

Electronic Supplementary Information

Porous Cesium impregnated MgO (Cs-MgO) Nanoflakes with excellent catalytic activity for Highly Selective Rapid Synthesis of Flavanone

Provas Pal,^a Sandip Kumar Pahari,^a Apurba Sinhamahapatra,^a Arnab Kanti Giri,^a Hari C. Bajaj,^a Asit Baran Panda^{*a,b}

^a *Discipline of Inorganic Materials and Catalysis, Central Salt and Marine Chemicals Research Institute (CSIR), G.B. Marg, Bhavnagar-364002, Gujarat, India. Fax: +91-2782567562; Tel: +91-2782567760 Ext. 704; E-mail: abpanda@csmcri.org,*

^b *Present address: Nano-Structured Materials Division, Central Glass & Ceramic Research Institute (CSIR), Raja SC Mullick Road, Kolkata-32, West Bengal, India.*

Corresponding Author: E-mail address: abpanda@csmcri.org,

Fax: +(91)278-2567760, Ext.: 704, Phone: +(91)278-2567562.

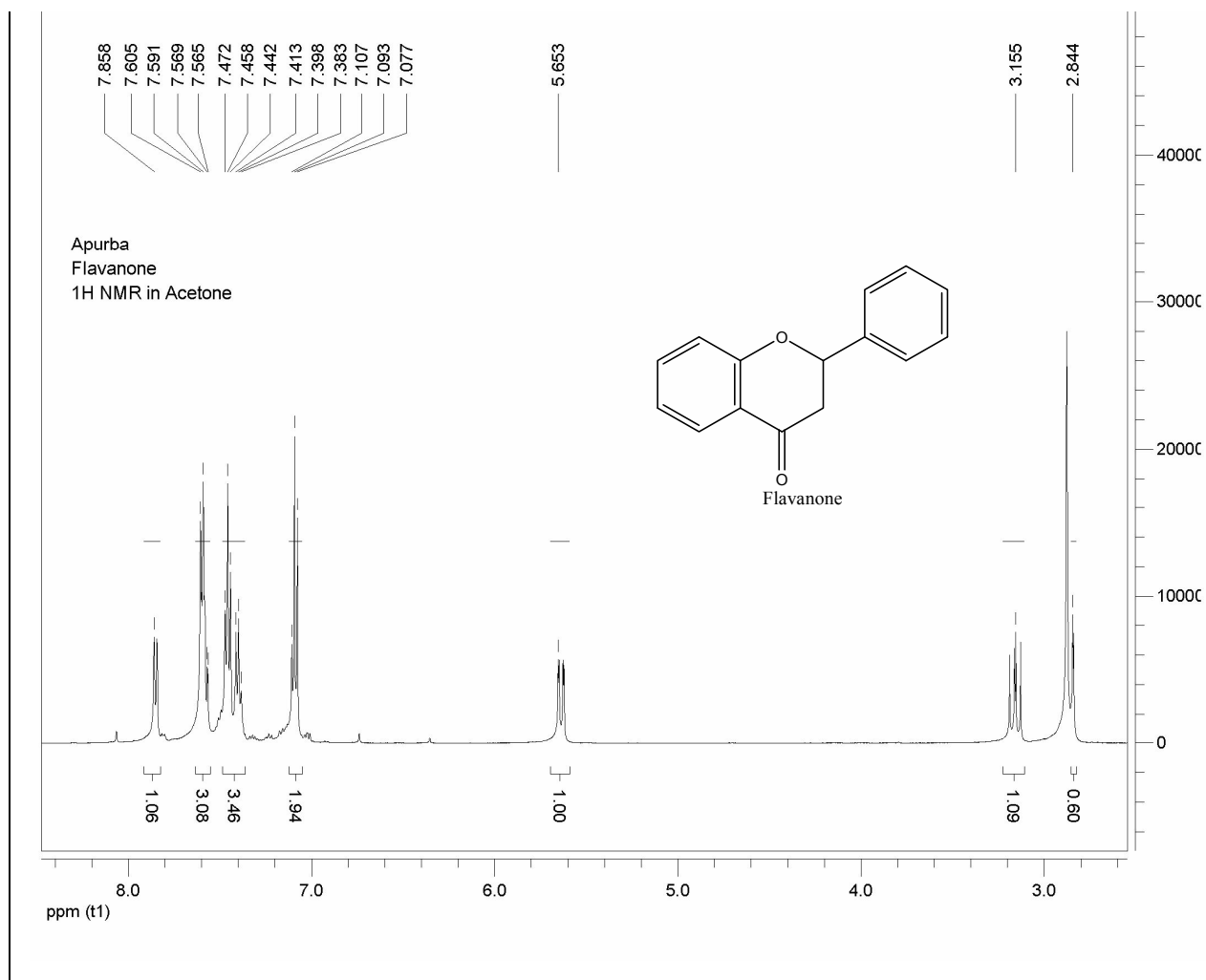


Figure S1 ^1H NMR Spectrum for flavanone

Flavanone 1H NMR in acetone (500 MHz): δ (ppm) 7.86 (1H, dd), 7.39-7.60 (6H, m), 7.07-7.10 (2H, m), 5.65 (1H, dd), 3.15 (1H, dd), 2.84 (1H, dd)

