



## Research Paper

## Glycerol acetalization with formaldehyde using heteropolyacid salts supported on mesostructured silica

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## ABSTRACT

In the present work, mesoporous silica supported heteropolyacid salts were studied systematically for glycerol acetalization with formaldehyde. Attention was focused on finding an appropriate loading of  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  ( $\text{Cs}_{2.5}$ ) on mesoporous silica supports and studying the influence of the architecture of mesoporous silica on activity. Supported  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  on 2D (SBA-15) and 3D (KIT-6 and SBA-16) pore lattice mesoporous silicas have been compared. The activity of all supported  $\text{Cs}_{2.5}$  catalysts was found superior to that of bulk  $\text{Cs}_{2.5}$  owing to the high surface area of the mesoporous supports. While the activity difference between 2D and 3D supports did not meet expectations, mesopore volume had a significant impact on activity, which is attributed to a good access to  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  acid sites. The catalysts could be reused for three times (24 h each time), losing only 10% glycerol conversion.

## 1. Introduction

Glycerol is a major by-product of biodiesel synthesis from natural triglycerides transesterification with methanol. It amounts to nearly 10 wt% of total biodiesel production [1]. Thus, a major issue is how to use glycerol efficiently so as to facilitate biodiesel commercialization. Several processes for the catalytic conversion of glycerol have been investigated, such as hydrogenolysis; dehydration; polymerization; oxidation; steam reforming, esterification, etherification and acetalization [1–8]. Acetals and ketals produced from glycerol acetalization reactions have received increasing attention recently as some of them could be used as biodiesel additives to improve its low temperature flow properties [9,10]. A great deal of research effort has been devoted to designing novel catalysts for the manufacture of high-value fuel additives such as acetals from low-cost glycerol [11–16].

The main drawback of glycerol acetalization is the production of water, which has to be removed in order to hinder the reversibility of this reaction and catalyst deactivation [17–19]. To solve the problem, various water-tolerant catalysts such as zeolites [12], periodic mesoporous organosilicas (PMO) [13], heteropoly acid salts and oxides [14] were used for glycerol acetalization. In our previous study,  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  (hereafter abbreviated as  $\text{Cs}_{2.5}$ ) heteropoly acid salt was proved to be more active than zeolite ZSM-5, AS-MES (arene sulfonic acid ethane-silica) and commercial catalyst Amberlyst-15 for glycerol acetalization with formaldehyde owing to its large surface area

(125  $\text{cm}^2/\text{g}$ ), high acid strength and hydrophobicity [15,20,21]. It is therefore necessary to investigate the use of supported heteropoly acid salts which would potentially allow a high dispersion of the active catalyst.

Heteropolyacid salts possess pure ultra-strong Brønsted acid sites which are stronger than Nafion and liquid  $\text{H}_2\text{SO}_4$  [22]. The protonated form of heteropolyacids is highly soluble in water and polar solvents, but the acidic salts with large cations such as  $\text{Cs}^+$  are often water-insoluble and possess high surface area [20–23]. The hydrophobicity of the heteropoly compounds follows the order: H-ZSM-5 (Si/Al = 628) > Cs3 > H-ZSM-5 (Si/Al = 40) >  $\text{Cs}_{2.5}$  >  $\text{SiO}_2\text{-Al}_2\text{O}_3$  >  $\text{Al}_2\text{O}_3$ , indicating that heteropoly acid salts possess satisfactory hydrophobicity for heterogeneous acetalization catalysts.

Supported heteropoly compounds normally have larger surface area than bulk heteropoly compounds which is useful for improving catalytic performances. Mesoporous materials are ideal supports for heteropoly compounds owing to their large surface areas (600–1000  $\text{m}^2/\text{g}$ ) and the feasibility of tuning pore structure geometry and composition. Mesoporous supports with different components have been studied for years, including silica [24–27], carbon [25,28–30], aluminas [31,32], zirconia [25,33–36]. Among those supports, mesoporous silica materials have been favored as supporting materials for heteropoly acids since they possess large pores which could be applied in many organic reactions using bulky molecule reactants. In addition, silica support interacts weakly with heteropoly compounds, thus the Keggin structure

