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Highly efficient glycerol acetalization over supported heteropolyacid catalysts

Lin Chen^[a], Bendaoud Nohair^[a], Dongyuan Zhao^[b], Serge Kaliaguine^{*[a]}

Abstract: The acetalization of glycerol with acetone to yield solketal was catalyzed by $Cs_{2.5}H_{0.5}PW_{12}O_{40}$ (Cs2.5) supported on mesoporous silica, under mild conditions. It gave high glycerol conversion and selectivity to targeted product even at room temperature (23°C). Another highly efficient glycerol acetalization reaction with paraformaldehyde using both bulk and supported Cs2.5 as catalysts was studied, which gave much higher activity compared with formaldehyde solution. For the reaction with acetone, the supported Cs2.5 showed higher activity than the bulk one which is owing to the high surface area of the mesoporous supports. Interestingly the supported Cs2.5 gave a lower conversion compared to the bulk for the reaction with paraformaldehyde. This is probably owing to the high viscosity of the reaction system with solid reagent paraformaldehyde. Overall, there is a complex relationship between catalyst, reaction conditions including molar ratio of reactants and temperature, reaction mechanism, and thermodynamics that affects the achieved activity and by-product formation. A discussion about these interactions is included for each reaction.

Introduction

Renewable energy is a focus today owing to the issue of global warming. Biodiesel stands out as an important alternative fuel which can be produced via transesterification of vegetable oils or animal fats. The production of biodiesel has increased significantly in EU.^[1] China, Brazil, US^[2] and other countries over past decades and the global production reached 37 billion gallons in 2016.^[3] Thus, glycerol as a byproduct representing 10 wt% of biodiesel production, as well as other traditional glycerol production from hydrolysis of C6 or even C5 sugars and classic soap manufacturing by saponification,^[4] has saturated the commercial market. High value biobased chemical products deriving from over produced glycerol have attracted much attention in recent years. Glycerol acetals and ketals are among the promising chemicals that could be formed from glycerol reaction with various aldehydes. They can be used as fuel additive to improve low temperature flow properties, scent, flavor, basis for surfactants and solvent for medical applications.^[5] The main issues are finding appropriate catalysts and optimizing the reaction conditions to reach complete glycerol conversion and high yield of target products. Traditional industry still mainly uses homogeneous catalysts such as sulfuric acid or PTSA

 [a] Lin Chen, Dr. Bendaoud Nohair, Prof. Serge Kaliaguine Department of Chemical Engineering Laval University Quebec, Canada , G1V0A6 E-mail: serge.kaliaguine@gch.ulaval.ca
 [b] Prof. Dongyuan Zhao Department of Chemistry Fudan University Shanghai, China, 200433 (paratoluene sulfonic acid) for the glycerol acetalization reaction which require heating to reflux for long reaction time (16 h). These catalysts are neither environmental friendly nor reusable.^[6] Heterogeneous catalysts have been studied extensively for glycerol utilization to replace homogeneous catalysts since they can be easily separated from the reaction media without corroding the reactor.

