organic molecules. NH_3 (20 mL) was then pulsed into the reactor every minute at room temperature under a flow of He (5 mL/min), until the acid sites were saturated with NH_3. The physisorbed NH_3 was removed by evacuating the catalyst sample at 100 °C for 1 h. The furnace temperature was increased from room temperature to 700 °C at a heating rate of 5 °C/min under a flow of He (10 mL/min). The desorbed NH_3 was detected using a GC-MSD (Agilent, MSD-6890 N GC).

2.3 Vapor-Phase 2-Propanol Conversion Reaction

Vapor-phase 2-propanol conversion reaction over $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts was carried out in a continuous flow fixed-bed reactor at atmospheric pressure. Each catalyst (0.3 g) charged into a tubular quartz reactor was pretreated with a mixed stream of nitrogen (20 mL/min) and oxygen (10 mL/min) at 230 °C for 1 h. 2-Propanol (6.54×10^{-3} mol/h) was sufficiently vaporized by passing through a pre-heating zone and continuously fed into the reactor together with oxygen and nitrogen carrier. The feed composition (molar ratio) was fixed at 2-propanol (0.27):oxygen (1.0):nitrogen (2.0). The catalytic reaction was carried out at 200 °C for 5 h. Reaction products were periodically sampled and analyzed with a gas chromatograph (HP 5890II). Yield for propylene was calculated by multiplying conversion of 2-propanol and selectivity for propylene.

3 Results and Discussion

3.1 Acid Strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ Catalysts

Acid strength of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts was measured by NH_3-TPD experiments. Figure 1 shows the NH_3-TPD profiles of selected $H_3PW_xMo_{12-x}O_{40}$ Keggin HPA and $H_6P_2W_xMo_{18-x}O_{62}$ Wells-Dawson HPA catalysts. It was found that the desorption peak temperature increased in order of $PMo_{12} < PW_6Mo_6 < PW_{12}$ for $H_3PW_xMo_{12-x}O_{40}$ catalysts, and $P_2Mo_{18} < P_2W_9Mo_9 < P_2W_{18}$ for $H_6P_2W_xMo_{18-x}O_{62}$ catalysts. The desorption peak temperature of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts showed the same trend with respect to tungsten substitution, in good agreement with the previous result reported for $H_3PW_xMo_{12-x}O_{40}$ Keggin HPA catalysts [9, 26]. The higher desorption peak temperature corresponds to the higher acid strength of HPA catalyst. In this work, therefore, the desorption peak temperature was used as an index for the acid strength of HPA catalyst.

Figure 2 shows the desorption peak temperature (acid strength) of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts, plotted as a function of tungsten substitution. The desorption peak temperature (acid strength) increased in order of PMo_{12} (207 °C) $<$ PW_3Mo_9 (234 °C) $<$ PW_6Mo_6 (240 °C) $<$ PW_9Mo_3 (290 °C) $<$ PW_{12} (593 °C) for $H_3PW_xMo_{12-x}O_{40}$ Keggin HPA catalysts, and P_2Mo_{18} (194 °C) $<$ $P_2W_3Mo_{15}$ (220 °C) $<$ $P_2W_9Mo_9$ (380 °C) $<$ $P_2W_{15}Mo_3$ (480 °C) $<$ P_2W_{18} (561 °C) for $H_6P_2W_xMo_{18-x}O_{62}$ Wells-Dawson HPA catalysts. It was revealed that the