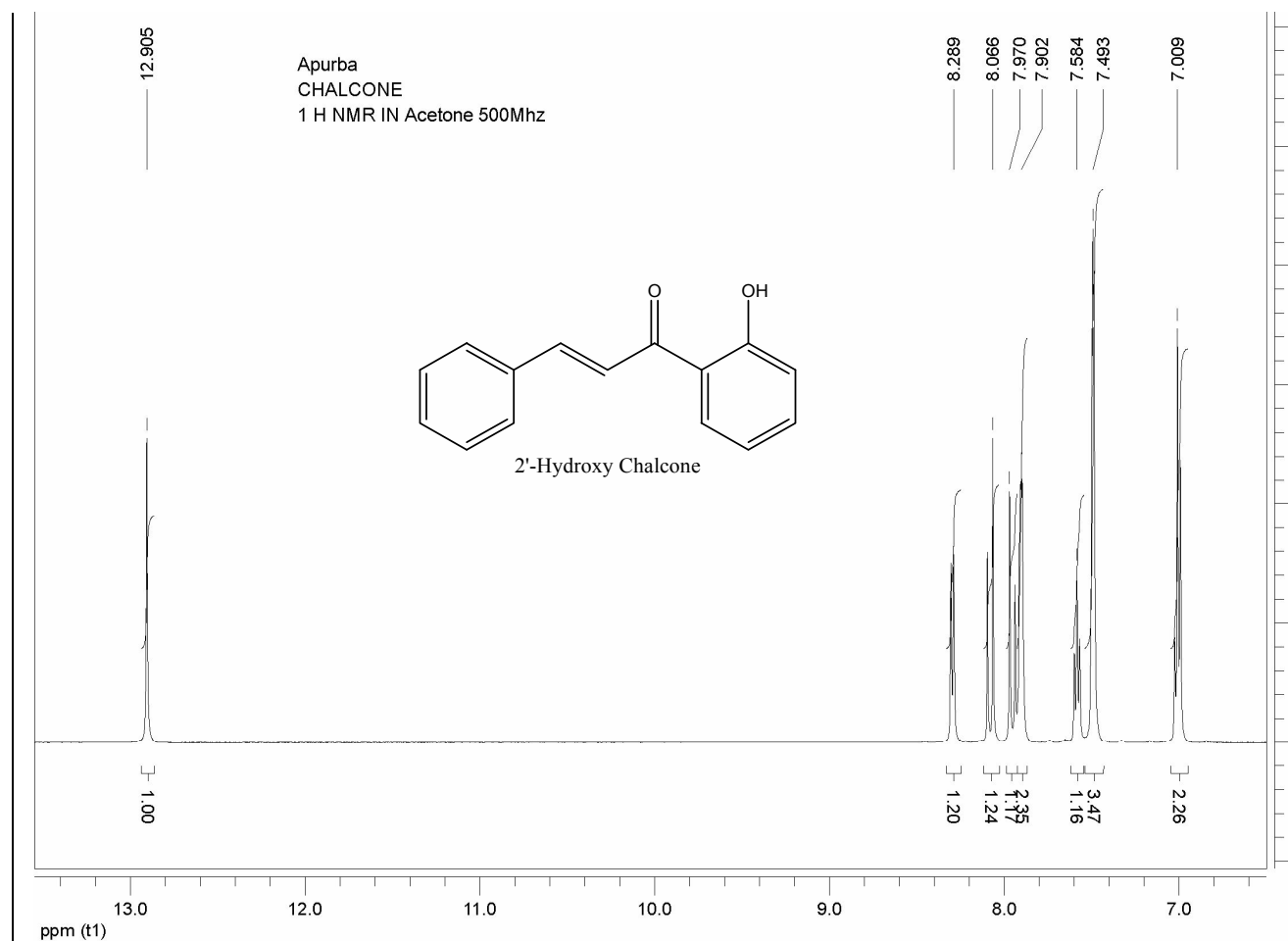


Figure S2 ^1H NMR Spectrum for 2'-hydroxy chalcone

2'-hydroxy chalcone 1H NMR in acetone (500 MHz): δ (ppm).12.9 (1H, s), 8.29 (1H, dd), 8.06 (1H, d), 7.97 (1H, d), 7.9 (2H, m), 7.58 (1H, m), 7.49 (3H, m), 7.01 (2H, t).

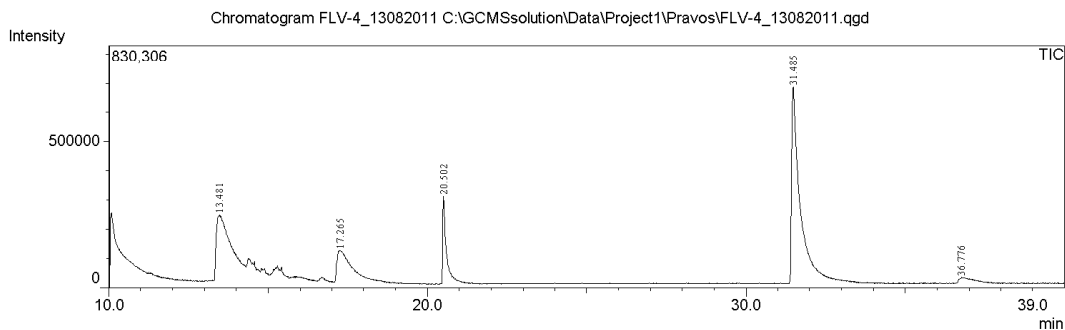
Central Salt and Marine Chemicals Research Institute

11/14/2011 15:42:27

C:\GCMSsolution\Data\Project1\Pravos\FLV-4_13082011.qgd

Sample Information

Analyzed by : Admin
 Analyzed : 8/13/2011 1:14:05 PM
 Sample Type : Unknown
 Sample Name : FLV-4_13082011
 Sample ID : FLV-4_13082011
 Vial # : 1
 Injection Volume : 1.000
 Data File : C:\GCMSsolution\Data\Project1\Pravos\FLV-4_13082011.qgd
 Method File : C:\GCMSsolution\Data\Project1\Pravos\IPA_cut.qgm
