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RAPID COMMUNICATION

Acidity and acid catalysis of polyatom-substituted $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin heteropolyacid catalysts

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Abstract−Acidity of polyatom-substituted $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin heteropolyacids (HPAs) was measured by NH_3-TPD experiments. Acidity decreased in the order of $H_3PW_{11}W_1O_{40}$>$H_4PW_{11}V_1O_{40}$>$H_4PW_{11}Nb_1O_{40}$>$H_4PW_{11}Ta_1O_{40}$. Vapor-phase dehydration of cyclohexanol was conducted as a model reaction to correlate the acidity with the acid catalysis of HPA catalysts. Yield for cyclohexene (a product by acid catalysis) increased with increasing acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts. The acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts could be utilized as a probe of acid catalysis for dehydration of cyclohexanol.

Key words: Heteropolyacid, Polyatom Substitution, Acid Catalysis, Dehydration of Cyclohexanol

INTRODUCTION

Heteropolyacids (HPAs) are early transition metal oxygen-anion clusters that exhibit a wide range of molecular sizes, compositions, and architectures [1,2]. Among various HPA structural classes, the Keggin HPAs have been employed as catalysts in commercial processes [3-5]. One of the great advantages of HPA catalysts is that their catalytic properties can be tuned in a systematic way by changing the identity of charge-compensating counter-cations, central heteroatoms, and framework polyatoms [6-11].

HPAs have been widely investigated as homogeneous and heterogeneous catalysts for acid-base and oxidation reactions [1-3,12,13]. HPAs retain stronger acidity than the conventional solid acid catalysts such as acidic oxides and zeolites [5]. Moreover, acid sites of HPA catalysts are more uniform and easier to control than those of other solid acid catalysts [5]. These make HPAs good candidates for acid catalytic applications under mild conditions.

Acid catalysis over HPAs has economical advantages and green benefits [14]. Among various HPA catalysts, tungsten-containing HPAs are widely used as catalysts in several acid-catalyzed reactions due to their high acid strength and thermal stability. Some of these examples include hydration of propylene [15] and isobutene [16], polymerization of tetrahydrofuran [17], and vapor-phase MTBE (methyl *tert*-butyl ether) and ETBE (ethyl *tert*-butyl ether) syntheses [18-21]. Although acid properties of HPA catalysts can be controlled by changing the composition of framework polyatom, no systematic investigation has been made on the acid properties and acid catalysis of group 5 metal (V, Nb, Ta)-substituted tungsten-containing HPA catalysts. Furthermore, only limited information on the catalytic properties of group 5 metal (V, Nb, Ta)-substituted tungsten-containing HPA catalysts is currently available.

In this work, acidity of group 5 metal-substituted tungsten-containing $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts was measured by NH_3-TPD experiments. Vapor-phase dehydration of cyclohexanol was carried out as a model reaction in order to investigate the acid catalysis of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts. The measured acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts was then correlated with the acid catalysis of the HPA catalysts.

EXPERIMENTAL

1. Polyatom-substituted $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPAs

Polyatom-substituted $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPAs were prepared according to a similar method reported in the literature [22-24]. Successful formation of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPAs was confirmed by FT-IR (Nicolet, Magna 750) and ^{31}P NMR (Bruker, AVANCE 600) analyses, as reported in our previous work [22]. In this work, $H_nPW_{11}M_1O_{40}$ Keggin HPAs with M=V, Nb, Ta, and W were denoted as $PW_{11}V_1$, $PW_{11}Nb_1$, $PW_{11}Ta_1$, and $PW_{11}W_1$, respectively.

2. Acidity Measurement of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPAs

Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPAs was measured by NH_3-TPD (temperature-programmed desorption) experiments. Each HPA catalyst (200 mg) was charged into a tubular quartz reactor of the TPD apparatus (BEL Japan, BELCAT B). The catalyst was pretreated at 200 °C for 2 h under a flow of He (50 ml/min) to remove any physisorbed organic molecules. NH_3 (50 ml/min) was then introduced into the reactor at 50 °C for 30 min. Physisorbed NH_3 was removed at 150 °C for 1 h under a flow of He (50 ml/min). After the sample was cooled, the furnace temper-

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ature was increased from room temperature to 700 °C at a heating rate of 5 °C/min under a flow of He (30 ml/min). The desorbed NH_3 was detected by using a TCD (thermal conductivity detector).