A drawback in forming acetals and ketals from glycerol is the production of water which would deactivate the catalyst and facilitate the reversibility of the reaction. To solve this problem, water tolerant heterogeneous catalysts, for example zeolite beta,^[7, 8] heteropoly compounds,^[9, 10] oxides and phosphates,^[11] organic-inorganic composites ^[12] have been studied extensively. As established in our previous study, the heteropoly compound Cs_{2.5}H_{0.5}PW₁₂O₄₀ (abbreviated as Cs2.5) is very active and selective for glycerol acetalization with aqueous formaldehyde solution (37%) since it has both high surface area and high acid strength.^[9] It was found more active than AS-MES (arene sulfonic acid ethane-silica), zeolite ZSM-5 and commercial catalyst Amberlyst-15. However, it is very difficult to reach complete glycerol conversion and high yield even under optimized reaction conditions with high acid sites concentration which is probably owing to the long lifetime of hemiacetal as an intermediate and the large amount of water involved in the reaction medium.^[9, 13] Thus finding an appropriate formaldehyde source might be crucial to achieve ideal activity result. Paraformaldehyde, a solid water-free source of formaldehyde, was rarely studied as aldehyde for glycerol acetalization since it could make the reaction medium highly viscous in absence of solvent.^[14] However, paraformaldehyde should favour the conversion of glycerol to yield more acetal as it contains 96% of formaldehyde compared to the more used formaldehyde solution (37%). Thus, effort should be put on exploring the usage of paraformaldehyde for glycerol conversion. It was also proved that glycerol acetalization with acetone could be carried out under mild reaction conditions with high yield of solketal, [1, 15] zeolite-beta was used for solketal production [8, 16, 17], high yield around 70% could be reached in 30 min while the reaction has to be carried out at 40-80 °C [18]. Organic resins Amberlyst-15 [8, ^{16]}, Amberlyst-36 ^[14] were also proved to be very active for this reaction. They also need to work around 70 °C for long reaction time. Heteropoly acid H₃PW₁₂O₄₀ was used for solketal synthesis at room temperature, but H₃PW₁₂O₄₀ is a homogeneous catalyst which is difficult to recycle [10]. The heteropoly acid salt Cs2.5 is water tolerant, and possesses acid strength comparable to H₃PW₁₂O₄₀ and high surface area ^[19]. This material is also interesting to explore as a catalyst for glycerol acetalization with acetone.

Although the surface area of Cs2.5 is high (around 125 m²/g), it is necessary to support Cs2.5 on mesoporous materials which have large surface area (~600-1000 m²/g), high thermal stability and tunable pore structure geometries. Silica,^[20, 21] zeolites,^[7, 22] titania,^[23] zirconia,^[15, 24] alumina,^[25] carbon,^[26] ^[27] and clay ^[28] are supports that have been widely applied for various reactions.

Silica is considered to be an appropriate support for heteropoly compounds since it interacts weakly with Cs2.5 and has suitable pore size to allow the interaction of large molecules with active sites. In our previous study, we have demonstrated that supported Cs2.5/KIT-6 meso-silica catalyst showed superior activity over bulk Cs2.5 for glycerol acetalization with formaldehyde solution.^[29] Tuning the architecture of mesoporous silica from 2D hexagonal SBA-15 to 3D interconnected KIT-6 and SBA-16 doesn't strongly affect the catalyst activity while expanded mesoporous support with large pore size improved catalytic performance. Thus, Cs2.5 supported on mesoporous silica allows reaching high catalytic activity.

This work uses the heteropoly compound Cs2.5 and supported Cs2.5/KIT-6 mesoporous silica as catalysts for the glycerol acetalization with paraformadehyde and acetone under mild reaction conditions. The influence of reaction parameters such as molar ratio of reactants, catalyst loading and reaction temperature were studied.

Results and Discussion

Glycerol acetalization with acetone

The effect of reaction conditions for glycerol acetalization with acetone was first studied using bulk Cs2.5 as catalyst. The reaction results in two cyclic products, (2,2-dimethyl-1,3dioxolan-4-yl)-methanol which is known as solketal (a in Scheme.1) and 1,3-dioxane-5-methanol (b in Scheme.1). As shown in Table.1, the molar ratio of acetone to glycerol plays an important role in order to reach high conversion. Over the ratio range of 1.5 to 6, the glycerol conversion increased from 25% to 92% even though the reaction time was reduced to less than 15 min and temperature to 60 °C at the highest ratio of 6. The reaction could also be run at room temperature achieving 94% glycerol conversion in 1h. A blank test was performed at room temperature in absence of catalyst showing no conversion. The reaction medium in the blank test was obviously separated in two phases (acetone and glycerol) after 2h reaction. The results in Table.1 show that glycerol acetalization with acetone for the production of solketal should be advantageous for scale up as it could be carried out at room temperature with almost complete glycerol conversion in 1h with high selectivity to solketal. The five member ring (5R) solketal (a) forms much faster than the six member ring b (6R). The molar ratio of a:b remains constant at 98:2 regardless of the reaction conditions. It is known that the 6R should be more stable than the 5R. Thermodynamic and kinetic can both affect the cyclization. According to Baldwin's "Rules for Ring closer".^[30] five-member rings are usually formed faster than the six-member rings and this selectivity is affected