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of heteropoly acids could be preserved. Ferreira's group has proved that silica supported heteropolyacid  $\text{H}_3\text{PW}_{12}\text{O}_{40}$  (HPW)/ $\text{SiO}_2$  is very active for glycerol acetalization with acetone and it has activity superior to other kinds of heteropolyacids such as  $\text{HPMo}/\text{SiO}_2$ ,  $\text{HSiW}/\text{SiO}_2$  and  $\text{HMoSi}/\text{SiO}_2$  [37]. However HPW has very low surface area ( $5\text{ m}^2/\text{g}$ ) and is water soluble. In our previous contribution, HPW was shown to be less active than  $\text{Cs}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  for water-sensitive reaction like glycerol acetalization [15]. Zhu and Yang [38] have prepared supported heteropolyacid salts  $\text{K}_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ ,  $(\text{NH}_4)_{2.5}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$ , and  $\text{Ce}_{0.83}\text{H}_{0.5}\text{PW}_{12}\text{O}_{40}$  on mesoporous silica MCM-41, all of which exhibit better activity than the bulk salts for alkylation of benzene with 1-dodecene. Their stability was maintained for up to three uses without apparent activity loss. Thus supported heteropoly acid salts on mesoporous silica should also be good candidates for glycerol acetalization reaction. The effect of mesoporous silica supports with various structures might also be significant for heterogeneous catalysts. Compared to 2D hexagonal structures (SBA-15, SBA-8, MCM-41 and KSW-2, etc), the topological curvatures of mesoporous silica with 3D structure (SBA-16, KIT-6) would reasonably provide good transportation channels to get facilitated access to acid sites. Indeed the long channels of SBA-15 may yield transport limitations at the points of connections of elemental particles forming rope like structures [39]. It was reported that sulfonic acid group functionalized mesoporous silica with 3D architecture of KIT-6 exhibited higher activity compared to 2D SBA-15 [40] for fatty acid esterification. So far there have been extensive studies using mesoporous silica with 2D hexagonal structure (SBA-15, MCM-41 and FSM-16) [38,41–43] for acetalization and other various reactions. To the best of our knowledge, supported Cs2.5 on mesoporous silica with 3D bicontinuous cubic KIT-6 and body-centered cubic SBA-16 structure have never been examined and studied as catalysts for glycerol acetalization. It is therefore necessary to investigate the effect of 3D pore structure on the activity, selectivity and stability. Pore size and pore volume of the mesoporous supports are other important factors that might affect catalyst activity. Researchers investigated the activity of tantalum oxide supported on mesoporous silica SBA-15 for production of 1,3-butadiene from ethanol and acetaldehyde with varied mesopore diameters ranging from 2.5 to 10.9 nm [44]. The result showed that the conversion increases with an increase in pore size of Ta/SBA-15 catalysts.

In this paper, the use of Cs2.5/SBA-16, Cs2.5/KIT-6 and Cs2.5/SBA-15 mesoporous silica supported solid acid catalysts prepared by a two step incipient impregnation method was explored for glycerol acetalization with formaldehyde. Moreover, the effects of loading, pore structure and pore size were examined and optimized. The stability of supported catalysts was also tested. The distribution of the two glycerol formal isomers (6R: six member ring isomer and 5R: five member ring isomer) was investigated aiming at achieving higher selectivity to the six member ring isomer [15].

## 2. Experimental

### 2.1. Preparation of materials

The KIT-6, SBA-15 and SBA-16 mesoporous silica were prepared according to procedures previously reported by our group [45] (Supporting Information).

Supported catalyst Cs2.5/KIT-6 was prepared by a method designated as incipient impregnation. For the first step, HPW which was dissolved in 1.0 ml of water (same pore volume as the mesoporous supports) was impregnated into the mesopores by capillary action, and then it was dried at  $60\text{ }^\circ\text{C}$  overnight. A secondary impregnation was carried out by impregnating  $\text{Cs}_2\text{CO}_3$  into the mesopores by the same method to react with HPW, yielding Cs2.5 within the mesoporous silica. The resulting impregnated mesoporous silica was calcined at  $300\text{ }^\circ\text{C}$  for 3 h. HPW/KIT-6 was also prepared as a reference catalyst using the same method. Cs2.5/SBA-15 was prepared using the exactly same

method as Cs2.5/KIT-6 since SBA-15 and KIT-6 supports have similar pore volume around  $1\text{ cm}^3/\text{g}$ . For Cs2.5/SBA-16, HPW was dissolved in  $913\text{ }\mu\text{l}$  of water according to the real pore volume of SBA-16 supports which was  $0.87\text{ cm}^3/\text{g}$ , and then impregnated into the mesopores.