 Report File :
 Tuning File : C:\GCMSsolution\System\Tune1\290910.qgt



Peak Report TIC

Peak#	R. Time	Area	Area%	Height	Height%	Name
1	13.481	8010804	29.38	220227	16.72	Benzaldehyde
2	17.265	3342121	12.26	104428	7.93	o-Hydroxyacetophenone
3	20.502	2418604	8.87	299211	22.72	Tetradecane
4	31.485	12817125	47.01	672303	51.06	Flavanone
5	36.776	675785	2.48	20626	1.57	2'-Hydroxychalcone
		27264439	100.00	1316795	100.00	

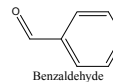
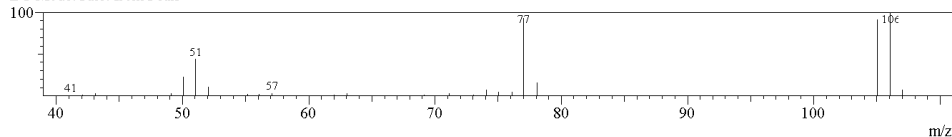
Spectrum

Line#:1 R. Time:13.5(Scan#:419)

MassPeaks:25

RawMode:Averaged 13.5-13.5(418-420) BasePeak:106(51968)

BG Mode:Calc. from Peak

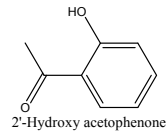
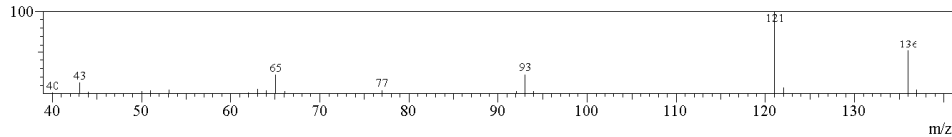


