Overall Comparison

&

Selection of Best Catalyst

Effect of active species SiW_{12}/SiW_{11}

The detailed comparison study of the catalytic activity of SiW_{12}/nMCM-48 and SiW_{11}/nMCM-48 for esterification and acetalization reactions showed that SiW_{12}/nMCM-48 was found to be better in bringing out the maximum conversion as well as selectivity of the desired products. A similar observation was also evident in case of comparison study of SiW_{12}/MCM-22 and SiW_{11}/MCM-22.

Thus, in a general term it can be stated that, the activity order of active species is Figure 1,

$SiW_{12} > SiW_{11}$

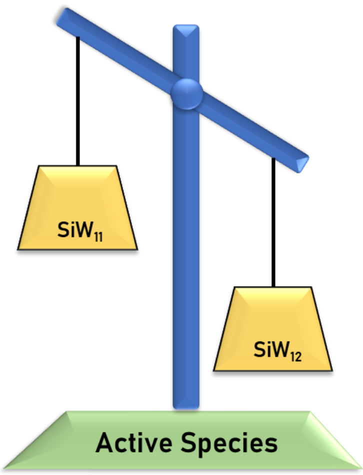


Figure 1 Activity order of active species

Effect of supports nMCM-48/MCM-22 on esterification and acetalization reactions

It is well known that, the 'Support' does not play always merely a mechanical role but it can also assist the catalytic properties of the active species. In this context the effect of both the supports (nMCM-48/MCM-22) on overall catalytic activity of the catalysts for esterification and acetalization reactions was determined by carrying out experiments in identical conditions (keeping the active species constant) and the results are displayed in Table 1.

It is observed that the catalysts with nMCM-48 as a support showed admirable catalytic activity as compared to that of MCM-22 based catalyst. This observed difference in the catalytic activity can be correlated to their unique structures, pore networks and acidic character. The acidic strength of nMCM-48 (168 mV) is relatively higher than that of MCM-22 (132 mV). The catalytic assistance of nMCM-48 is better mainly due to its unique structure. However, the presence of Al (Lewis acid) sites in MCM-22 does alter the overall nature of the catalyst and it has an impact on catalytic activity (conversion as well as selectivity of desired products).

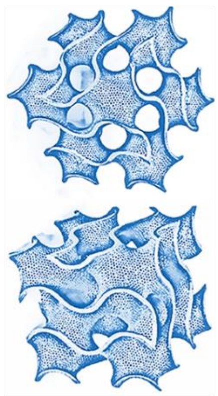
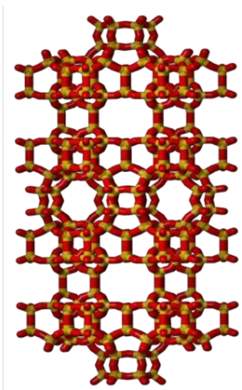
Properties	nMCM-48	MCM-22
Structure	3D cubic branched channels 	Layered 2D sinosuidal channels 
Framework	Purely Siliceous	Aluminosilicate
Surface area (m^2/g)	1307	344
Acidity (mV)	168	132

Table 1 Comparison of activity of all catalysts under identical conditions

Reaction	Catalyst	% Conv /Sel*	TON/ TOF (h^{-1})	Acidic strength (mV)	Very Strong acid sites (mEq/g)	Strong acid sites (mEq/g)	Total acid sites (mEq/g)	BET Surface area (m^2/g)
[a]Esterification of Levulinic acid	**SiW_{12}/nMCM-48**	**99/100**	**2469/617**	**700**	**1.4**	**3.5**	**4.9**	**588**
	SiW_{12}/MCM-22	38/94	948/237	456	2.2	1.5	3.7	234
	SiW_{11}/nMCM-48	**49/84**	**1300/325**	**460**	**0.9**	**3.0**	**3.9**	**516**
	SiW_{11}/MCM-22	32/78	847/212	383	1.1	2.1	3.2	324
[b]Esterification of Succinic acid	**SiW_{12}/nMCM-48**	**98/84**	**1227/153**	**700**	**1.4**	**3.5**	**4.9**	**588**
	SiW_{12}/MCM-22	67/34	839/105	456	2.2	1.5	3.7	234
	SiW_{11}/nMCM-48	**35/18**	**465/58**	**460**	**0.9**	**3.0**	**3.9**	**516**
	SiW_{11}/MCM-22	29/15	385/48	383	1.1	2.1	3.2	324
[c]Acetalization of Glycerol	**SiW_{12}/nMCM-48**	**89/69**	**7355/10978**	**700**	**1.4**	**3.5**	**4.9**	**588**
	SiW_{12}/MCM-22	21/69	1750/2623	456	2.2	1.5	3.7	234
	SiW_{11}/nMCM-48	**27/72**	**2389/3582**	**460**	**0.9**	**3.0**	**3.9**	**516**
	SiW_{11}/MCM-22	18/62	1593/2388	383	1.1	2.1	3.2	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