Table 1. Optimization of reaction conditions for glycerol acetalization with							
acetone on non supported Cs2.5							
Reaction Temperature (°C)	Weight of catalyst (g)	Molar ratio of Acetone: Glycerol Reactior Time (min)		Conversion (%)	Selectivity a:b		
65	0.25	1.5	120	25	98:2		
65	0.25	3	120	59	98:2		
60	0.25	6	15	92	98:2		
23	0.25	6	60	94	98:2		
23	0	6	120	0	0		

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by both the stability of the products and entropic factors.^[31]



Scheme 1. Reaction mechanism for glycerol acetalization with acetone

The activity of supported Cs2.5 on mesoporous silica KIT-6 was also investigated. 30% Cs2.5 is chosen as an appropriate loading according to our previous work.^[29] The Cs2.5 loading is confirmed by XRF, which shows that the weight fraction of SiO₂ corresponds to 68.6%. Thus the real Cs2.5 loading should be 31.4%. The physical properties and acid site density of Cs2.5 and supported Cs2.5/KIT-6 are shown in Table.2. The surface area of supported catalyst 30% Cs2.5/KIT-6 (574 m²/g) is much higher than the bulk Cs2.5 (125 m²/g). The pore volume and surface area of mesoporous KIT-6 support decreased upon impregnation with Cs2.5. As shown in Fig.1, although Cs2.5 and Cs2.5/KIT-6 gave basically the same ultimate glycerol conversion and yield of solketal (95% and 93% respectively), the reaction rate is faster over supported Cs2.5 than the bulk, giving glycerol conversion of 95% in 15 min with 98% selectivity to solketal at room temperature, whereas it needs one hour to achieve the similar activity by using bulk Cs2.5. The higher reaction rate is probably owing to the large surface area of the supported catalyst (574 m²/g) attributed by the mesoporous KIT-6 support (768 m²/g), making the reactants have faster access to the acid sites of Cs2.5. The molar ratio of products a:b remains constant at 98:2 using supported catalyst, which means that glycerol acetalization with acetone favours the formation of five member ring isomer as previously discussed.

Fig 1. Evolution of glycerol conversion (left) and yield of solketal (right) over supported Cs2.5 and bulk Cs2.5. Reaction conditions: bath temperature 25°C, acetone/glycerol molar ratio: 6:1, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.25g/batch

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Table 2.	Physical	properties	and	acidities	of Cs2	.5 and	supported	Cs2.5/	KIT-6
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sample	BET area (m²g⁻¹)	pore size (nm)	pore volume (cm ³ g ⁻¹)	acid capacity (mmol/g)
30% Cs2.5/KIT-6	574	8.1	0.688	0.06
$Cs_{2.5}H_{0.5}PW_{12}O_{40}$	125	Mesopores:5 Micropores:1	0.096	0.19
KIT-6 (SiO ₂)	768	8.1	0.977	١
$H_3PW_{12}O_{40}$	5	١	١	0.9

Pore size is the pore diameter calculated by NLDFT. Pore volume is the total pore volume filled by N_2 at relative pressure 0.99. Acid capacity is determined by NH_3 -TPD.

