<u>Electronic Supplementary Information</u>

Silica and zirconia supported tungsten, molybdenum and gallium oxide catalysts for the synthesis of furfural

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Materials

The chemicals used in this work were listed here. Softwood derived hemicellulose (Xylan, Aldrich Chemicals, USA, xylose ≥70%, glucose 15%, arabinose 10%), xylose (LOBA Chemicals, India, 99.5%), arabinose (s. d. fine, India, 100%), xylo-oligosaccharide (DP = 2-7, Cascade Analytical Reagents and Biochemicals, USA, 95%), glucose (s. d. fine, India, 100%), fructose (LOBA Chemicals, India, 99%), 5-hydroxymethylfurfural (Aldrich Chemicals, USA, >99%), furfural (LOBA Chemicals, India, 98%), toluene (LOBA Chemicals, India, 99.5%), ethanol (Analytical Reagents, India, 99.9%), ethylene glycol (s. d. fine, India, 99%), HCl (LOBA Chemicals, India, 35%), HNO_3 (LOBA Chemicals, India, 69-72%), ammonia solution (Rankem, India, 25%), fumed silica (Aldrich Chemicals, USA, 99.8%), tetraethyl orthosilicate (TEOS, Aldrich Chemicals, USA, 98%), zirconyl nitrate (LOBA Chemicals, India, 99%), ammonium metatungstate hydrate (AMT, Aldrich Chemicals, USA, 66.5%), ammonium heptamolybdate tetrahydrate (AHM, LOBA Chemicals, India, 98%), gallium nitrate (Acros Organics, 99.99%), and *p*-nitro aniline (Thomas Baker, India, 99%) were purchased and used as received. Zeolite, HMOR (Si/Al = 10) was obtained from Zeolyst International and before use, it was calcined at 823 K in air for 16 h.

Catalyst synthesis

Various metals were incorporated in either silica (SiO_2) or zirconia (ZrO_2) through different synthesis techniques (wet-impregnation and sol-gel method). Metal loading was kept constant at 10 *wt*% for all the catalysts. Before use all the supports were activated at 423 K under evacuation for 6 h. The synthesis processes are described below.

For the synthesis of catalysts by wet-impregnation (WI) method, as a metal precursor, ammonium metatungstate hydrate (AMT), ammonium heptamolybdate tetrahydrate (AHM), and gallium nitrate salt solutions were used in the synthesis of WO_3/SiO_2, MoO_3/SiO_2, and Ga_2O_3/SiO_2 catalysts, respectively. In a typical synthesis procedure, 1.0 g of SiO_2 support was dispersed uniformly in 8 mL of de-ionized water within 0.5 h. Then requisite amount of metal salt solution (metal concentration = 10 *wt*% with respect to silica; in 2 mL de-ionized water) was added slowly to the dispersed silica and stirred vigorously for 16 h at *RT*. Now the excess water was removed from the system with rotary evaporator and the solid obtained was dried (first at

333 K for 16 h and then at 383 K for 6 h under evacuation). Finally the materials were calcined in air to obtained supported metal oxide catalysts. The calcination temperatures applied were 823 K for tungsten (2 h) and molybdenum (5 h), and 573 K for gallium (1 h) catalyst. The catalysts prepared by wet-impregnation method are named as WO_3/SiO_2 (WI), MoO_3/SiO_2 (WI) and Ga_2O_3/SiO_2 (WI).

In sol-gel (SG) synthesis, W, Mo, and Ga oxides were supported on both SiO_2 and ZrO_2 based on the processes described in the literature[1-5] with minor modification in the procedure. The detail procedures were described below.

For synthesis of WO_3/SiO_2 (SG) catalyst, typically, mixture of 10 mL TEOS and 20 mL deionized water was made homogeneous and hydrolysed at 333 K for 14 h. Resulting ethanol was removed from the system and after thorough water washing and separation silica gel was obtained. Prepared silica gel was made acidic with careful addition of 3.8 M HCl (pH=1-1.5). In another beaker, 0.67 g AMT (calculated amount for 10 $wt\%$ W based on theoretical yield of silica) was dissolved in de-ionized water to obtain 6.5×10^{-3} M solution. pH of this solution was maintained at 1-1.5 by addition of 3.8 M HCl at RT and the solution was aged under static condition for 48 h. Now, acidic tungstate gel was mixed slowly with acidic silica gel under vigorous stirring for 1 h. Resulting solution was aged at RT under static condition for 12 h. The gel thus obtained was washed with water and dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation). Finally light yellow coloured WO_3/SiO_2 (SG) was obtained after calcination of material at 823 K for 2 h in the presence of air.