Line#:2 R. Time:17.3(Scan#:873)

MassPeaks:19

RawMode:Averaged 17.3-17.3(872-874) BasePeak:121(42151)

BG Mode:Calc. from Peak

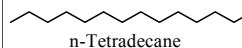
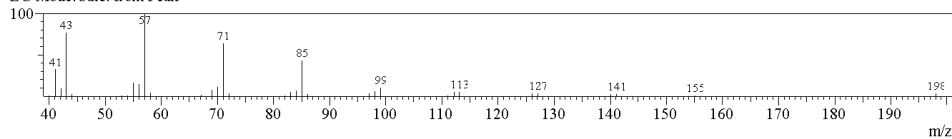


Line#:3 R. Time:20.5(Scan#:1261)

MassPeaks:33

RawMode:Averaged 20.5-20.5(1260-1262) BasePeak:57(63590)

BG Mode:Calc. from Peak



Central Salt and Marine Chemicals Research Institute

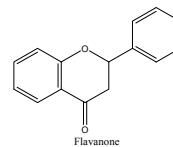
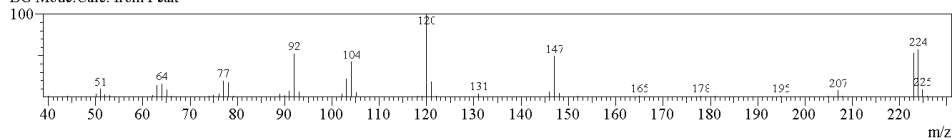
11/14/2011 15:42:27

Line#4 R.Time:31.5(Scan#:2579)

MassPeaks:52

RawMode:Averaged 31.5-31.5(2578-2580) BasePeak:120(113641)

BG Mode:Calc. from Peak

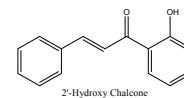
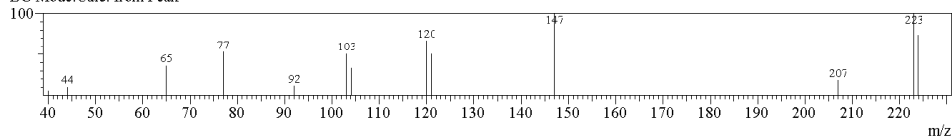


Line#5 R.Time:36.8(Scan#:3214)

MassPeaks:13

RawMode:Averaged 36.8-36.8(3213-3215) BasePeak:223(3154)

BG Mode:Calc. from Peak



2 / 2

Figure S3 GCMS result for the reaction mixture of benzaldehyde and 2'-hydroxy chalcone