To confirm the heterogeneous nature of Cs2.5. Fig.2 reports the results of a test performed at 25 °C in the same conditions as in Fig.1 using bulk Cs2.5. After 3 min of reaction, the stirring was stopped and the whole reaction medium was centrifuged for 10 min at 25 °C. As shown in Fig.2a the first reaction step (glycerol to hemiketal) is almost completed (84%) after 3 min and no significant change is observed after centrifugation (87%). The minor difference is likely due to conversion during centrifugation before the catalyst is entirely separated from the reaction medium. The constant conversion afterwards indicates no homogeneous catalysis by leached Cs2.5. Fig 2b shows the evolution of solketal yield in the same test. At three minutes, before catalyst removal, the yield of solketal as expected does not change. Then some change in yield is observed which corresponds to the reaction (hemiacetal to solketal secondary reaction) still going on before the whole catalyst is separated by centrifugation. Thereafter no change is observed clearly showing that no homogeneous reaction happened in these conditions. Moreover the pH of the centrifuged reaction medium was measured to be 6-7 whereas the catalyst containing medium had a pH close to 5. Similar test has been performed with supported Cs2.5/KIT-6, the result is essentially same as those reported for bulk catalyst.

Table 3 compares the activities of various acidic catalysts for the glycerol acetalization with acetone including the heteropoly compounds tested in this work (row 1-4) and functionalized oxides (row 5-7), supported metal catalyst and mesoporous silica framework incorporated metal atom (row 8-10), sulphonic

groups functionalized activated carbon and mesostructured silica (row 11-12), zeolites (row 13-14), commercial Amberlyst resin (row 15) reported in literature. For heteropoly compounds, the water-tolerant Cs2.5 shows superior activity over HPW for glycerol acetalization with acetone (row 1 and 4). Activity for glycerol acetalization with formaldehyde solution (37%) over Cs2.5 was also found higher than that of HPW in our previous work.^[9] Therefore catalyst hydrophobicity is a key factor for water-sensitive reactions like glycerol acetalization.

Fig 2. Evolution of glycerol conversion (left) and yield of solketal (right) over bulk Cs2.5 separated at 3 min. Reaction conditions: bath temperature 25°C, acetone/glycerol molar ratio: 6:1, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.25g/batch

Supported Cs2.5 catalyst still shows higher activity than the bulk one owing to its large surface area and better accessibility of the reactants to the active sites (row 1 and 2). The highly acidic SO_4^{2-}/ZrO_2 catalyst (acidity 0.69mmol/g), could also work at room temperature with similar high glycerol conversion in rather short reaction time, like supported Cs2.5. While other categories of acidic catalysts, for example, Nb₂O₅ is not suitable since it took much longer reaction time and reached only ~80% glycerol conversion even though it is also water-tolerant. For supported silica materials, 1% Re/SiO₂ gave high activity but the reaction needs to proceed under the inert N₂ atmosphere and ultra sound for 10 min which complicates the reaction procedure. MoPO/SBA-15 SiO₂ is very active for the reaction, but a recycling test showed that glycerol conversion at the 1st, 2nd, 3rd and 4th cycles was found to be 100, 70, 68, and 62%,

Table 3. Comparison of activity of different catalysts for glycerol acetalization with acetone								
No.	Heterogeneous catalysts	Acetone /Glycerol	Reaction Temperature (°C)	Reaction time	Glycerol conversion	Catalysts loading (relative to glycerol)	Reference	
1	Cs2.5	6:1	RT(25)	60 min	94%	5 wt%	This paper	
2	Cs2.5/KIT-6	6:1	RT(25)	15 min	95%	5 wt%	This paper	
3	HPW/SiO ₂	6:1	70	4h	97%	5 wt%	[32]	
4	HPW 🔺	10:1	RT	2h	58%	1 mol%	[10]	
5	SO42-/ZrO2	6:1	RT	90 min	98%	5 wt%	[15]	
6	Nb ₂ O ₅	1.5:1	70	6h	80%	5 wt%	[33]	
7	Nb ₂ O ₅ -Al ₂ O ₃	4:1	50	2h	84%	3 wt%	[34]	
8	MoPO/SBA-15 SiO2	3:1	RT	2h	100%	5 wt%	[11]	
9	Re/SiO ₂	10:1	30	1h	100%	5 wt%	[20]	
10	Zr or Hf/TUD-1	2:1	80	6h	65%	3 wt%	[35]	
11	Activated carbon- SO₃H	4:1	RT	6h	97%	3 wt%	[36]	
12	SiO ₂ -SO ₃ H (arene sulfonic)	6:1	70	15-30min	80%	5 wt%	[1]	
13	Dealuminated BEA zeolite	1:1	30	30 min	80%	5 wt%	[37]	
14	zeolite beta	1.2:1	70	40 min	90%	19 wt%	[8]	
15	Amberlyst-36	1.5:1	38.1-40	8h	Acetal yield 88%	5 wt%	[14]	

