Comparison of activity of SiW_{12}/MCM-22 and SiW_{11}/MCM-22

The comparison of activity of SiW_{12}/SiW_{11} anchored to MCM-22 based catalysts was examined for esterification and acetalization in identical reaction conditions.

From the data (Table 1), the conversion of substrates, selectivity of desired product, TON and TOF of all the reactions in SiW_{12}/MCM-22 were found to be superior as compared to that in SiW_{11}/MCM-22. Moreover, the activity of both the catalysts corroborated to their acidic strength. The acidic strength and acidic sites of SiW_{12}/MCM-22 (456 mV and 3.7 mEq/g) is relatively higher than that of SiW_{11}/MCM-22 (383 mV and 3.2 mEq/g). Hence, the catalytic activity of MCM-22 based catalysts are directly related to their acidic strength and here also, the absence of one tungsten-oxygen unit lowers the catalytic activity. Furthermore, the surface area of SiW_{12}/MCM-22 (234 m^2/g) is lower as compared to SiW_{11}/MCM-22, which contradicts their activity. Thus, the catalysts are not surface types, however, the surface area may help in overall activity as the active species (SiW_{12}/SiW_{11}) resides in the pores and the reaction also happens in the bulk. Majorly, the role of both the catalysts are governed by their acidic character, the SiW_{12}/SiW_{11} anchored to MCM-22 systems are of pseudo-liquid type (I) heterogeneous catalysts.

Table 1 Comparison of activity of SiW_{12}/MCM-22 and SiW_{11}/MCM-22 under identical conditions

Catalyst	**SiW_{12}/MCM-22**	SiW_{11}/MCM-22
% Conv/Sel*	**[a]65/94** **[b]97/59** **[c]63/66**	[a]57/88 [b]71/39 [c]48/66
TON/TOF (h^{-1})	**[a]1621/203** **[b]1214/121** **[c]2625/3918**	[a]1510/189 [b]944/94 [c]2120/3178
Acidic strength (mV)	**456**	383
Very Strong acid sites (mEq/g)	**2.2**	1.1
Strong acid sites (mEq/g)	**1.5**	2.1
Total acid sites (mEq/g)	**3.7**	3.2
BET Surface area (m^2/g)	**234**	324

[a]**Esterification of Levulinic acid:** Reaction conditions- Mole ratio 1:2; catalyst amount 50 mg; temperature 90 °C; time 4 h.
[b]**Esterification of Succinic acid:** Reaction conditions- Mole ratio 1:3; catalyst amount 100 mg; temperature 80 °C; time 8 h.
[c]**Acetalization of Glycerol:** Reaction conditions- Mole ratio 1:1; catalyst amount 15 mg; temperature 30 °C; time 40 min.
*Selectivity of [a] Ester (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

From above studies, the activity order of MCM-22 based catalysts for all three transformations is

SiW_{12}/MCM-22 > SiW_{11}/MCM-22

The obtained values of activation energy for all reactions are tabulated in Table 2.

Table 2 Activation energy

Reaction	**SiW_{12}/MCM-22**	SiW_{11}/MCM-22
Levulinic acid esterification	**36 kJ/mol**	49 kJ/mol
Succinic acid esterification	**68 kJ/mol**	82 kJ/mol
Glycerol acetalization	**48 kJ/mol**	67 kJ/mol

From the above data it was observed that the lower values of activation energy for all three reactions were obtained for SiW_{12}/MCM-22, in agreement with the catalytic studies and confirmed that the said catalyst is better amongst two.