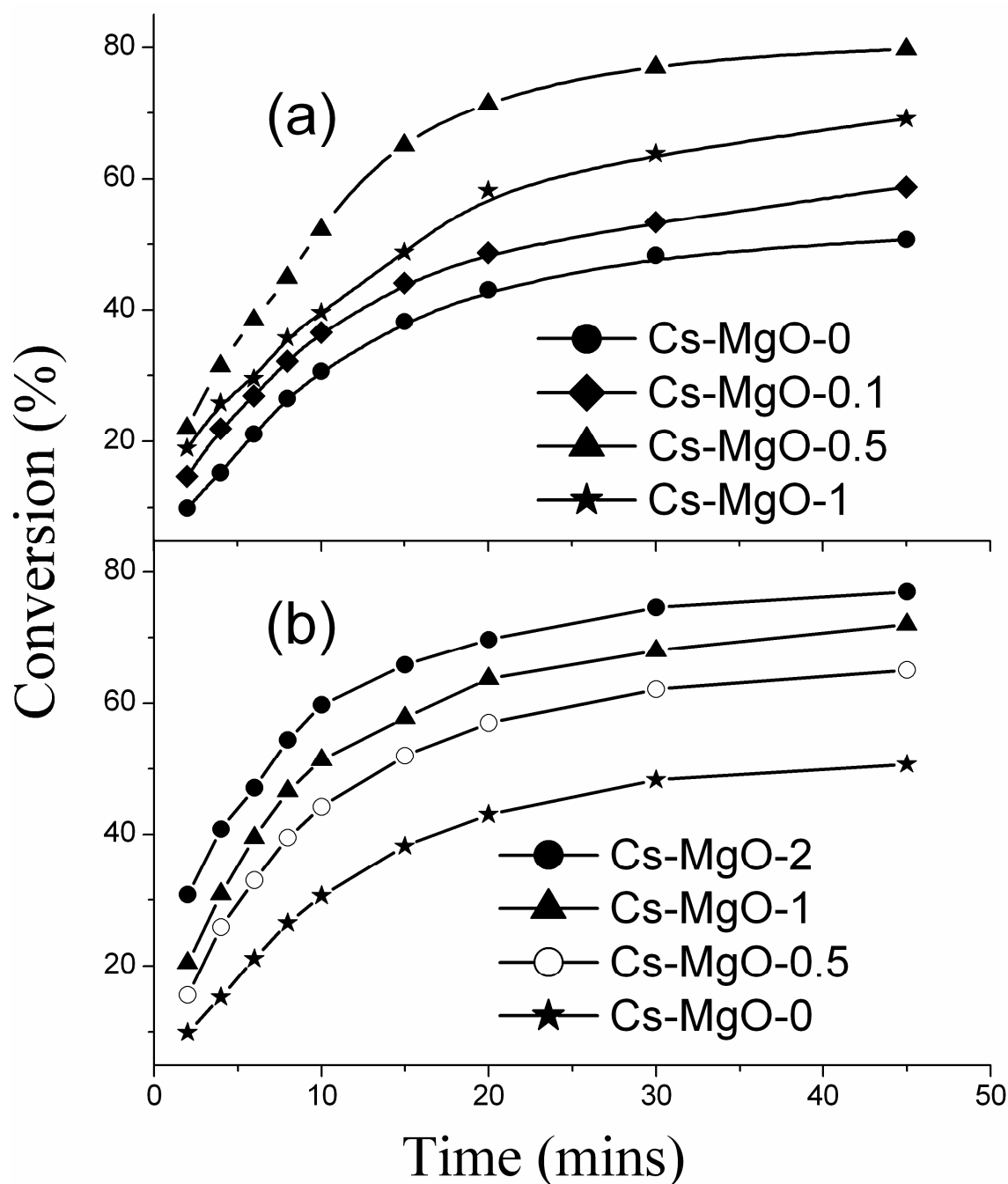


Fig. S4 2'-hydroxyacetophenone conversion as a function of time over synthesized MgO catalysts with constant catalyst amount 30 mg (a) and surface area (equivalent to 30 mg pure MgO) (b) keeping all other parameters constant (8 mmol of 2'-hydroxy acetophenone, 10 mmol of benzaldehyde, 100 mmol of DMF and reaction temperature of 140°C).

To understand the synergic effect of medium base site and surface area of the synthesized catalyst on the rate of reaction, reactions were performed with (i) constant amount of catalyst (30 mg, used

lower than optimized catalyst loading for better clarity) and (ii) constant surface area (equivalent to 30 mg pure MgO) with 8 mmol 2'-hydroxy acetophenone and 10 mmol benzaldehyde in 100 mmol DMF. Similar trained of reaction profile was observed (as Fig. 7a, in main manuscript) with higher constant amount of sample (114 mg). No change in trained of progress of reaction (although the conversion was decreased with lower amount of catalyst) was observed even after reduction of catalyst amount (Fig. S4a). However, the catalytic activity was gradually increased with the increased amount of Cs on MgO with constant surface area (Fig. S4b). From this it can be concluded that the catalytic activity of the synthesized MgO catalyst is a synergic effect of cesium dispersion and surface area.