respectively, which does not correspond to a truly stable heterogeneous catalyst. Lewis acidic mesoporous metal substituted silicates catalysts Zr or Hf/TUD-1 need long time (6h) to reach the reaction equilibrium at 80°C. Activated carbon-SO₃H might be very active for glycerol acetalization owing to its extremely large surface area (1240-1550 m²/g), high acidity (1.88 mmol/g) and also being water-tolerant, while it also took long time (6h) to reach the equilibrium of the reaction. Arene sulfonic functionalized mesoporous silica SBA-15 only gave 80% glycerol conversion under optimized reaction conditions. Zeolites catalysts seem to be active and allowed reaching 80% to 90% glycerol conversion in 40 min, but the works did not explore the optimization of reaction conditions. For example, the molar ratio of the reactants, which is a very important parameter for glycerol acetalization with acetone was not varied. Thus, the activity of Cs2.5 catalysts and previous published works can hardly be compared.

To study the stability of the spent bulk and supported Cs2.5 for glycerol acetalization with acetone, the catalysts were used for three times. After each test, the catalyst was centrifuged (10000 rpm for 10 min), and then washed with ethanol and water, calcined in air at 573K for 3h to regenerate the catalyst. As shown in Fig.3 and Fig.4, the glycerol conversion is basically same after three time use (~98%) for both bulk and supported Cs2.5, indicating no deactivation occurred. Only the bulk Cs2.5 shows some decrease in secondary reaction rate at the third cycle (Fig.3b). This result demonstrates that bulk and supported Cs2.5 are more stable for glycerol acetalization with acetone than with formaldehyde solution, since in our previous publications^[9, 29], supported Cs2.5 would lose 10% of glycerol conversion owing to the large amount of water (37% formaldehyde solution) in the reaction medium.

Fig 3. Stability study on Cs2.5 for glycerol acetalization with acetone. Reaction conditions: bath temperature 25°C, acetone/glycerol molar ratio: 6:1, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.5g/batch

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Fig 4. Stability study on Cs2.5/KIT-6 for glycerol acetalization with acetone. Reaction conditions: bath temperature 25°C, acetone/glycerol molar ratio: 6:1, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.5g/batch

Glycerol acetalization with paraformaldehyde

The reaction with paraformaldehyde was also performed over the heteropoly compound Cs2.5. The results were compared with our previous results obtained with formaldehyde solution (37% aqueous solution). The reaction of glycerol acetalization with formaldehyde solution was shown to proceed more slowly than with acetone under the same reaction conditions, as it needed at least several hours to reach reaction equilibrium.^[9] The reaction mechanism involves two reversible steps as shown in Scheme.2. In the first step formaldehyde reacts with a hydroxyl group to form hemiacetal 1,2-propanediol,3-(hydroxymethoxy). The second step is the condensation of two hydroxyl groups of the hemiacetal. There are two kinds of acetal formed from the hemiacetal. One is the five-member ring 1,3dioxolane-4-methanol (hereafter designated as 5R), whereas the other one is a six-member ring 1,3- dioxan-5-ol (hereafter designated as 6R). The first step is faster than the second one and would not require a catalyst.[38] As shown in Fig.5, it is noteworthy that for both formaldehyde solution and paraformaldehyde, the glycerol conversions are always higher than the yields of acetal. The reason is that the condensation of hemiacetal hydroxyl groups is a slow reaction. Thus even after glycerol conversion reaches a plateau, the glycerol formal yield is still increasing, owing to the long reaction time of the second step.^[9]