MCM-22 possesses 2D sinusoidal channels with layered structure and is zeolitic in nature having Al sites as Lewis acid sites while nMCM-48 is purely silicious, exhibits 3D branched channels with cubic mesophase. It also possesses higher surface area. The 3D cubic structure as well as the higher surface area of nMCM-48 based catalysts, provides a larger access of reactants to acidic sites and also promotes the outgoing of products. Hence, for the catalytic activity **nMCM-48** comes out to be the **better support** as compared to that of MCM-22.

Thus, the structure, geometry and inherent properties of the support matters in the overall catalytic activity and this is in good agreement with the well-known fact, as mentioned above, that support does not play always merely a mechanical role but it can also assist the catalytic properties of the active species.

The assistance order of support for esterification and acetalization reaction can be represented as (Figure 2),

nMCM-48 > MCM-22

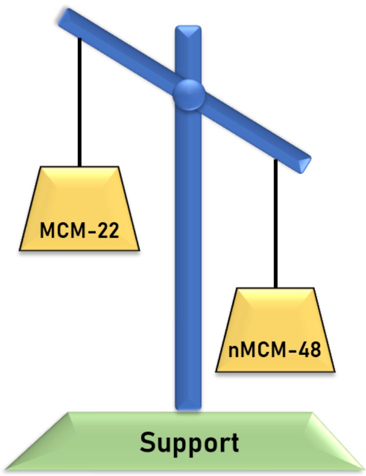


Figure 2 Assistance order of support

Effect of catalyst on activation energy

The final data of optimization study using all four catalysts for esterification as well as acetalization reactions are summarized in table 2.

Table 2 Activation energy of esterification and acetalization reactions with all catalysts in their respective optimized conditions

Reaction	Catalyst	% Conv/Sel*	TOF (h^{-1})	Activation energy (kJ/mol)
[a]Esterification of Levulinic acid	**SiW_{12}/nMCM-48**	**99/100**	**617**	**26**
	SiW_{11}/nMCM-48	49/84	325	29
	SiW_{12}/MCM-22	65/94	203	36
	SiW_{11}/MCM-22	78/94	148	49
[b]Esterification of Succinic acid	**SiW_{12}/nMCM-48**	**98/84**	**153**	**55**
	SiW_{11}/nMCM-48	83/43	183	75
	SiW_{12}/MCM-22	97/59	121	68
	SiW_{11}/MCM-22	76/41	168	82
[c]Acetalization of Glycerol	**SiW_{12}/nMCM-48**	**89/69**	**10978**	**35**
	SiW_{11}/nMCM-48	66/65	8757	65
	SiW_{12}/MCM-22	63/66	3935	48
	SiW_{11}/MCM-22	74/62	4900	67

*Selectivity of [a]Ester (Butyl levulinate), [b]Diester (Dibutyl succinate) and [c]1,3-dioxane

It is evident from the results that amongst all four catalysts, SiW_{12}/nMCM-48 provides excellent catalytic activity for all transformations in terms of % conversion of substrate as well as in obtaining the highest selectivity towards desired products. Furthermore, from above studies we observed that the amongst both the POMs, SiW_{12} is relatively more active than SiW_{11} and amongst supports, nMCM-48 proves to be a better support. The amalgamation of these two best components generates an excellent catalytic system, SiW_{12}/nMCM-48 which miraculously works in lowering the activation energy of all transformations. Relatively higher activation energy in other catalysts is also related to their less acidic strength where less acidic sites are available and so more energy is required to overcome the barrier, as compared to SiW_{12}/nMCM-48.

Thus, the order of catalysts in overcoming the energy barrier efficiently in terms of activation energy is as follow.

SiW_{12}/nMCM-48 > SiW_{12}/MCM-22 > SiW_{11}/nMCM-48 > SiW_{11}/MCM-22

Hence, the catalyst **SiW_{12}/nMCM-48** comes out to be the **best catalyst** amongst all the synthesized ones and the combination of acidic active species as well as 3D cubic structure and higher surface area of support brings out the maximum exploitation of the catalyst for smooth conversion of bioplatform molecules to value added products.