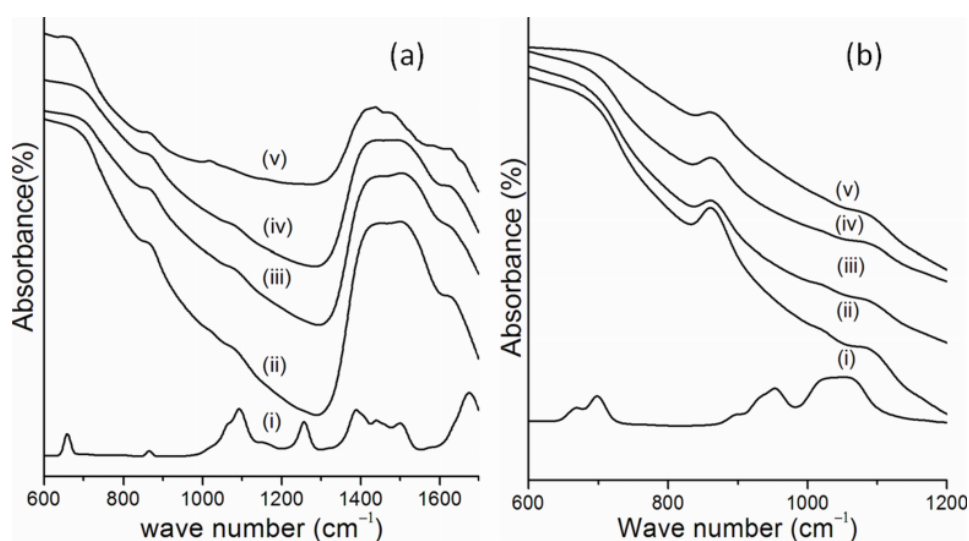


Fig. S5. (a) FT-IR spectra of pure DMF (i), DMF adsorbed MgO (ii), in situ flushing of (ii) with N₂ for 15 min (iii), 30 min(iv) and 60 min (v). (b) FT-IR spectra of pure DMSO (i), DMSO adsorbed MgO (ii), in situ flushing of (ii) with N₂ for 15 min (iii), 30 min(iv) and 60 min (v).

To identify the origin of enhanced promotion effect for DMF, the FTIR experiment of the DMF and DMSO adsorbed MgO-0.5 catalyst was performed at 140 °C with time under N₂ flow (as mentioned in the experimental section). In the FT-IR spectra of DMF adsorbed sample, the bands at 1628, 1414, 1086, 868 and 690 cm⁻¹ associated with C=O stretching, C-N stretching, C-H deformation, C'-N symmetric stretching and NCO deformation respectively was identified, which confirms the presence of DMF on the surface of catalyst (Fig. S5a). However, the C=O stretching band at 1675 cm⁻¹ of pure DMF shifted to 1628 cm⁻¹ in the spectra of DMF adsorbed on the MgO surface and confirms the chemisorptions of DMF on the surface of MgO instead of physisorption. In the FT-IR spectra of DMSO adsorbed sample the bands at 1088, 1020 cm⁻¹ associated with physisorbed S=O stretching (Fig. S5b). The band at 861 cm⁻¹ associated with chemisorbed S=O stretching, whereas S=O stretching of pure DMSO appeared at 1066 cm⁻¹, and band at 693 cm⁻¹ associated with C-S stretching. FT-IR results indicate that both chemisorbed as well as physisorbed DMSO was present in the catalyst surface. From the IR studies it is evident that the vibration band for C=O stretching of DMF shifted ~47 cm⁻¹ whereas the band for S=O stretching shifted ~205 cm⁻¹ after chemisorption on MgO surface. The shifting of bands for S=O stretching for DMSO was much higher than that of C=O stretching of DMF. The results evidenced that the DMSO adsorbed more strongly on the surface of catalyst than DMF.¹ To confirm this, FT-IR spectra of DMF and DMSO adsorbed samples was recorded after N₂ flashing for varying time at 140 °C (Fig. S5). It was observed that even after 1 h N₂ flashing the band at 861 cm⁻¹ associated with chemisorbed S=O stretching was present prominently, whereas band at 1628 cm⁻¹ associated with C=O stretching of DMF significantly decreased. Similar observation was also reported by Morito *et al.*¹ The strong chemical bonding of DMSO with catalyst surface leads to the partial deactivation of catalyst; and as a result the promotion effect of DMSO was less pronounced as compare to that of DMF. Amiridis and his group² reported the formation of sulfate species on the DMSO adsorbed MgO catalyst and predicted the generated sulfate species are the responsible for the promotion of reaction. In DMF as solvent, probably the promotion effect is originated from free lone pair of nitrogen, which helped the proton abstraction step and stabilized the polar intermediate.