The glycerol conversion and acetal yield are obviously higher with paraformaldehyde than with formaldehyde solution after 24h reaction. For paraformaldehyde, only 1h is required to reach 95% glycerol conversion with almost complete conversion after 4h, and yields up to 70%. Only 55% glycerol conversion was reached after 24h for glycerol acetalization with formaldehyde solution. These activity results are consistent with the mechanism presented in Scheme.2. Paraformaldehyde is the polymerization product of formaldehyde, the assay percent range of which is as high as 96%, while formaldehyde solution has only 37% of formaldehyde involving large amount of water (the concentration of formaldehvde in the reaction medium is 19%). Due to the high concentration of reactant by using paraformaldehyde (28%) which favours the reaction moving forward, the yield of hemiacetal and final product, glycerol formal, dramatically increased compared to using formaldehyde solution. This highlights the importance of the source of formaldehyde. The activity is 2-3 folds higher by using paraformaldehyde under the same reaction conditions. As far as we know, most of the researches regarding glycerol acetalization with formaldehvde are still using formaldehyde solution [8, 13, 14, 39] as the formaldehyde source, since some people believe that paraformaldehyde is an insoluble polymer, which could make the reaction medium inhomogeneous together with reactant glycerol and solid catalyst, leading to low and moderate $conversion.^{\left[13, \ 14\right]}$ It is true that the reaction medium is inhomogeneous during the first hour of the reaction, but we could see increasing amount of water condensing on the wall of the batch reactor. Besides the targeted product glycerol formal can act as a good solvent which helps reducing the viscosity of the reaction medium. Thus high activity could be reached with solid paraformaldehyde without adding solvent. Due to the high_{\!\varDelta}

viscosity of the reaction medium for the first hour, we also tried to solve the problem by first dissolving paraformaldehyde with glycerol at 70°C and then starting the reaction by adding catalyst. No significant improvement in activity was observed (Fig.6). Thus the inhomogeneity of the reaction medium in the first hour of reaction does not affect the average reaction rate.

The molar ratio of 6R to 5R is also dramatically affected by using paraformaldehyde. With formaldehyde solution, the distribution of 5R to 6R is around 70% to 30%, while with paraformaldehyde, the distribution of 5R and 6R is almost 30% to 70% under the same reaction condition. This means that glycerol acetalization with paraformaldehyde can produce more 6R than 5R. We have explored the distribution of 5R and 6R for glycerol acetalization with formaldehyde solution in our previous work since 6R is a very useful compound that could be converted to 1,3-propanediol.^[9] High reaction temperature, amount of acid sites and ratio of reactants are important factors that may be raised to produce more 6R. In this work, we found that glycerol reacting with paraformaldehyde can also yield much more 6R acetals than with formaldehyde solution.

For comparison, the reaction conditions that were optimized for glycerol acetalization with formaldehyde solution ^[9] were also used for the reaction with paraformaldehyde, namely 90 °C and 1.33g of catalyst Cs2.5, molar ratio of glycerol to paraformaldehyde: 1:1.5. The reaction reaches equilibrium in 1h with ~99% glycerol conversion and 70% yield of glycerol formal under the optimized reaction conditions. In the conditions described above, namely a lower temperature of 70°C, a lower catalyst content of 0.25g/batch, the initial reaction rate is much lower, but the final values for glycerol conversion and GF yield were the same under the optimized reaction conditions (Fig.7), glycerol acetalization reaction with paraformaldehyde can reach equilibrium within one hour.