In a typical synthesis of MoO_3/SiO_2 (SG), 0.64 g AHM (calculated amount for 10 $wt\%$ Mo based on theoretical yield of SiO_2) was dissolved in 40 mL ethylene glycol and solution was stirred for 0.5 h. Then to this solution, 10 mL TEOS was added and resulting mixture was heated at 353 K for 5 h under vigorous stirring. The solution was then diluted with 20 mL of de-ionized water and acidified with 0.5 mL concentrated HNO_3. The solution was then kept at 353 K under stirring until it becomes a thick gel. The gel formed was washed with water, dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation), and finally calcined at 823 K for 5 h in air to obtain powdered MoO_3/SiO_2 (SG).

Typically for the synthesis of Ga_2O_3/SiO_2 (SG), to the solution of 1.25 g gallium nitrate (calculated amount for 10 $wt\%$ Ga based on theoretical yield of SiO_2) 21 mL ethanol and 10 mL of TEOS was added and the mixture was stirred for 0.5 h at RT. A thick gel was formed after the slow addition of ammonia solution to the previous mixture. The gel was washed with ethanol, dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation), and finally calcined at 573 K for 1 h in air to get final catalyst.

In a typical synthesis of ZrO_2, 5.0 g zirconyl nitrate hydrate was dissolved in 98.27 g distilled water. To it, 5% diluted ammonia solution was added drop by drop with vigorous stirring until pH of solution become 9.1 and stirring was continued for 1 h at 298 K. Then the solid mass was aged for 12 h at RT without stirring. The precipitate obtained was washed with water till pH becomes neutral and dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation). Finally light brown powdered ZrO_2 was obtained after calcination at 773 K for 4 h in presence of air.

For the synthesis of WO_3/ZrO_2 (SG) catalyst, 1.88 g zirconyl nitrate was dissolved in 30 mL deionized water and pH of this solution was adjusted to 10 with a slow addition of 25% ammonia solution. In another container, aqueous solution of AMT (0.22 g AMT + 7 mL deionized water) was prepared and made alkaline with dropwise addition of 25% ammonia (pH = 10). Now zirconyl nitrate solution was added slowly to alkaline AMT solution and a white gel was formed. The gel was aged at RT for 24 h under static condition. The gel obtained was washed with water and dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation). Finally powdered WO_3/ZrO_2 (SG) was obtained after calcination at 823 K for 2 h in presence of air.

In a typical synthesis of MoO_3/ZrO_2 (SG) catalyst, 1.88 g zirconyl nitrate was dissolved in 30 mL deionized water and made homogeneous by stirring for 0.25 h. To it an aqueous solution (7 mL) of calculated amount of AHM (0.21 g; to maintain 10 $wt\%$ Mo based on theoretical amount of ZrO_2) was added and stirred vigorously. 25% ammonia was then added to the system under constant stirring until pH = 10 was reached and the gel formed was aged at RT for 12 h under static condition. Later this gel was washed with water, dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation), and finally calcined at 823 K for 5 h in air to obtain powdered MoO_3/ZrO_2.

Typically for the synthesis of Ga_2O_3/ZrO_2 (SG) catalyst, 1.88 g zirconyl nitrate was dissolved in 30 mL deionized water and pH of this solution was maintained at 10 with a slow addition of 25% ammonia solution. In another container, aqueous solution of gallium nitrate (0.41 g salt + 7 mL de-ionized water) was prepared and made alkaline with dropwise addition of 25% ammonia (pH = 10). Now zirconyl nitrate solution was added slowly to alkaline salt solution and formation of gel was observed. The gel was aged at *RT* for 24 h under static condition. The gel obtained was washed with water and dried (first at 333 K for 16 h and then at 383 K for 6 h under evacuation). Finally powdered Ga_2O_3/ZrO_2 (SG) was obtained after calcination of material at 573 K for 1 h in presence of air.

Catalyst characterization techniques

The synthesized supported metal oxide catalysts were characterized with Thermogravimetry Analysis (TGA-DTG), X-ray Diffraction (XRD), Temperature Programmed Desorption of ammonia (TPD-NH_3), Inductively Coupled Plasma-Optical Emission Spectroscopy (ICP-OES) and Ultraviolet-Visible (UV-Vis) spectroscopy techniques.

Thermal stability of catalysts was analyzed with Mettler Toledo TGA/SDTA 851 series, USA instrument at a heating rate of 10 K min^{-1}. The recording temperature range of graph was set at 298-1273 K.