### 2.2. Characterization

Powder (XRD) patterns were recorded on a Rigaku D/MAX-RB diffractometer with a Cu  $\text{K}\alpha$  radiation, operating at 40 kV. Small-angle X-ray scattering (SAXS) measurements were taken on a Nanostar U SAXS system (Bruker, Germany) using Cu  $\text{K}\alpha$  radiation (40 kV, 35 mA).

Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature using a QUANTACHROME NOVA 2000 instrument. Before adsorption, the samples were evacuated for 5 h at  $250\text{ }^\circ\text{C}$ . Specific surface area was calculated using the BET (Brunauer-Emmett-Teller) method in the relative pressure range of 0.05–0.2. The total pore volume was estimated from the volume of  $\text{N}_2$  adsorbed at a relative pressure of  $P/P_0 = 0.99$ . Nonlocal density functional theory (NLDFT) was also used to analyze the pore size distribution. For this analysis, the kernel of NLDFT equilibrium capillary condensation isotherms of  $\text{N}_2$  at  $-196\text{ }^\circ\text{C}$  on silica was selected for the model isotherms (using the adsorption branch model for SBA-15 structure, equilibrium model for KIT-6 structure and assuming cylinder/spherical pores for analysis of SBA-16 structure). The TPD experiments were performed using a RXM-100 instrument from ASDI.  $\text{NH}_3$  was pulsed to samples at  $80\text{ }^\circ\text{C}$  and the temperature was raised at a rate of  $5\text{ }^\circ\text{C min}^{-1}$ . The density of acid sites was evaluated from the measured amounts of desorbed  $\text{NH}_3$ .  $^{29}\text{Si}$  and  $^{31}\text{P}$  MAS NMR was carried out on a Bruker Avance 300 MHz spectrometer equipped with 4 and 7 mm probe heads. FTIR spectra were collected using a Nicolet Magna 850 Fourier transform infrared spectrometer (Thermo Scientific, Madison, WI).

### 2.3. Catalytic tests

The catalytic properties of the catalysts were studied in the acetalization of glycerol by formaldehyde. In a typical experiment, 5 g (54.3 mmol) of glycerol was stirred with 5.308 g (65.5 mmol) formaldehyde solution (37%).

The liquid phase catalytic tests were conducted in a glass batch reactor. In one series of experiments, different masses of the different catalysts were used in order to keep the same total content of acid sites (0.26 g Cs2.5) in the reactor. Before reaction, all catalysts were activated in vacuum at  $180\text{ }^\circ\text{C}$  for 2 h. The reaction was carried out in absence of any additional solvent. At the end of each test, a sample of the reaction medium (the supported solid catalyst was removed from the solution for GC analysis using a 13 mm filter syringe) was injected into a gas chromatograph (Varian CP-3800) using a flame ionization detector (FID) with a Stabliwax<sup>®</sup>  $30\text{ m} \times 0.53\text{ mm} \times 1\text{ }\mu\text{m}$  capillary column for identification of the reaction products, measurement of glycerol conversion and yield of glycerol formal.

## 3. Results and discussion

### 3.1. Supported Cs2.5/KIT-6 with various loadings

#### 3.1.1. Compositional and structural information

The powder X-ray diffraction (XRD) patterns of Cs2.5/KIT-6 are shown in Fig. 1. The peaks assigned to Cs2.5 became stronger as the loading was increased from 10 to 40 wt%. Usually, at low loading of 10%, no diffraction peaks of Cs2.5 are observed due to the high dispersion [42,46]. In our case, catalyst with 10% loading Cs2.5 shows clearly all peaks that belong to Cs2.5, meaning that Cs2.5 aggregates inside ordered mesoporous silica forming Cs2.5 nanoparticles. The crystal domain size of bulk Cs2.5 salt calculated using Scherrer equation is around 10.7 nm, whereas the supported Cs2.5 with 10–40% loadings had crystal sizes of 13, 11.3, 10.2 and 10.9 nm which are

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