Comparison of the activity of SiW_{12}/nMCM-48 and SiW_{11}/nMCM-48

To check the effect of active species (SiW_{12}/SiW_{11}) for esterification and acetalization reactions, experiments were carried out under identical reaction conditions over SiW_{12}/SiW_{11} anchored to the nMCM-48.

From Table 1, it is apparent that the catalytic activity of SiW_{12}/nMCM-48 is much higher than that of SiW_{11}/nMCM-48 for all the reactions. The rate of conversion of substrates, selectivity of the desired product as well as TON and TOF for SiW_{12}/nMCM-48 catalyzed reactions are found to be excellent. This can be explained as follows.

1. The surface of SiW_{12}/nMCM-48 (588 m^2/g) is much higher than that of SiW_{11}/nMCM-48 (516 m^2/g). The higher surface area of SiW_{12}/MCM-48 promotes the catalytic activity more. Hence, it is expected to be more active.
2. The total acidic sites of SiW_{12}/nMCM-48 is 4.9 mEq/g while that of SiW_{11}/nMCM-48 is 3.9 mEq/g. Hence the latter is expected to be less active.

Thus, predominantly the activity of both the catalysts is directly proportional to their surface area and it can be concluded that the present systems are surface type catalysts.

Table 1 Comparison of activity of SiW_{12}/nMCM-48 and SiW_{11}/nMCM-48 under identical conditions

Catalyst	**SiW_{12}/nMCM-48**	SiW_{11}/nMCM-48
% Conv/Sel*	**[a]99/100** **[b]98/84** **[c]89/69**	[a]49/84 [b]35/18 [c]27/72
TON/TOF (h^{-1})	**[a]2469/617** **[b]1227/153** **[c]7355/10978**	[a]1300/325 [b]465/58 [c]2389/3582
Acidic strength (mV)	**700**	460
Very Strong acid sites (mEq/g)	**1.4**	0.9
Strong acid sites (mEq/g)	**3.5**	3.0
Total acid sites (mEq/g)	**4.9**	3.9
BET Surface area (m^2/g)	**588**	516

[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

Thus, from above observations, the catalytic activity order is

SiW_{12}/nMCM-48 > SiW_{11}/nMCM-48

for both esterification as well as acetalization reactions.

The activation energy obtained from the kinetic experiments, for all said transformations are summarized in Table 2.

Table 2 Activation energy

Reaction	SiW_{12}/nMCM-48	SiW_{11}/nMCM-48
Levulinic acid esterification	**26 kJ/mol**	29 kJ/mol
Succinic acid esterification	**55 kJ/mol**	75 kJ/mol
Glycerol acetalization	**35 kJ/mol**	65 kJ/mol

It is seen from the table that for all three reactions, the activation energy in case of SiW_{12}/nMCM-48 was found to be less as compared to that of SiW_{11}/nMCM-48 confirming, SiW_{12}/nMCM-48 is more active.

Thus, from both, the catalytic as well as kinetic studies, SiW_{12}/nMCM-48 proves to be a better catalyst than SiW_{11}/nMCM-48.