Fig 5. Evolution of glycerol conversion (left) and yield of glycerol formal (right) over bulk Cs2.5. Reaction conditions: bath temperature 70°C, glycerol/formaldehyde molar ratio: 1:1.2, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.25g/batch

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Fig.6 Evolution of glycerol conversion (left) and yield of glycerol formal (right) over bulk Cs2.5. Reaction conditions: bath temperature 70°C, glycerol/formaldehyde molar ratio: 1:1.2, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.25g/batch

Scheme 2. Reaction mechanism for glycerol acetalization with formaldehyde

Fig 7. Evolution of glycerol conversion (left) and yield of GF (right) for glycerol acetalization with paraformaldehyde over bulk Cs2.5. Reaction conditions: glycerol/formaldehyde molar ratio: 1:1.2, stirring speed: 400 rpm.

Fig 8. Evolution of glycerol conversion (left) and yield of GF (right) for glycerol acetalization with paraformaldehyde over supported Cs2.5/KIT-6 and bulk Cs2.5. Reaction conditions: bath temperature 70°C, glycerol/formaldehyde molar ratio: 1:1.2, stirring speed: 400 rpm, the amount of Cs2.5 was kept constant at 0.25g/batch

The use of supported Cs2.5 was also explored for glycerol acetalization with paraformaldehyde and compared with bulk Cs2.5 (Fig.8). Surprisingly, the reaction with supported Cs2.5 proceeds more slowly than with bulk Cs2.5, but gave similar ultimate glycerol conversion around 99 % and a lower GF yield. In our previous work, Cs2.5/KIT-6 was shown to be more active than bulk Cs2.5 for glycerol acetalization with formaldehyde solution and acetone.^[29] Finding a lower reaction rate on supported Cs2.5 is therefore very unusual. According to Kapkowski et al, the viscosity of a reaction medium may strongly affect the reagent contact with the catalyst surface during the nano catalysis on mesoporous silica.[20] The two reactants glycerol and paraformaldehyde solution constitute a highly viscous system, thus the access of the reactants to the acid sites inside the mesoporous silica channel might be restricted (Fig.8).

Fig 9. Stability study on bulk Cs2.5 (left) and Cs2.5/KIT-6 (right) for glycerol acetalization with paraformaldehyde. Reaction conditions: bath temperature 70°C, acetone/glycerol molar ratio: 6:1, stirring speed: 400 rpm, the amount of Cs2.5 was at 0.5g/batch (left) and 0.25g/batch (right)

Similarly, to study the stability of the spent bulk and supported Cs2.5 for glycerol acetalization with paraformaldehyde, the catalysts were used for three times. After each test, the catalyst was centrifuged (10000 rpm for 10 min), and then washed with ethanol and water, calcined in air at 573K for 3h to regenerate the catalyst. Fig.9 shows that the glycerol conversion is also basically the same after three time use for both bulk and supported Cs2.5, indicating no deactivation occurred.

Conclusions

This work demonstrates the highly efficient glycerol acetalization with acetone and paraformaldehyde under mild solvent free reaction conditions over heteropoly compound Cs2.5 and supported Cs2.5 on 3D mesoporous silica KIT-6. High glycerol conversion and selectivity to targeted products were achieved by using the supported heteropoly compound Cs2.5 with a glycerol conversion of 95% in 15 min and 98% selectivity to solketal at room temperature for glycerol acetalization with acetone. One hour was needed to achieve the similar conversion by using bulk Cs2.5. Thus the supported catalyst shows superior activity to the

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bulk one. For the glycerol acetalization reaction with paraformaldehyde, however supported Cs2.5 gave lower reaction rate compared to the bulk one owing to the high viscosity of the solvent free reaction medium that affected the reagent contact with the catalyst surface.

