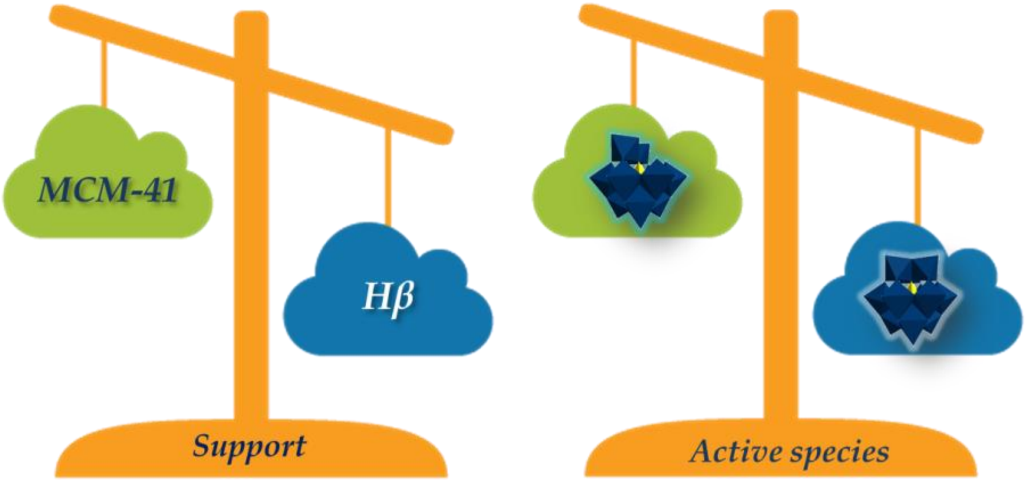
# APPENDIX

# COMPARISON OF ACTIVITY OF THE SYNTHESIZED CATALYSTS



**Effect of active species $SiW_{12}/SiW_{11}$ on biodiesel synthesis**

In order to see the effect of active species for biodiesel synthesis, both esterification and transesterification reactions were carried out under similar reaction conditions over $SiW_{12}/SiW_{11}$ anchored to the supports, MCM-41 and Hβ.

**Table 1.** Comparison of activity of $SiW_{12}/SiW_{11}$ and MCM-41 based catalysts for biodiesel synthesis.

| Reaction | Catalyst | Surface area ($m^2/g$) | Acidic strength, mV | % Conversion | TOF, $h^{-1}$ |
|---|---|---|---|---|---|
| Esterification of OA [a] | 30% $SiW_{12}$/MCM-41 | 349 | 438 | 99 | 123.8 |
| | 30% $SiW_{11}$/MCM-41 | 536 | 260 | 70 | 87.5 |
| Trans-esterification of SO [b] | 30% $SiW_{12}$/MCM-41 | 349 | 438 | 88 | 36.2 |
| | 30% $SiW_{11}$/MCM-41 | 536 | 260 | 58 | 23.2 |

[a] *Mole ratio (OA: MeOH)= 1 : 40, Catalyst wt. = 100 mg, Temperature = 60 °C, Reaction time = 10 h,* [b] *Weight ratio (SO: MeOH) = 1 : 4, Catalyst wt. = 200 mg, Temperature = 65 °C, Reaction time = 8 h.*

Table 1 describes the activity of MCM-41 anchored $SiW_{12}/SiW_{11}$ for biodiesel synthesis under the same conditions. It is clear that activity of 30% $SiW_{12}$/MCM-41 is higher than that of 30% $SiW_{11}$/MCM-41 for both transesterification as well as esterification reactions. This can be explained as follows.

The activity of the catalysts was found to be consistent with the acidic strength of both the catalysts. The acidic character of polyoxometalates is mainly due to the acidic addenda atoms i.e. tungsten in the present case and removal of one tungsten-oxygen unit from the parent $SiW_{12}$ is expected to decrease the acidity and as a result activity of the $SiW_{11}$. This can be seen by the decrease in the values of acidic strength of 30% $SiW_{11}$/MCM-41 as compared to 30% $SiW_{12}$/MCM-41 (Table 1).

The surface area of 30% $SiW_{11}$/MCM-41 (536 $m^2/g$) is higher than 30% $SiW_{12}$/MCM-41 (349 $m^2/g$). This suggests that the catalytic activity of both the catalysts is not directly proportional to the surface area confirming that the present catalytic systems are not surface type heterogeneous in which the catalytic activity is directly proportional to surface area. Hence, it can be concluded that the present catalytic system is pseudo-liquid type (I) heterogeneous catalyst where activity is directly proportional to the acidic strength of the catalyst [1]. The order of the catalytic activity was 30% $SiW_{12}$/MCM-41 > 30% $SiW_{11}$/MCM-41 for both esterification as well as transesterification reactions.

