December, 1980] © *1980 The Chemical Society of Japan* NOTES *Bull. Chem. Soc. Jpn.*, *53*, *3719—3720 (1980)* 3719

Catalysis by Heteropolyacid. V. Catalytic Alkylation of Toluene by Mixed-coordination type, $H_4[SiMo_{12-n}W_nO_{40}]$, Heteropolyacid

Kenji Nomiya, Hidehiko Saijoh, and Makoto Miwa*

Department of Industrial Chemistry, Faculty of Engineering, Seikei University, Musashino-shi, Tokyo 180

(Received June 5, 1980)

Synopsis. To compare the specific difference between molybdenum and tungsten ions on the catalytic reaction, we investigated the alkylation of toluene with benzyl chloride by mixed-metal heteropolyacids, $H_4[SiMo_{12-n}W_nO_{40}]$ ($n=0$, 1, 10, and 11). Molybdenum-rich compound is more active than tungsten-rich one.

Recently it has been reported that protonated form of Keggin-structure heteropolyanion, showing strong Brønsted acidity, catalyzes the polycondensation of benzyl alcohols[1] and the Friedel-Crafts-type reaction.[2] Among those heteropolyacids, the mixed-coordination type, which is constituted from two kinds of metal with original Keggin-framework retained and with the total number of metal unchanged, has been marked in comparison with original type. Not so many mixed-coordination compounds, which behave as Brønsted acid, have been known. Mo–W system is one of such examples. In order to examine the role of the metal constituting the Keggin-unit, we have prepared $H_4[SiMo_{12-n}W_nO_{40}]$-type compounds. The compounds corresponding to $n=1$, 10, and 11 showed the catalytic activity for the alkylation of toluene with benzyl chloride resulting in *o*- and *p*-tolylphenylmethane. In this paper, the data will be compared with those by saturated compounds of $n=0$ and 12. Molybdenum and tungsten ions have been known to form similar type of complexes and their chemistry has always been treated as an identical family. The heteropolyanions discussed here show the different catalytic activity, although the cause has not been clarified.

Table 1. Analytical results

$(n\text{-}Bu_4N)_4[SiMo_{12-n}W_nO_{40}]$	Found (Calcd) (%) C	H	N
$n=1$	26.03 (26.71	5.09 5.01	1.90 1.95)
$n=10$	20.59 (20.94	3.93 3.92	1.56 1.53)
$n=11$	20.42 (20.45	3.95 3.83	1.51 1.49)

Table 2. IR data of $H_4[SiMo_{12-n}W_nO_{40}]$ (KBr disk, cm^{-1})

$n=0$	$n=1$	$n=10$	$n=11$	$n=12$	Assignment[5]
958	955	971	972	982	$\nu(M\text{-}O_d)$
910	908	915	915	930	$\nu(Si\text{-}O)$
860	855	870	870	885	$\nu(M\text{-}O\text{-}M)$
780	775	790	785	792	$\nu(M\text{-}O\text{-}M)$

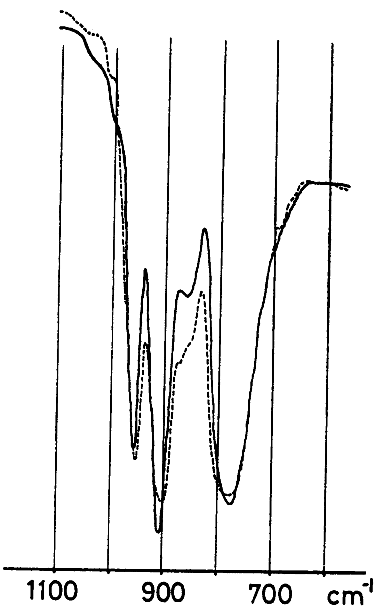

Fig. 1. IR spectra of the $n=1$ compound and the mixture of $n=0$ and 12 compounds with molar ratio of 11 : 1; full line : the $n=1$ compound, broken line : the mixture.

The $n=0$, 1, and 12 compounds were prepared according to the literature,[3,4] and the $n=10$ and 11 compounds were obtained by its modification from the stoichiometric reaction of Na_2SiO_3, Na_2MoO_4 and Na_2WO_4 in aqueous acidic solution. The heteropolyanions were isolated as tetrabutylammonium salts and analyzed. The results are presented in Table 1. The characteristic IR bands of the anions in 1000—750 cm^{-1} region are listed in Table 2, indicating that the original Keggin-unit is retained. These are distinct from those of the mixtures of the $n=0$ and 12 compounds with corresponding molar ratios. For example, IR bands of the $n=1$ compound were shown in Fig. 1. These are clearly different from those of the mixture of the $n=0$ and 12 compounds with molar ratio of 11 : 1. The four-protonated forms of heteropolyanions identified by IR spectra were used for the alkylation reaction of toluene with benzyl chloride.

The reaction was performed at *ca.* 110 °C by refluxing the solution of toluene 92 g (1 mol) and benzyl chloride 6.3 g (0.05 mol) in the presence of the heteropolyacid of *ca.* 9.7×10^{-5} mol, where the molar ratio of reactant is designated to avoid the polymerization of benzyl chloride. Although heteropolyacids are undissolved in the solution, they promote the reaction homogeneously. The reaction time was unified to the sufficient time for the lowest active catalyst. After *ca.* 17 h, the reaction was stopped by cooling and the solution once filtered. By shaking the filtrate with chloroform, product and heteropolyacid were separated. Unreacted substrate and chloroform were removed by distillation. The products, *o*- and *p*-tolylphenylmethane, were obtained

Table 3. Experimental conditions and yields

Catalyst		Reaction time	Yields
$H_4[SiMo_{12-n}W_nO_{40}]$	($\times 10^{-5}$ mol)	h	%
$n=0$	9.90	17.5	78
$n=1$	9.68	17.5	71
	9.44	17.0	60
$n=10$	9.92	17.0	56
	9.84	17.0	58
$n=11$	9.61	17.0	58
$n=12$	9.90	17.0	43

by reduced pressure-distillation of the residual solution (8 mmHg, 130 °C). Conditions and yields were presented in Table 3, the yields being estimated from the total amounts of products.

Generally, to compare a reactivity, it is necessary to obtain a rate constant in the initial reaction stage. However, observing the procedure of this experiment, it is not so far from the truth to discuss the activity by the yield at an appropriate time. In Table 3, the $n=0$ compound shows the maximum activity, whereas the $n=12$ compound does the minimum one, and the mixed-coordination compounds do the intermediate and almost equal activity. Moreover, it was shown that (1) all reactions proceed catalytically, (2) Mo-rich compound is more active than that of the W-rich one for the alkylation, however, (3) the activity is not always proportional to the number of exchanged or unexchanged metal.

The pH values of the aqueous solutions of the catalysts studied here have shown no significant difference.

References

1) K. Nomiya, T. Ueno, and M. Miwa, *Bull. Chem. Soc. Jpn.*, **53**, 827 (1980).

2) K. Nomiya, Y. Sugaya, S. Sasa, and M. Miwa, *Bull. Chem. Soc. Jpn.*, **53**, 2089 (1980).

3) E. O. North and W. Haney, *Inorg. Synth.*, Vol. I, p. 127.

4) M. Fiolwitz, R. K. C. Ho, E. G. Klemperer, and W. Shum, *Inorg. Chem.*, **18**, 93 (1979).

5) C. Rocchicciolo-Deltcheff, R. Touvenot, and R. Franck, *Spectrochim. Acta*, *Part A*, **32**, 587 (1976).