Experimental Section

Catalyst preparation

Bulk Cs_{2.5}H_{0.5}PW₁₂O₄₀, abbreviated as Cs_{2.5}, was prepared by adding an aqueous solution of Cs₂CO₃ (0.1M) dropwise to a H₃PW₁₂O₄₀ (abbreviated as HPW, 0.08M) solution while stirring ^[40]. The resulting precipitate was dried at room temperature overnight and then evaporated to dryness at 318K. The obtained powder was calcined at 573 K for 3 h in air.

Supported catalyst Cs2.5/KIT-6 mesoporous silica was prepared by an incipient impregnation method.

Preparation of KIT-6 support: A 10.0 g amount of triblock copolymer P123 (BASF) was fully dissolved by stirring in 362.0 g of water and 18.5 g of HCl (Fischer 36.5-38.0%) at room temperature. The solution was heated to 35 °C before adding 10.0 g of butanol (Sigma-Aldrich). After about 1 h, 26.0 g of TEOS (tetraethyl orthosilicate, Aldrich) was added to the solution. The molar composition of the reaction mixture TEOS/P123/BuOH/HCl/H₂O was 1.0/0.014/1.08/1.42/160.

Impregnation of HPW: HPW was first dissolved in 1.0 ml of water (same pore volume as the mesoporous KIT-6 supports) and impregnated into the mesopores by capillary action, followed by drying at 60 °C overnight. Formation of Cs2.5/KIT-6: Cs₂CO₃ was introduced into the mesopores by the same method (dissolved in 1.1 ml water, same pore volume as the mesoporous HPW/KIT-6 material) to react with HPW, yielding Cs2.5

within the mesoporous silica. The resulting impregnated mesoporous silica was calcined at 300 °C for 3 h in air.

Nitrogen adsorption/desorption isotherms were measured at liquid nitrogen temperature (-196 °C) using a QUANTACHROME NOVA 2000 instrument. Prior to adsorption, the samples were evacuated for at least 5 h at 250 °C. The BET specific surface area was calculated using the BET (Brunauer-Emmett-Teller) equation in the relative pressure range of 0.05 –0.2. The total pore volume was determined from the volume of N₂ adsorbed at a relative pressure of P/P0 = 0.99. Pore size distribution was analyzed by using the Nonlocal Density Functional Theory (NLDFT) method. For this analysis, the kernel of NLDFT equilibrium capillary condensation isotherms of N₂ at -196 °C on silica was applied for the model isotherms (using the equilibrium model for KIT-6 structure), which was supplied by Autosorb software from Quantachrome instrument.

The NH₃-TPD experiments were performed using an RXM-100 instrument from ASDI. After the sample had been preheated in argon at 300°C for 2 h, pure NH₃ gas was admitted over the samples at 80 °C for 30 min, and then the temperature was raised at a rate of 5 °C min-1 from 80 °C to 700 °C for TPD test under an argon carrier gas flow (flow rate of 10ml/min). The density of acid sites was evaluated from the measured amounts of desorbed NH₃. The Cs2.5 loading was confirmed by XRF (X-ray fluorescence) using a PANalytical WD-XRF instrument. Catalytic reactions

The catalytic properties of the catalysts were studied in the acetalization of glycerol by paraformaldehyde or acetone. In a typical experiment with paraformaldehyde, 5 g (54.3mmol) of glycerol was stirred with 2.05 g (65.5 mmol) paraformaldehyde (96%) without solvent. In the experiment with acetone, 5 g (54.3mmol) of glycerol was stirred with acetone (HPLC grade, >99.9%) under different reaction conditions in absence of solvent. The liquid phase catalytic tests were conducted in a glass batch reactor equipped with a condenser. In one series of experiments, the mass of catalysts having different Cs2.5 loadings was adjusted in order to keep the total content of acid sites (0.25 g Cs2.5) constant in the reactor. Before reaction, all catalysts were activated in vacuum at 180 °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 bulk or 6).

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) equipped with a flame ionization detector (FID) and a Stabliwax® 30m×0.53mm×1µm capillary column for identification of the products, measurement of glycerol conversion and yield of glycerol formal or solketal.

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