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Synthesis of acetals and ketals catalyzed by tungstosilicic acid supported on active carbon[*]

YANG Shui-jin (杨水金)[†1], DU Xin-xian (杜心贤)[1], HE Lan (贺 兰)[1], SUN Ju-tang (孙聚堂)[2]

(*^{1}Department of Chemistry and Environmental Engineering, Hubei Normal University, Huangshi 435002, China*)

(*^{2}School of Chemistry and Molecular Sciences, Wuhan University, Wuhan 430072, China*)

[†]E-mail: yangshuijin@163.com

Abstract: Catalytic activity of activated carbon supported tungstosilicic acid in synthesizing 2-methyl-2-ethoxycarbonylmethyl-1,3-dioxolane, 2,4-dimethyl-2-ethoxycarbonylmethyl-1,3-dioxolane, cyclohexanone ethylene ketal, cyclohexanone 1,2-propanediol ketal, butanone ethylene ketal, butanone 1,2-propanediol ketal, 2-phenyl-1,3-dioxolane, 4-methyl-2-phenyl-1,3-dioxolane, 2-propyl-1,3-dioxolane, 4-methyl-2-propyl-1,3-dioxolane was reported. It has been demonstrated that activated carbon supported tungstosilicic acid is an excellent catalyst. Various factors involved in these reactions were investigated. The optimum conditions found were: molar ratio of aldehyde/ketone to glycol is 1/1.5, mass ratio of the catalyst used to the reactants is 1.0%, and reaction time is 1.0 h. Under these conditions, the yield of 2-methyl-2-ethoxycarbonylmethyl-1,3-dioxolane is 61.5%, of 2,4-dimethyl-2-ethoxycarbonylmethyl-1,3-dioxolane is 69.1%, of cyclohexanone ethylene ketal is 74.6%, of cyclohexanone 1,2-propanediol ketal is 80.1%, of butanone ethylene ketal is 69.5%, of butanone 1,2-propanediol ketal is 78.5%, of 2-phenyl-1,3-dioxolane is 56.7%, of 4-methyl-2-phenyl-1,3-dioxolane is 86.2%, of 2-propyl-1,3-dioxolane is 87.5%, of 4-methyl-2-propyl-1,3-dioxolane is 87.9%.

Key words: Tungstosilicic acid, Aceta, Ketal, Active carbon, Catalysis

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INTRODUCTION

Acetals and ketals are among the most important perfume materials and industrial materials of organic synthesis. There are now many methods to synthesize them. The H_2SO_4 conventionally used as catalyst in factories (Li and Fan, 1981) causes many problems, such as erosion of equipment, difficulty for after-treatment, low quality of the products, etc. With the use of anhydrous copper sulfate (Hanzlik and Leinwetter, 1978), molecular sieve (Wang and Qian, 1993), montmorillonite K 10 (Li *et al*., 1996), $TiSiW_{12}O_{40}/TiO_2$ (Yang *et al*., 2003a), cadmium iodide (Dhrubojyoti *et al*., 1999) as catalysts for the

acetals and ketals, the catalytic activity are very high. Catalysts based on heteropolyacids have many advantages over liquid acid catalysts. They are non-corrosive and environmentally friendly, present fewer disposal problems. Their repeated use is possible and their separation from liquid products is easier compared to homogeneous catalysts.

Heteropolyacids (HPA) and their salts have been extensively studied because of their interesting catalytic properties (Kozhevnikov, 1998; Mizuno and Misono, 1998; Yang *et al*., 2003b). Their uses for synthesis of antioxidants, medicinal preparations, vitamins and biologically active substances have been reported and some are already applied in practice. These catalysts are very important for fine chemicals industries, and pharmaceutical and food and flavors industries, etc. HPA and its salts showed excellent catalytic activity accelerating esterification and have

recently attracted much attention as catalysts for various industrial processes, because their acidic and redox properties can be controlled at atomic/molecular levels (Wang *et al.*, 1998). Kozhevnikov (1998), Mizuno and Misono (1998), and Wang *et al.*(1998) reviewed the homogeneous catalysts and fine organic synthesis products catalyzed by heteropoly compounds.