3. Acid Catalysis over $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPAs

To investigate the acid catalysis of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts, vapor-phase dehydration of cyclohexanol was carried out as a model reaction. Vapor-phase dehydration of cyclohexanol over $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts was performed in a continuous flow fixed-bed reactor at atmospheric pressure. Each catalyst (200 mg) charged into a tubular quartz reactor was pretreated with a stream of air (25 ml/min) at 240 °C for 1 h. Cyclohexanol (4.8×10^{-3} mol/h) was sufficiently vaporized by passing through a pre-heating zone and was continuously fed into the reactor together with air carrier (25 ml/min). Feed composition (molar ratio) was fixed at cyclohexanol (0.08): air (1.0). Catalytic reaction was carried out at 220 °C for 5 h. Reaction products were periodically sampled and analyzed with an on-line gas chromatograph (HP 5890II). Conversion of cyclohexanol and selectivity for products were calculated on the basis of carbon balance. Yield for cyclohexene was calculated by multiplying conversion of cyclohexanol and selectivity for cyclohexene.

RESULTS AND DISCUSSION

1. Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA Catalysts

Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts was measured by NH_3-TPD experiments. Fig. 1 shows the NH_3-TPD profiles of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts. It was found that peak area decreased in the order of $PW_{11}W_1$>$PW_{11}V_1$>$PW_{11}Nb_1$>$PW_{11}Ta_1$. Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts was determined from the peak area of desorbed NH_3. Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts is summarized in Table 1. Acidity decreased in the order of $PW_{11}W_1$>$PW_{11}V_1$>$PW_{11}Nb_1$>$PW_{11}Ta_1$. The acidity trend of $PW_{11}W_1$>$PW_{11}V_1$ is in good agreement with the result reported in a previous work [25]. Among the $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts, $PW_{11}W_1$ catalyst exhibited the largest acidity.

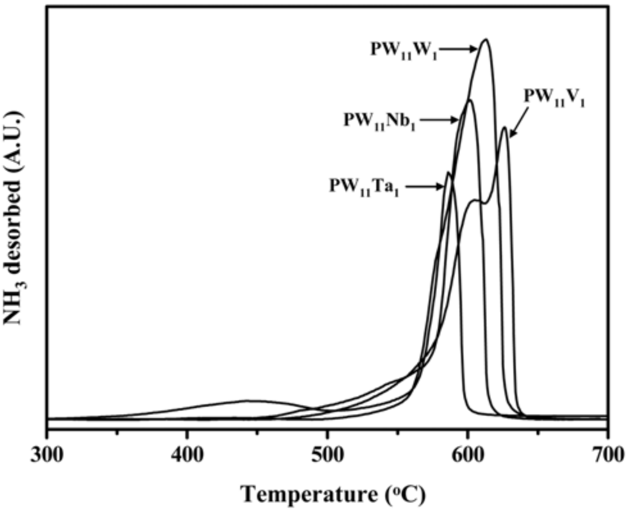

Fig. 1. NH_3-TPD profiles of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts.

Table 1. Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts

Catalyst	Acidity (μmol-NH_3/g-catalyst)
$PW_{11}V_1$	281.4
$PW_{11}Nb_1$	234.5
$PW_{11}Ta_1$	175.6
$PW_{11}W_1$	325.1

2. Acid Catalysis for Vapor-phase Dehydration of Cyclohexanol

To correlate the acid catalysis with the acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts, vapor-phase dehydration of cyclohexanol was carried out as a model reaction. In the catalytic reactions, cyclohexene was produced by the acid catalytic function of HPA via dehydration reaction, while cyclohexanone was formed

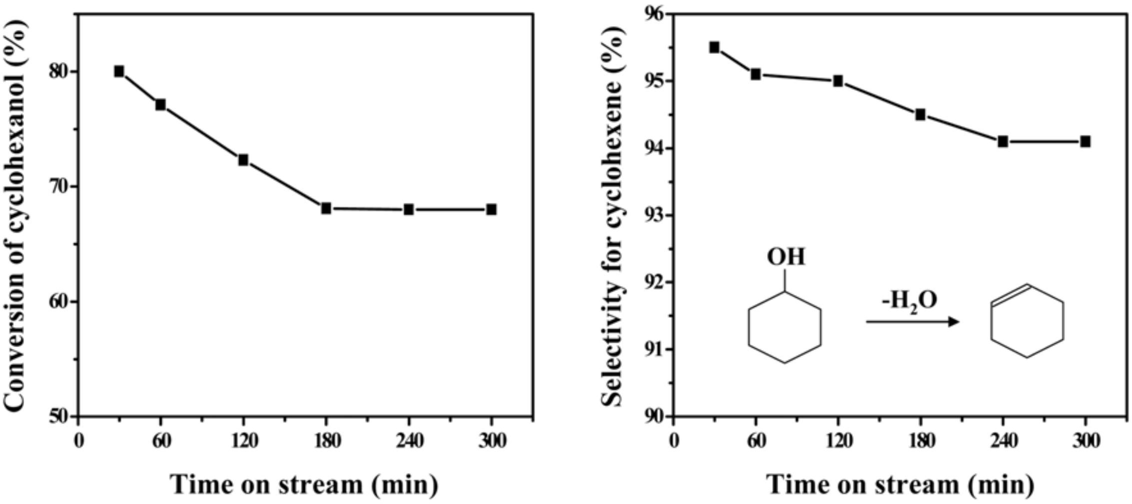

Fig. 2. Typical catalytic performance of $PW_{11}Nb_1$ catalyst in the vapor-phase dehydration of cyclohexanol with time on stream at 220 °C.