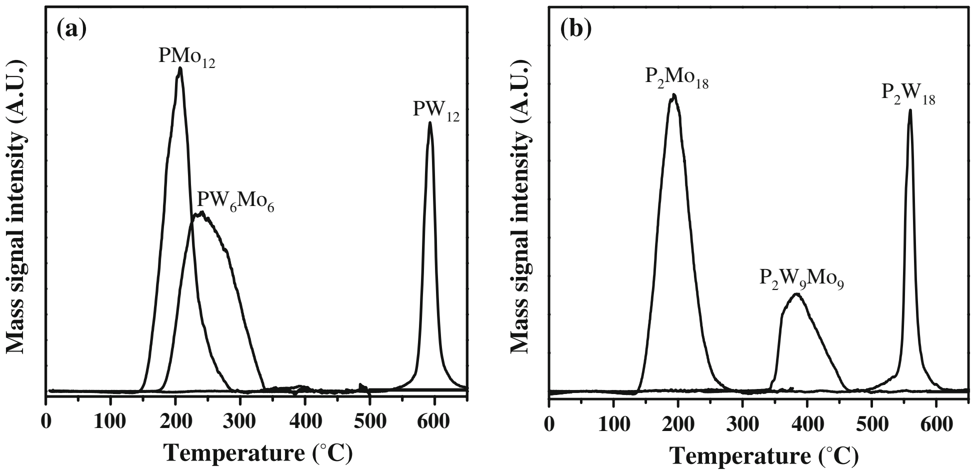

Fig. 1 NH_3-TPD profiles of (**a**) PMo_{12}, PW_6Mo_6, and PW_{12} Keggin HPA catalysts and (**b**) P_2Mo_{18}, $P_2W_9Mo_9$, and P_2W_{18} Wells-Dawson HPA catalysts

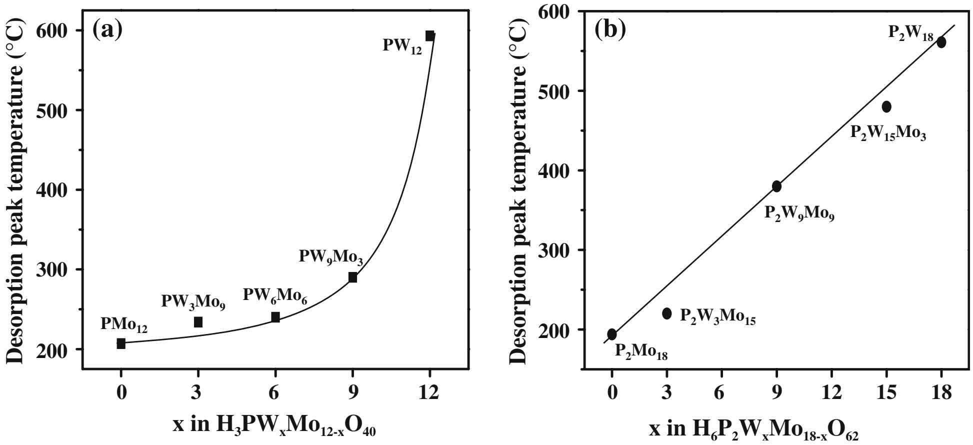

Fig. 2 Desorption peak temperature (acid strength) of (**a**) $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and (**b**) $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts, plotted as a function of tungsten substitution

desorption peak temperature (acid strength) of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts showed the same trend with respect to tungsten substitution, and increased with increasing tungsten substitution in both Keggin and Wells-Dawson HPA catalysts.

3.2 Acid Catalysis for Vapor-Phase 2-Propanol Conversion Reaction

In order to correlate the acid catalysis with the acid strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts, vapor-phase 2-propanol conversion reaction was carried out as a model reaction. In the catalytic reaction, propylene and acetone were produced as major products. Negligible amounts of CO, CO_2, and isopropyl ether were detected as by-products. It is known that propylene is formed by the acid catalysis of HPA, while acetone is produced by the oxidation catalysis of HPA [27, 28]. In our catalytic reaction, selectivity for propylene was more than 75%, while selectivity for acetone was less than 25%. This means that HPA catalysts dominantly affected the acid catalysis under our experimental conditions, indicating that 2-propanol conversion reaction was suitable as a model reaction to probe the acid catalysis of HPA catalysts.