XRD analysis of samples was carried out with Rigaku Miniflex diffractometer using a Ni-filtered monochromatic Cu K_α radiation (λ = 1.54 Å).

Micromeritics AutoChem-2920 instrument equipped with thermal conductivity detector was used for the TPD analysis. Before analysis, all the samples were activated at 873 K in He gas flow. Adsorption of NH_3 gas (10% NH_3 + 90% He) on the catalyst surface was allowed at 323 K for 1 h followed by catalyst surface cleaning with 100% He to remove physisorbed NH_3. Then the recording was carried out at 10 Kmin^{-1} heating rate in the temperature range of 373-873 K for NH_3 desorption.

Elemental analysis was carried out in Spectro Acros ICP-OES instrument installed with winlab software.

UV-Vis spectra were recorded with Jesco V-570 spectrophotometer in the range of 200-600 nm. This analysis also helps in determining Hammett acidity value (H_0) of the catalysts. For analysis of solid powdered catalyst, we used the same instrument operated in a wavelength range of 200-600 nm.

Catalytic reaction

For catalytic reaction, softwood hemicellulose (xylan) composed of ≥70% xylose, 10% arabinose and 15% glucose unit was used. Typically, reactions were carried out with 0.3 g hemicelluloses (xylan) or xylose, 0.075 g catalyst and water or water + toluene (1:1 *v/v*) = 60 mL charged in Parr autoclave. Inert atmosphere in autoclave was ensured with N_2 gas flushing thrice inside the autoclave and finally filled with 0.2 MPa N_2 gas. Then reaction was conducted at desired temperature. After the reaction catalyst was separated from reaction mixture by centrifugation.

Analysis of reaction solutions

Water soluble products were identified and quantified with Agilent 1260 Infinity series HPLC operated with Millipore water as mobile phase (0.6 mL min^{-1} flow rate), combined with Pb^{2+} column (300 mm × 7.8 mm, oven temperature of 353 K), and refractive index detector (cell temperature of 313 K). Toluene (organic solvent) soluble products were identified and quantified with Varian make gas chromatograph, equipped with HP-5 column (50 m × 0.22μm *ID*), and flame ionization detector (FID).

Calculations

Detail calculations for the xylose/hemicellulose conversions and product yields were described below.

% conversion of xylose = [{Initial mole of xylose − mole of xylose remaining (HPLC)} / Initial mole of xylose] × 100

% Hemicellulose conversion = [(Total solid charged in the reaction − Solid recovered after reaction) / (Weight of initial hemicellulose charged in the reactor)] × 100

Hemicellulose molecular weight was taken as 132 considering loss of 18 (due to water removal) from xylose/arabinose (molecular weight of 150) during polymerization to form

6

hemicellulose. So 132 g hemicellulose will form 150 g xylose + arabinose (considering 100% conversion and selectivity).

% yield of xylose + arabinose = [mole of xylose + arabinose (HPLC) / mole of xylose + arabinose (theoretical)] × 100

Molecular weight of furfural is 96. So, 96 g of furfural formation is possible from 150 g xylose + arabinose (considering 100% yield and selectivity).

% yield of furfural = [mole of furfural (GC [org] + HPLC [water]) / mole of furfural (theoretical)] × 100

For the quantification of oligomers, standard containing dimer to heptamer was procured and then calibration curve was drawn.

Table S1 ICP-OES analysis of metal oxide catalysts prepared with the theoretical loading of 10$wt\%$