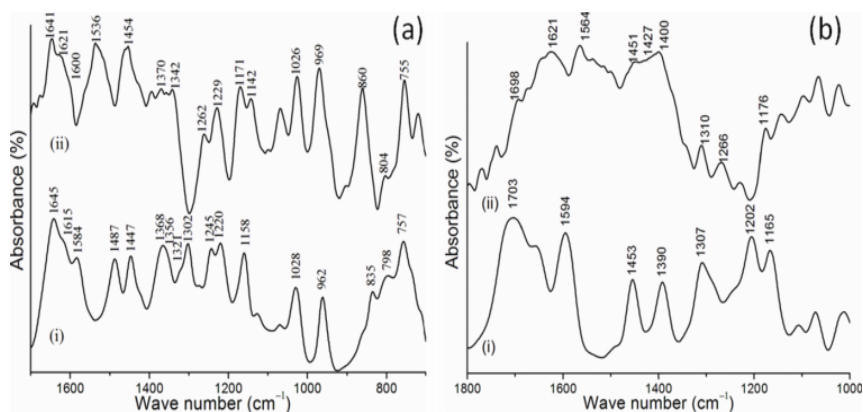


Fig. S6. (a) FT-IR spectra of pure 2'-hydroxyacetophenone (i) and 2'-hydroxyacetophenone adsorbed MgO at 140 °C (ii). (b) FT-IR spectra of pure benzaldehyde (i) and benzaldehyde adsorbed MgO at 140 °C (ii).

We have also performed the FT-IR study of 2'-hydroxyacetophenone and benzaldehyde adsorbed MgO-0.5 catalyst at 140°C to identify the type of interactions of the reactant with catalyst surface (Fig. S6). In the FT-IR spectra of 2'-hydroxyacetophenone adsorbed catalyst, a new band at 1336 cm⁻¹ was observed and the respective band of OH stretching vibration at 1321 and 1356 cm⁻¹ along with strong band at 1302 cm⁻¹ for C-O stretching of pure 2'-hydroxyacetophenone were disappeared. This phenomenon suggests a strong interaction of phenolic OH group of 2'-hydroxyacetophenone with catalyst surface through “acid-base” interaction. Similar observation was reported by Amiridis and his group³ and confirmed the band at 1336 cm⁻¹ is for C-O stretching. Whereas, two bands at 1641 and 1621 cm⁻¹ of 2'-hydroxyacetophenone adsorbed catalyst can be assigned to the physisorbed and chemisorbed C=O stretching respectively. On interaction of C=O group with catalyst the bond weakened and the wave number of corresponding C=O band at 1646 cm⁻¹ decreased. The reduction of wave number of chemisorbed C=O was much higher than that of physisorbed C=O. In the FT-IR spectrum of 2'-hydroxyacetophenone adsorbed catalyst, the appearance of band related to physisorbed OH group was not identified, whereas band related to the both physisorbed and chemisorbed C=O was identified. From this, it can be concluded that the 2'-hydroxyacetophenone was strongly bound on the catalyst surface through phenolic OH group and some carbonyl group was chemically bounded with the surface of catalyst, and some are weakly bounded. However, it is difficult to identify the enolate species due to the existence of band related to phenolic group in that region (1300-1400 cm⁻¹).

The strong band at 1703 cm⁻¹ assigned to C=O stretching was present in the FT-IR spectra of the both pure benzaldehyde and benzaldehyde adsorbed catalyst, but the intensity in the spectra of benzaldehyde

adsorbed catalyst was very less, suggests that the benzaldehyde is bonded weakly on the MgO surface. A intense new band was observed in the spectrum of benzaldehyde adsorbed catalyst at 1621 cm^{-1} assigned to the stretching vibration of weakened C=O bond, formed through the interaction of benzaldehyde and catalyst surface by substitution of aldehydic hydrogen. Absence of band at 1390 cm^{-1} of benzaldehyde, for aldehydic C-H bond, supports these observations. The new band at 1266 cm^{-1} for benzaldehyde adsorbed catalyst can be assigned to ring-C (aldehydic carbon) bond stretching vibration after substitution of aldehydic hydrogen. Other new bands in the spectrum of benzaldehyde adsorbed catalyst at 1564 , 1400 , 1427 cm^{-1} can be assigned to the asymmetric and symmetric stretching vibration of bridging surface benzoate ion coordinated to the one or two surface metal ions.³ The FT-IR spectra of mixed reactants and solvents adsorbed catalyst are very helpful to predict the probable reaction mechanism. However, these spectra are too complicated to identify as several overlapped bands appeared in the spectrum.

References:

- [1] N. Morito, W. Suetka, S. Shimodaira, *Spectrochimica Acta*. **1971**, *27A*, 131-137.
- [2] M. T. Drexler, M. D. Amiridis, *J. Catal.* **2003**, *214*, 136-145.
- [3] J. Lichtenberger, S. C. H. Leak, M. D. Amiridis, *J. Catal.* **2006**, *238*, 165-176.