by the oxidation catalytic function of HPA via dehydrogenation reaction [26]. Formation of CO, CO_2, and phenol (aromatization product of cyclohexanol) was negligible. In our catalytic reaction, selectivity for cyclohexene was more than 90%, while selectivity for cyclohexanone was less than 10%. This means that HPA catalysts dominantly affected the acid catalysis under our experimental conditions, indicating that dehydration of cyclohexanol was suitable as a model reaction to probe the acid catalysis of the HPA catalysts.

Fig. 2 shows the typical catalytic performance of $PW_{11}Nb_1$ catalyst in the vapor-phase dehydration of cyclohexanol with time on stream at 220 °C. $PW_{11}Nb_1$ catalyst experienced a deactivation at the initial stage. Selectivity for cyclohexene also decreased during the initial reaction period, but reached a steady-state after a 4 h-reaction. The balance selectivity corresponds to the selectivity for cyclohexanone. The catalytic performance behavior of the other HPA catalysts with respect to reaction time was similar to that of $PW_{11}Nb_1$ catalyst.

3. Correlation between Acidity and Acid Catalysis

Steady-state catalytic performance data obtained after a 5 h-reaction were used for the correlation with the acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts. Yield for cyclohexene decreased in the order of $PW_{11}W_1$ (69.7%)>$PW_{11}V_1$ (66.6%)> $PW_{11}Nb_1$ (64.0%)>$PW_{11}Ta_1$ (61.9%). This trend was well consistent with the trend of acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts (Table 1). Among the catalysts tested, $PW_{11}W_1$ catalyst with the largest acidity showed the highest yield for cyclohexene.

Fig. 3 shows the correlation between acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) catalysts and yield for cyclohexene over $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) catalysts. It should be noted that yield for cyclohexene increased with increasing acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts. This means that acidity 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 acidity to meet the need for acid reaction by controlling the composition of HPA catalyst. However, it was observed that the acid strength of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) catalysts was not correlated with the acid catalysis for dehydration of cyclohexanol.

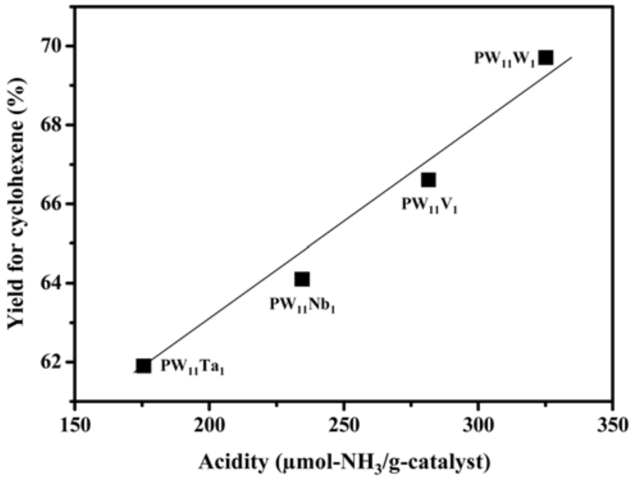

Fig. 3. Correlation between acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) catalysts and yield for cyclohexene over $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) catalysts. Catalytic performance data were obtained after a 5 h-reaction.

CONCLUSIONS

Acidity and acid catalysis of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) Keggin HPA catalysts were examined for the first time. Acidity of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts determined by NH_3-TPD measurements decreased in the order of $PW_{11}W_1$> $PW_{11}V_1$>$PW_{11}Nb_1$>$PW_{11}Ta_1$. In the vapor phase dehydration of cyclohexanol, yield for cyclohexene (a product formed by acid catalysis of HPA) also decreased in the order of $PW_{11}W_1$>$PW_{11}V_1$>$PW_{11}Nb_1$ >$PW_{11}Ta_1$. The correlation between acidity and acid catalysis for cyclohexene formation revealed that acid catalysis increased with increasing acidity of the HPA catalyst. Thus, the acidity could be utilized as a probe of acid catalysis of $H_nPW_{11}M_1O_{40}$ (M=V, Nb, Ta, and W) HPA catalysts for dehydration of cyclohexanol.

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