Among heteropolyacids, polytungstic acids are the most widely used catalysts owing to their high acid strength, thermal stability, and low reducibilities. In surface type catalysis, the reactions take place on the internal pore and external surfaces of solid catalysts. In general, the reaction rate is proportional to the catalyst surface area. Supporting the heteropolyacids on solids with high surface areas is a useful method for improving catalytic performance in liquid-solid and gas-solid surface heterogeneous reactions. Activated carbon has been found to be able to entrap a certain amount of heteropoly acids.

This work is aimed at studying the interaction between tungstosilicic acid and carbon in catalysts prepared by equilibrium impregnation with water solvent. The species present in all solids were characterized by X-ray powder diffraction and thermogravimetry and differential thermal analysis techniques. Also, the catalyst activity in the acetalation and ketalation reaction was determined.

EXPERIMENTAL DETAILS

Materials and measurements

Ethyl acetoacetate, cyclohexanone, butanone, benzaldehyde, butyraldehyde, glycol, 1,2-propanediol and cyclohexane were of analytical reagent grade. Tungstosilicic acid ($H_4SiW_{12}O_{40}$) was synthesized as described in literature (Hu *et al.*, 1993) and examined by IR spectra. The IR (infrared) spectra were obtained using an IMP 410 IR spectrometer (Nicolet, USA). The X-ray powder diffraction pattern of the powder sample was measured by a D/MAX-3C X-ray diffractometer (Rigaku, Japan) employing CuK_α radiation. The data were collected over diffraction angle of 5° to 70° in 2θ with a step scanning. The accelerating voltage and the applied current were 40 kV and 30 mA, respectively. TG and DTA analysis were carried out with Pyris Diamond TG/DTA thermogravimeter

(Perkin-Elmer, USA) in dynamic nitrogen atmosphere and at a heating rate of 10 °C/min. ^{1}H NMR spectra were determined on a Mercury-VX 300 MHz spectromer with tetramethylsilane as internal standard in $CDCl_3$.

Preparation of $H_4SiW_{12}O_{40}$/C

The solution of tungstosilicic acid was prepared by dissolving 15.0 g tungstosilicic acid in 40 ml of water solution. The support used was commercial wood-based activated carbon (C) ground to mean particle size of 1 mm, with a surface area of 950 m^2/g and average pore diameter below 2 nm. Before being utilized, this material was washed first in solution of NaOH 0.1 mol/L, then in HCl 0.1 mol/L to eliminate the soluble acidic and alkaline impurities. Finally, it was chemically treated in solution of HNO_3 (30%, w/v) and heated by reflux for 2 h. The treatment with nitric acid makes the carbon more acidic. Then 5.0 g activated carbon was dropped into the above solution under vigorous stirring, and the resulting solution was impregnated for 6 h. Black solid $H_4SiW_{12}O_{40}$/C washed with distilled water, the powder was dried under 105 °C for 24 h. Finally the catalysts were stored in a desiccator till time of use. $H_4SiW_{12}O_{40}$/C were identified by XRD and TG/DTA.

Synthesis of acetals and ketals

The reaction was carried out in a three-neck flask (100 ml) equipped with a stirrer, a reflux condenser and a thermometer. The molar ratio of glycol to aldehyde/ketone was 1.5:1, 0.2 mol ethyl acetoacetate, cyclohexanone, butanone, benzaldehyde, butyraldehyde were added separately with 0.3 mol glycol (ethylene glycol or 1,2-propylene glycol) to the catalyst. The solution was heated to boiling and refluxed until no water flowed off. Then the solution was distilled to get colourless liquid as the end product.

RESULTS AND DISCUSSION

Characterization of catalyst $H_4SiW_{12}O_{40}$/C

1. XRD spectra

The X-ray diffraction pattern of $H_4SiW_{12}O_{40}$/C is shown in Fig.1.