**Table 2.** Comparison of activity of $SiW_{12}/SiW_{11}$ and Hβ based catalysts for biodiesel synthesis.

| Reaction | Catalyst | Surface area ($m^2/g$) | Acidic strength, mV | % Conversion | TOF, $h^{-1}$ |
|---|---|---|---|---|---|
| Esterification of OA [a] | 30% $SiW_{12}$/Hβ | 419 | 657 | 86 | 107.5 |
| | 30% $SiW_{11}$/Hβ | 439 | 390 | 82 | 100.8 |
| Trans-esterification of SO [b] | 30% $SiW_{12}$/Hβ | 419 | 657 | 95 | 39.3 |
| | 30% $SiW_{11}$/Hβ | 439 | 390 | 96 | 39.6 |

[a] *Mole ratio (OA: MeOH)= 1 : 20, Catalyst wt. = 100 mg, Temperature = 60 °C, Reaction time = 10 h.* [b] *Weight ratio (SO: MeOH) = 1 : 4, Catalyst wt. = 200 mg, Temperature = 65 °C, Reaction time = 8 h.*

Similar trend was found in the case of catalysts comprising $SiW_{12}/SiW_{11}$ and Hβ support. The catalytic activity was found to be depending on the acidic strength of the catalysts irrespective of the surface area of the catalysts (Table 2). The order of activity was 30% $SiW_{12}/H\beta$ > 30% $SiW_{11}/H\beta$ for esterification of oleic acid where very strong acidic sites are required. However the activity of both the catalysts was almost similar for transesterification reaction.

### Effect of active species $SiW_{11}/SiW_{12}$ on valorisation of glycerol

**Table 3.** Comparison of activity of $SiW_{12}/SiW_{11}$ anchored to MCM-41 for valorisation of glycerol.

| Reaction | Catalyst | Surface area ($m^2/g$) | Acidic strength, mV | Conv./Sel., % | TOF, $h^{-1}$ |
|---|---|---|---|---|---|
| Acetalization[a] | 30% $SiW_{12}$/MCM-41 | 349 | 438 | 91/74 | 113.9 |
| | 30% $SiW_{11}$/MCM-41 | 536 | 260 | 85/82 | 98.9 |
| Carboxylation[b] | 30% $SiW_{12}$/MCM-41 | 349 | 438 | 75/77 | 117.3 |
| | 30% $SiW_{11}$/MCM-41 | 536 | 260 | 62/75 | 97.7 |

[a] *mole ratio Gly./Benzaldehyde: 1/1; time: 60 min; temperature: 30 °C; catalyst amount: 100 mg,* [b] *mole ratio Gly./Urea: 1/1; time: 8 h; temperature: 150 °C; catalyst amount: 100 mg.*

**Table 4.** Comparison of activity of $SiW_{12}/SiW_{11}$ anchored to Hβ for valorisation of glycerol.

| Reaction | Catalyst | Surface area ($m^2/g$) | Acidic strength, mV | Conv./Sel., % | TOF, $h^{-1}$ |
|---|---|---|---|---|---|
| Acetalization[a] | 30% $SiW_{12}/H\beta$ | 419 | 657 | 97/68 | 1214 |
| | 30% $SiW_{11}/H\beta$ | 439 | 390 | 95/78 | 1106 |
| Carboxylation[b] | 30% $SiW_{12}/H\beta$ | 419 | 657 | 73/72 | 114.2 |
| | 30% $SiW_{11}/H\beta$ | 439 | 390 | 68/75 | 107.2 |

[a] *mole ratio Gly./Benzaldehyde: 1/1; time: 60 min; temperature: 30 °C; catalyst amount: 50 mg,* [b] *mole ratio Gly./Urea: 1/1; time: 8 h; temperature: 150 °C; catalyst amount: 100 mg.*

Table 3 and 4 shows the effect of $SiW_{12}/SiW_{11}$ on acetalization as well as carboxylation reactions. For both the supports it was found that $SiW_{12}$ based catalysts show higher TOFs than $SiW_{11}$. The results were consistent with the acidity of the catalysts. However, the selectivities were better for $SiW_{11}$ based catalysts as for glycerol acetalization reaction because of ring transformation of dioxolane to dioxane in the presence of strong acidic $Siw_{12}$ based catalysts as discussed in the earlier chapter (Page no. 201). The order of activity of the catalysts for glycerol valorisation was 30% $SiW_{12}$/MCM-41 > 30% $SiW_{11}$/MCM-41 for MCM-41 based catalysts and 30% $SiW_{12}$/Hβ > 30% $SiW_{11}$/Hβ for zeolite Hβ based catalysts in terms of conversion.

**Effect of Supports**

**Table 5.** Effect of supports on biodiesel synthesis via esterification of oleic acid and transesterification of soybean oil.

| Reaction | Catalyst | Surface area ($m^2/g$) | Acidic strength, mV | n-butyl amine acidity (mmol/g) Very strong /Strong | % Conv./ TOF, $h^{-1}$ |
|---|---|---|---|---|---|
| Esterification of OA [a] | 30% $SiW_{12}$/MCM-41 | 349 | 438 | 0.9/2.5 | 73/91.2 |
| | 30% $SiW_{12}$/Hβ | 419 | 657 | 1.46/2.60 | 86/107.5 |
| | 30% $SiW_{11}$/MCM-41 | 536 | 260 | 0.9/2.4 | 61/76.2 |
| | 30% $SiW_{11}$/Hβ | 439 | 390 | 1.40/2.16 | 82/100.8 |
| Transesterification of SO [b] | 30% $SiW_{12}$/MCM-41 | 349 | 438 | 0.9/2.5 | 88/36.2 |
| | 30% $SiW_{12}$/Hβ | 419 | 657 | 1.46/2.60 | 95/39.4 |
| | 30% $SiW_{11}$/MCM-41 | 536 | 260 | 0.9/2.4 | 58/23.2 |
| | 30% $SiW_{11}$/Hβ | 439 | 390 | 1.40/2.16 | 96/39.6 |