Figure 3 shows the typical catalytic performance of $H_3PMo_{12}O_{40}$ catalyst in the vapor-phase 2-propanol conversion reaction with time on stream at 200 °C. $H_3PMo_{12}O_{40}$ catalyst experienced a slight deactivation at the initial stage. However, $H_3PMo_{12}O_{40}$ catalyst showed a steady-state catalytic performance after a 3 h-reaction. The catalytic performance behavior of the other catalysts with respect to reaction time was similar to that of $H_3PMo_{12}O_{40}$ catalyst.

Steady-state catalytic performance data obtained after a 5 h-reaction were used for the correlation with the acid strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts. Figure 4 shows the yield for propylene over $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts, plotted as a function of tungsten substitution. Yield for propylene increased monotonically with increasing tungsten substitution in both series of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts. The yield for propylene increased in the order of PMo_{12} (53.7%) $<$ PW_3Mo_9

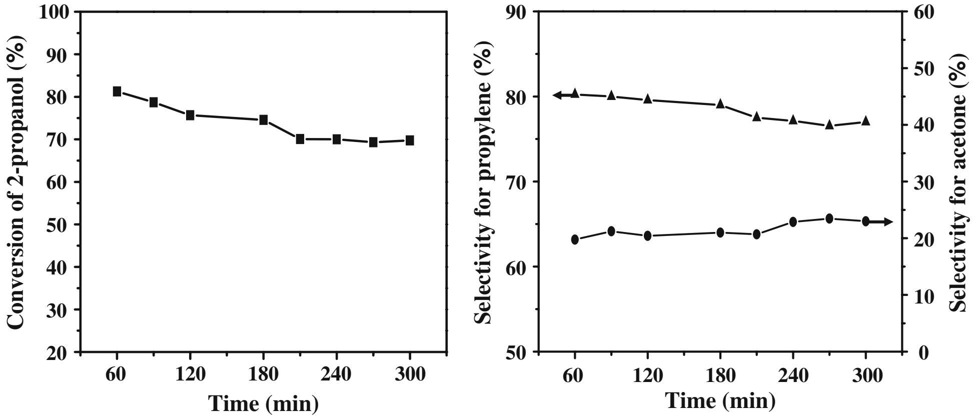

Fig. 3 Typical catalytic performance of $H_3PMo_{12}O_{40}$ catalyst in the vapor-phase 2-propanol conversion reaction with time on stream at 200 °C

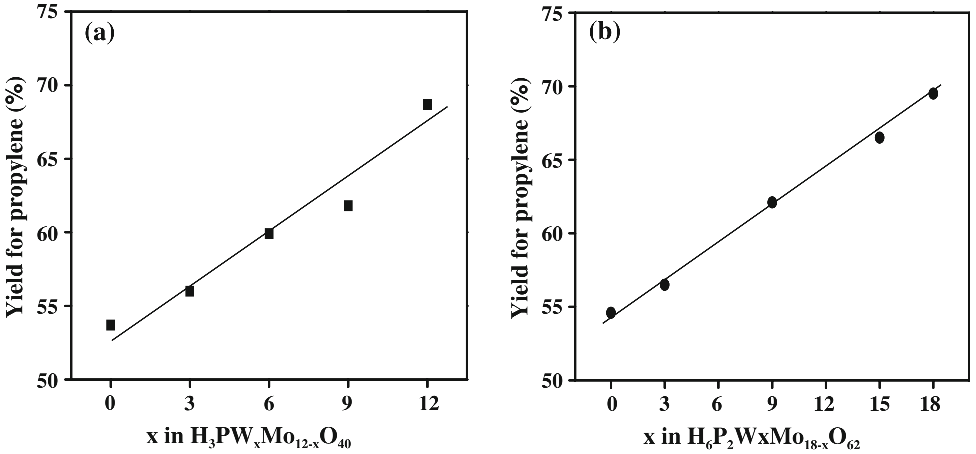

Fig. 4 Yield for propylene over (**a**) $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and (**b**) $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts, plotted as a function of tungsten substitution