X-ray powder diffraction analysis is used widely

to study the structure of heteropoly complexes. The wide diffusive peak at 27° for C in the X-ray diffraction pattern verifies its amorphous nature.
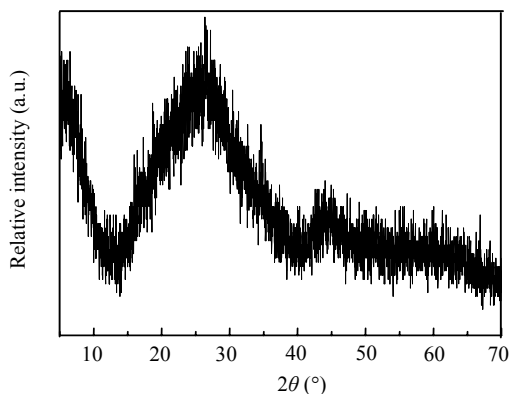

Fig.1 X-ray diffraction patterns of $H_4SiW_{12}O_{40}$/C

2. Thermal behavior studies

The TG-DTA patterns of $H_4SiW_{12}O_{40}$/C are shown in Fig.2. In the DTA diagram of $H_4SiW_{12}O_{40}$/C, the exothermic peak was assigned to the Keggin's anion decomposition at 579 °C. The TG diagram of the sample shows a decrease of the weight below 444.3 °C (less than 2.1%) and a rapid and continuous weight loss from 444.3 °C to 693.9 °C (almost 74.6%). Thermal behavior of $H_4SiW_{12}O_{40}$/C is similar to that of $H_4SiW_{12}O_{40}$. In the $H_4SiW_{12}O_{40}$ sample, it was observed the endothermic peak associated with appearance of the anhydrous phase $H_4SiW_{12}O_{40}$ is seen at 169 °C, and the exothermin peak assigned to the Keggin's anion decomposition at 526 °C.
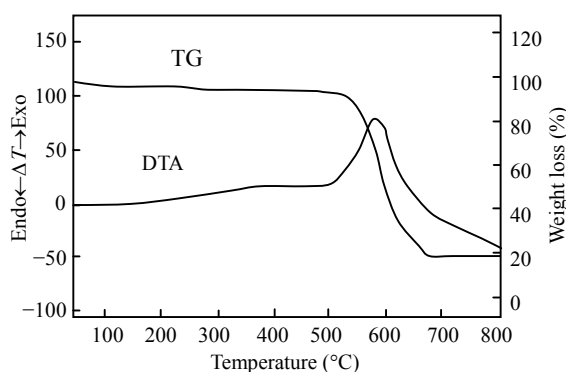

Fig.2 TG-DTA patterns of $H_4SiW_{12}O_{40}$/C

Evolutionary operation experiment design of reaction conditions

For example, butyraldehyde glycol acetal was synthesized from butyraldehyde and glycol in the presence of $H_4SiW_{12}O_{40}$/C. The factors influencing the synthesis were discussed and the best conditions were found.

1. Effect of molar ratio of butyraldehyde to glycol on yield

Table 1 shows the effect of molar ratio of butyraldehyde to glycol on yield. The molar ratio of butyraldehyde to glycol directly influences the yield.

Table 1 Effect of molar ratio of butyraldehyde to glycol on the yield[*]

n (butyraldehyde): n (glycol)	1:1.3	1:1.4	1:1.5	1:1.6	1:1.7
Yield (%)	84.1	84.9	87.5	86.2	86.2

[*]Butyraldehyde: 0.2 mol; mass ratio of catalyst to reactants: 1.0%; temperature: 86~113 °C; reaction time: 60 min

The yield increases with the increase of molar ratio of butyraldehyde to glycol. When the ratio is 1:1.5, the yield is the highest. To increase molar ratio of butyraldehyde to glycol will cause a lower yield, because of the lowering of the temperature. So the optimum molar ratio of butyraldehyde to glycol is 1:1.5.

2. Effect of catalyst dosage on the yield

The effect of catalyst dosage on the yield is shown in Table 2.

Table 2 Effect of catalyst dosage on the yield[*]

Catalyst dosage (%)	0.5	0.75	1.0	1.25
Yield (%)	80.1	80.6	87.5	86.2

[*]Butyraldehyde: 0.2 mol; mole ratio of butyraldehyde to glycol: 1:1.5; temperature: 86~113 °C; reaction time: 60 min

Table 2 shows that the yield increases with increase of the catalyst concentration. When the mass ratio of the catalyst to the reactants was 1.0%, the yield was 87.5 %. The yield did not vary greatly when more catalyst was added. Therefore, the mass ratio of the catalyst to the reactants was 1.0 % for these experiments.