*Reaction conditions: [a] Mole ratio (OA: MeOH) = 1:20, Catalyst amount = 100 mg, Temperature = 60 °C, Reaction time = 10 h, TON= moles of product / moles of catalyst. [b] Weight ratio (SO: MeOH) = 1:4, Catalyst amount = 200 mg, Temperature = 65 °C, Reaction time = 8 h*

It is known that, 'Support' does not play always merely a mechanical role but it can also modify the catalytic properties of the POMs. The nature of the support and its textural properties are the important factors for a successful reaction towards the better catalytic activity. In order to see the effect of supports, the catalytic activities of SiW$_{12}$/SiW$_{11}$ anchored to different supports MCM-41 and zeolite Hβ have been compared under identical reaction conditions for biodiesel synthesis (Table 5) as well as valorisation of glycerol (Table 6).

**Table 6.** Effect of supports on valorisation of glycerol under similar reaction conditions.

| Reaction | Catalyst | Surface area, m$^2$/g | Pore width, Å | Acidic strength, mV | Conv./ Sel., % | TOF, h$^{-1}$ |
|---|---|---|---|---|---|---|
| Acetalization with benzaldehyde [a] | 30% SiW$_{12}$/MCM-41 | 349 | 29.2 | 438 | 75/75 | 939 |
| | 30% SiW$_{12}$/Hβ | 419 | 16.8 | 657 | 97/68 | 1214 |
| | 30% SiW$_{11}$/MCM-41 | 536 | 39.6 | 260 | 65/85 | 757 |
| | 30% SiW$_{11}$/Hβ | 439 | 17.1 | 390 | 95/78 | 1106 |
| Carboxylation with urea [b] | 30% SiW$_{12}$/MCM-41 | 349 | 29.2 | 438 | 75/77 | 117.3 |
| | 30% SiW$_{12}$/Hβ | 419 | 16.8 | 657 | 73/72 | 114.2 |
| | 30% SiW$_{11}$/MCM-41 | 536 | 39.6 | 260 | 62/75 | 97.7 |
| | 30% SiW$_{11}$/Hβ | 439 | 17.1 | 390 | 68/75 | 107.2 |

[a] *mole ratio Glycerol/Benzaldehyde: 1/1; reaction time: 60 min; temperature: 30* $^{o}$*C; catalyst amount: 50 mg,* [b] *mole ratio Glycerol/Urea: 1/1; reaction time: 8 h; temperature: 150* $^{o}$*C; catalyst amount: 100 mg.*

In almost all the reactions, 30% SiW$_{12}$/Hβ exhibited excellent activity as compared to that of 30% SiW$_{12}$/MCM-41. Similarly activity of 30% SiW$_{11}$/Hβ was better than that of 30% SiW$_{11}$/MCM-41. The obtained difference in catalytic activity may be due to the nature of supports and this can be explained as follows.

The acidity of support is responsible for the catalytic activity, as it is well known that MCM-41 as well as zeolite Hβ both exhibit acidic character. The zeolite Hβ (1.14 mmol n-butyl amine/g) is much more acidic than MCM-41 (0.82 mmol n-butyl amine/g) as MCM-41 has only hydrogen bonding sites whereas Hβ has both Bronsted as well as Lewis acid sites. Therefore the higher value of total acidity for 30% $SiW_{12}$/Hβ as well as for 30% $SiW_{11}$/Hβ was observed collectively from $SiW_{12}$/$SiW_{11}$ as well as support Hβ. This can be clearly seen in Table 5 that very strong acidic character is increased to a great extent for Hβ based catalysts. The trend in the activity of all the catalysts was in good agreement with their acidic strength. The catalyst 30% $SiW_{12}$/Hβ having highest acidic strength and produced better conversions.

In addition, the pore structure of zeolite support is very different from that of MCM-41. Zeolite Hβ has framework structure consisting of three dimensional intersecting channel systems [2]. The channels are interconnected and consisting of two different sizes with maximum of 12 ring channels pore opening [3-4]. Whereas MCM-41 consists of 2D hexagonal porous channels spread uniformly over wide range [5-6]. Though surface area of MCM-41 (659 $m^2/g$) is higher than zeolite Hβ (587 $m^2/g$), after incorporation of $SiW_{12}$ the surface area of 30% $SiW_{12}$/MCM-41 was decreased as compared to 30% $SiW_{12}$/Hβ. This suggests that in the case of MCM-41, due to the 2D channel systems some of the channels have been blocked whereas in Hβ zeolite, 3D channels allow better dispersion as well as better mass transfer between the reactants and the product molecules leading to the better activity.

**References**

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