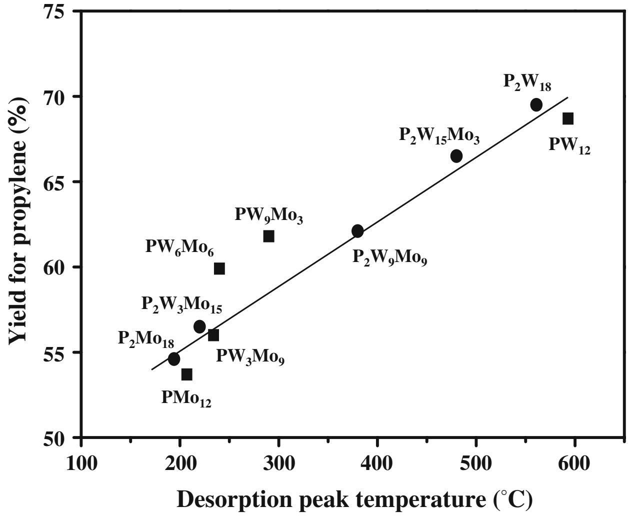

Fig. 5 Correlation between desorption peak temperature (acid strength) and yield for propylene, established for $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts

(560%) < PW_6Mo_6 (59.9%) < PW_9Mo_3 (61.8%) < PW_{12} (68.7%) for $H_3PW_xMo_{12-x}O_{40}$ Keggin HPA catalysts, and P_2Mo_{18} (54.6%) < $P_2W_3Mo_{15}$ (56.5%) < $P_2W_9Mo_9$ (62.1%) < $P_2W_{15}Mo_3$ (66.5%) < P_2W_{18} (69.5%) for $H_6P_2W_xMo_{18-x}O_{62}$ Wells-Dawson HPA catalysts. These trends were well consistent with the trends of acid strength of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts (Fig. 2). The acid catalysis and acid strength increased with increasing tungsten substitution in both Keggin and Wells-Dawson HPA catalysts.

3.3 Correlation Between Acid Strength and Acid Catalysis

Figure 5 shows the correlation between desorption peak temperature (acid strength) and yield for propylene, established for $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts. It should be noted that yield for propylene increased with increasing desorption peak temperature (acid strength) across both HPA families, regardless of the identity of HPA catalyst (without HPA structural sensitivity). This means that the acid strength of HPA catalyst can be utilized as a probe of acid catalysis for this model reaction. It also implies that an HPA catalyst can be rationally designed to have a suitable acid strength to meet the need for acid reaction by controlling the structure and composition of HPA catalyst.

4 Conclusions

Acid strength and acid catalysis of $H_3PW_xMo_{12-x}O_{40}$ Keggin HPA and $H_6P_2W_xMo_{18-x}O_{62}$ Wells-Dawson HPA catalysts were examined and compared. The desorption peak temperature (acid strength) of $H_3PW_xMo_{12-x}O_{40}$ ($x = 0$, 3, 6, 9, and 12) and $H_6P_2W_xMo_{18-x}O_{62}$ ($x = 0$, 3, 9, 15, and 18) catalysts determined by NH_3-TPD measurements increased with increasing tungsten substitution in both series of HPA catalysts. In the 2-propanol conversion reaction, yield for propylene (a product formed by acid catalysis of HPA) increased with increasing tungsten substitution in both families of HPA catalysts. The correlation between acid strength and acid catalysis for propylene formation revealed that the acid catalysis increased with increasing acid strength of the HPA catalyst, regardless of the identity of HPA catalyst (without HPA structural sensitivity). Thus, the acid strength could be utilized as a probe of acid catalysis of $H_3PW_xMo_{12-x}O_{40}$ and $H_6P_2W_xMo_{18-x}O_{62}$ catalysts for 2-propanol conversion reaction.

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