3. Effect of reaction time on the yield

Reaction time is also an important factor for the reaction. Table 3 shows the effect of the reaction time on the yield.

We can see from Table 3 that the yield increases with increase of time. After 60 min, the yield is the highest. So we choose 60 min as optimum reaction time.

Table 3 Effect of reaction time on the yield*

Reaction time (min)	40	60	80	100
Yield (%)	83.2	87.5	82.3	77.6

*Butyraldehyde: 0.2 mol; mole ratio of butyraldehyde to glycol: 1:1.5; mass ratio of catalyst to reactants: 1.0%; temperature: 86~113 °C

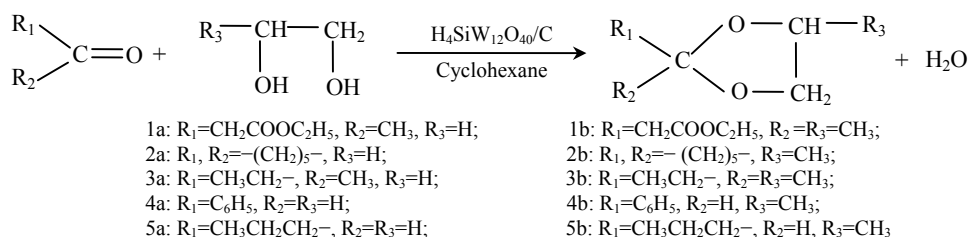## Comparison of catalytic activity of different catalysts

Table 4 gives the catalytic activity of $FeCl_3 \cdot 6H_2O$ (Yu and Peng, 1994), TiO_2/SO_4^{2-} (Wang *et al.*, 1992a), $Fe_2(SO_4)_3 \cdot xH_2O$ (Li *et al.*, 1989), and $H_4SiW_{12}O_{40}/C$.

The following conclusions were obtained: All of the catalysts showed certain catalytic activity for the synthesis of 2-propyl-1,3-dioxolane, with the catalytic

Table 4 Comparison of catalytic activity of different catalysts*

Catalyst	n (butyraldehyde): n (glycol)	Reaction time (h)	Yield (%)
$FeCl_3 \cdot 6H_2O$	1:1.5	1.5	73.9
TiO_2/SO_4^{2-}	1:1.5	1.5	67.0
$Fe_2(SO_4)_3 \cdot xH_2O$	1:1.5	6.0	56.0
$H_4SiW_{12}O_{40}/C$	1:1.5	1.0	87.5

*Butyraldehyde: 0.2 mol; mole ratio of butyraldehyde to glycol: 1:1.5; mass ratio of catalyst to reactants: 1.0%; temperature: 86~113 °C

activity of $H_4SiW_{12}O_{40}/C$ being the highest among these four catalysts.

Analysis and identification of the product

A purified product was analyzed by IR and ^1H NMR spectrum. The IR spectrum of 2-propyl-1,3-dioxolane shows peaks at 1146, 1123, 1057, 1023, 946 cm^{-1}, which are in accordance with the standard IR spectrum of 2-propyl-1,3-dioxolane; ^1H NMR (CDCl₃, 300 Hz): 4.60 (m, 1H, CH), 3.83 (m, 4H, OCH₂CH₂O), 1.63 (m, 2H, CH₂), 1.25 (m, 2H, CH₂), 0.96 (t, 3H, CH₃); n_D^{20} =1.4190 (n_D^{20} =1.4182 (Wang *et al.*, 1992a)); b.p.: 130~133 °C.

SYNTHESIS OF ACETALS AND KETALS

Factors on the synthesis of acetals and ketals

Syntheses of ten important acetals and ketals were carried out as follows. The amount of reactant of aldehyde/ketone was fixed to 0.2 mol with cyclohexane (8 ml) as water-stripped reagent. The results of these synthesis reactions are summarized in Fig.3 and Table 5.

From the data listed in Table 5, we can find that $H_4SiW_{12}O_{40}/C$ was highly active, leading to yields of ten ketals and acetals up to 87.9% and no less than

1a: R₁=CH₂COOC₂H₅, R₂=CH₃, R₃=H;
2a: R₁, R₂=−(CH₂)₅−, R₃=H;
3a: R₁=CH₃CH₂−, R₂=CH₃, R₃=H;
4a: R₁=C₆H₅, R₂=R₃=H;
5a: R₁=CH₃CH₂CH₂−, R₂=R₃=H;

1b: R₁=CH₂COOC₂H₅, R₂=R₃=CH₃;
2b: R₁, R₂=−(CH₂)₅−, R₃=CH₃;
3b: R₁=CH₃CH₂−, R₂=R₃=CH₃;
4b: R₁=C₆H₅, R₂=H, R₃=CH₃;
5b: R₁=CH₃CH₂CH₂−, R₂=H, R₃=CH₃

Fig.3 Synthesis of acetals or ketals catalyzed by $H_4SiW_{12}O_{40}/C$

Table 5 Physical properties, yields, IR and ^1H-NMR spectral data on acetals or ketals (1a~5b)*

Product	b.p. (°C)	n_D^{20}	Yield (%)	IR (cm^{-1})	^1H-NMR (δ)
1a	126−128/6.7 kPa	1.4321	61.5	1738, 1375, 1244, 1188, 1047	4.16, 3.98, 2.62, 1.46, 1.22
1b	150−155/6.7 kPa	1.4278	69.1	1740, 1377, 1244, 1188, 1043	4.10, 3.98, 3.42, 2.53, 1.30, 1.20
2a	176−180	1.4580	74.6	2937, 2863, 1163, 1104	3.91, 1.58
2b	172−176	1.4493	80.1	2937, 2864, 1163, 1103	4.12, 3.95, 3.34, 2.28, 1.19, 1.21
3a	116−119	1.4106	69.5	1254, 1215, 1194, 1130	3.90, 1.62, 1.31, 0.94
3b	126−129	1.4101	78.5	1250, 1218, 1194, 1157	4.11, 3.83, 3.34, 1.60, 1.34, 1.26, 0.90
4a	224−228	1.5264	56.7	1096, 1071, 1028, 947	7.37, 5.82, 4.05, 3.70
4b	218−222	1.5095	86.2	1097, 1067, 1011, 976	7.40, 5.97, 5.81, 4.10, 3.50, 1.38, 1.32
5a	130−133	1.4190	87.5	1146, 1123, 1023, 946	4.60, 3.83, 1.63, 1.25, 0.96
5b	140−144	1.4152	87.9	1150, 1123, 1024, 970	4.87, 4.10, 3.93, 3.35, 1.58, 1.40, 1.25, 0.96

*Reaction conditions: mole ratio of aldehyde/ketone to glycol: 1:1.5; mass ratio of catalyst to reactants: 1.0%; reaction time: 1.0 h

56.7% after 1.0 h. Moreover, the reaction temperature was controlled at the reflux temperature and the amount of $H_4SiW_{12}O_{40}$/C was much lower than other catalyst used in these reactions (Wang *et al.*, 1992b; Zhang *et al.*, 1995). All these helped to solve the technical problems faced by the industrial processes.

Characterization of acetals and ketals

The products have been purified and confirmed by the measurement of infrared spectrum and ^{1}H NMR. IR and ^{1}H NMR spectral data on acetals or ketals (1a~5b) are listed in Table 5.

CONCLUSIONS

The optimum conditions of synthesis for 2-propyl-1,3-dioxolane are: molar ratio of butyraldehyde to glycol is 1:1.5, and catalyst dosage used is 1.0% of feed stocks, and the reaction time is 60 min. Under the above conditions, the yield of 2-propyl-1,3-dioxolane can be up to 87.5%.

Activated carbon supported tungstosilicic acid was applied as catalyst in the synthesis of ten important ketals and acetals and revealed high catalytic activity. Under certain conditions (molar ratio of aldehyde/ketone to glycol is 1:1.5, the mass ratio of the catalyst used in the reactants is 1.0%, the reaction time is 1.0 h), the yields of ketals and acetals can reach 56.7%~87.9%. It has been demonstrated that the activated carbon supported tungstosilicic acid is an excellent catalyst. From the above results and discussion, we can see that the synthesis of ten important ketals and acetals by the activated carbon supported tungstosilicic acid has good prospects.

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