Synthesis technique	Catalyst	Actual metal loading (wt%)
Sol-gel	Fresh WO_3/SiO_2	9.95
	Spent WO_3/SiO_2	9.93
	Fresh MoO_3/SiO_2	9.01
	Spent MoO_3/SiO_2	9.03
	Fresh Ga_2O_3/SiO_2	9.36
	Spent Ga_2O_3/SiO_2	9.30
Wet-impregnation	Fresh WO_3/SiO_2	9.79
	Spent WO_3/SiO_2	5.32
	Fresh MoO_3/SiO_2	8.74
	Spent MoO_3/SiO_2	4.11
	Fresh Ga_2O_3/SiO_2	9.22
	Spent Ga_2O_3/SiO_2	6.89
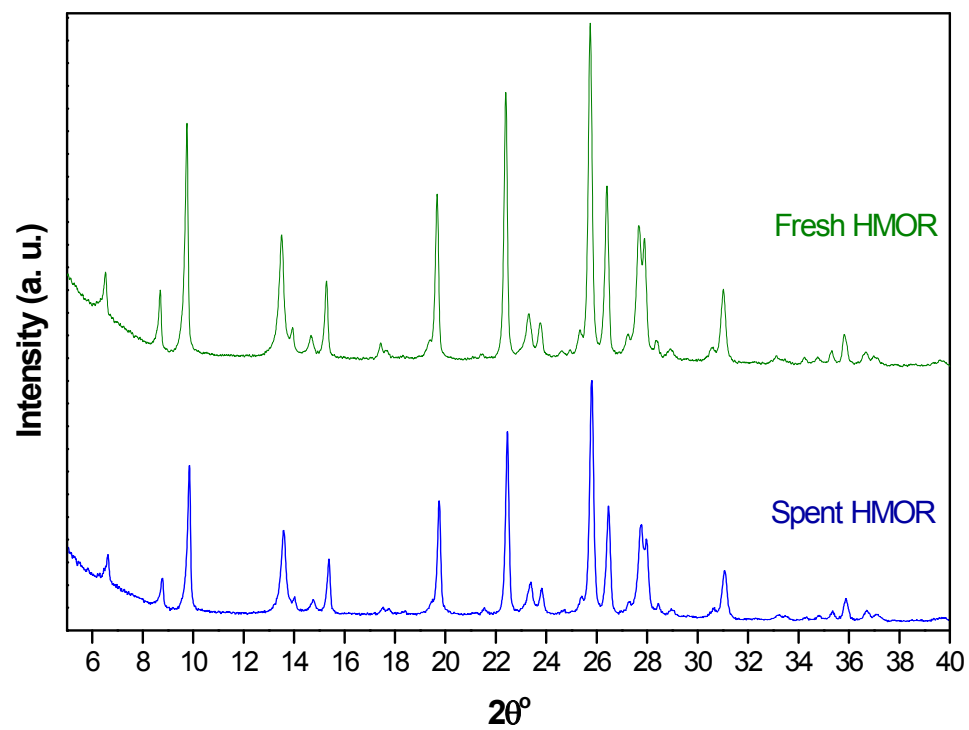
Fig. S1 XRD patterns for HMOR (Si/Al = 10) catalyst before use (fresh) and after use (spent, after calcination at 823 K, 12 h, in air) in hemicellulose conversion.
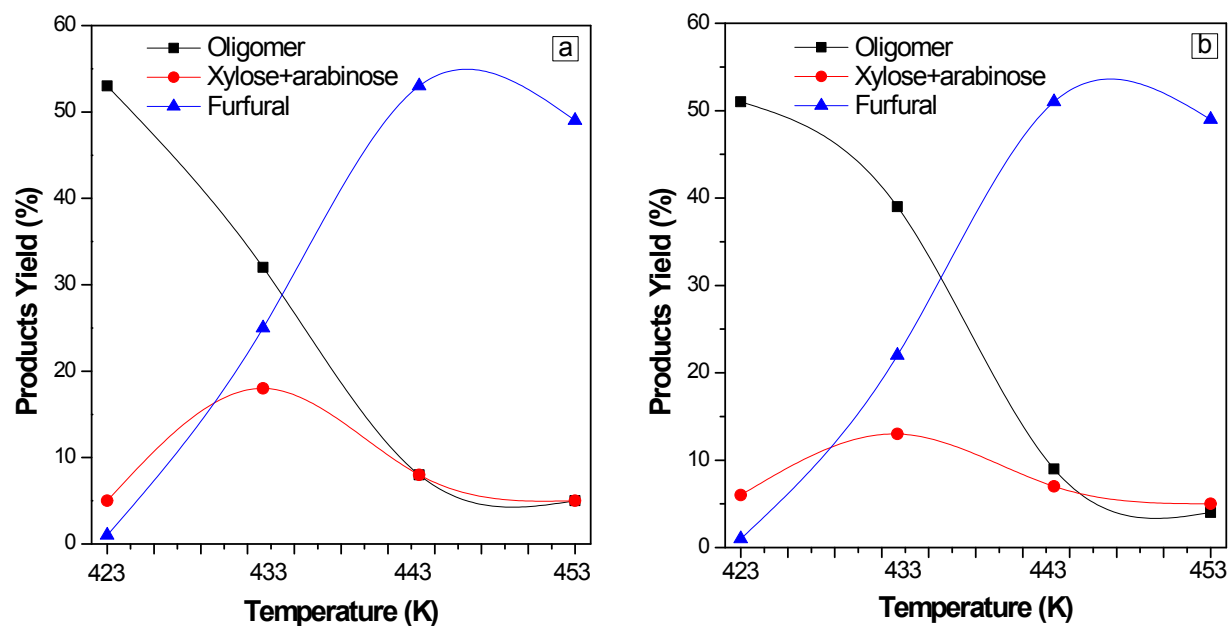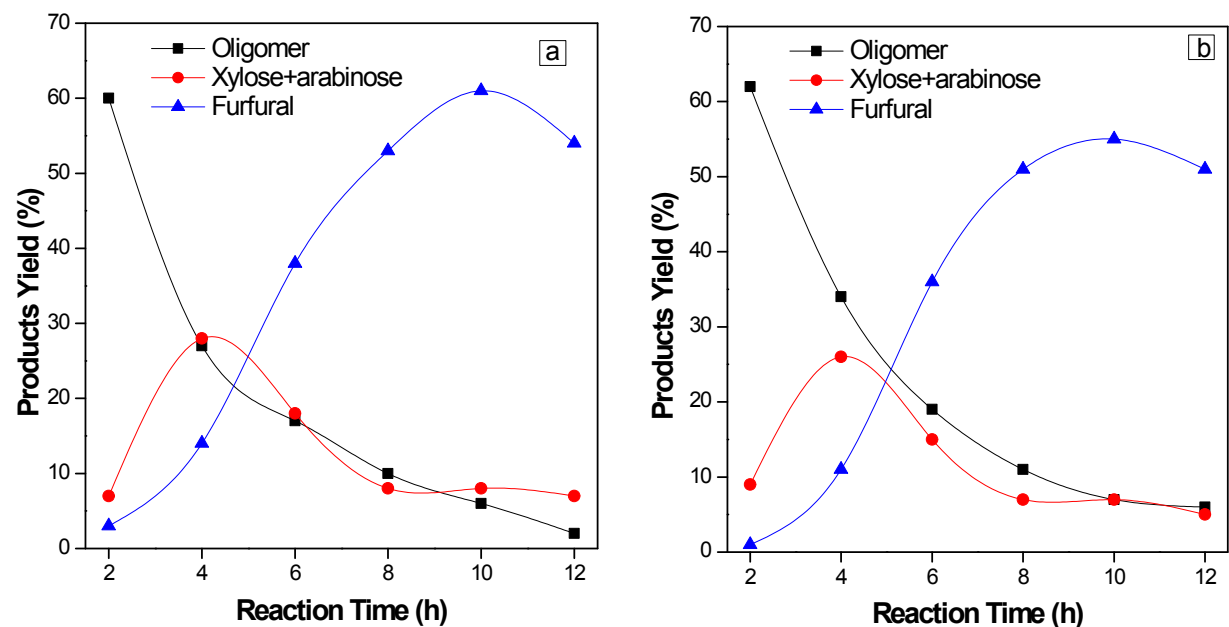
Fig. S2a, b Optimization of reaction temperature for one-pot hemicellulose conversion to furfural in presence of sol-gel (SG) synthesized catalysts; a. WO_3/SiO_2, b. Ga_2O_3/SiO_2. Reaction conditions: hemicellulose (0.3 g), catalyst (0.075 g), water + toluene = 60 mL (1:1 *v/v*), 8 h.

Fig. S3a, b Optimization of reaction time for one-pot hemicellulose conversion to furfural in presence of sol-gel (SG) synthesized catalysts; a. WO_3/SiO_2, b. Ga_2O_3/SiO_2. Reaction conditions: hemicellulose (0.3 g), catalyst (0.075 g), water + toluene = 60 mL (1:1 *v/v*), 443 K.

Optimization of catalyst amount

Use of minimum quantity of catalyst can boost its applicability quotient. Consequently, a study with both WO_3/SiO_2 (SG) and Ga_2O_3/SiO_2 (SG) was undertaken at 443 K by altering the S/C ratio (*wt/wt*) from 1 to 8 keeping substrate amount constant (1*wt*%). Similar yield of furfural (55-61%) after 10 h reaction was detected with the S/C ratio maintained in the range of 1-4, but with the increase in ratio to 8, decrease in the yield (ca. 47%) with lower hemicellulose conversion (86%) was seen. This was quite obvious as insufficient amount of acid sites were present in the system to catalyze reactions. Hence, in next reactions, S/C ratio of 4 was fixed.

Optimization of substrate concentration

Besides, lowering the catalyst quantity it is also beneficial if higher substrate amount can be used and hence reactions were conducted using 1, 5 and 10*wt*% hemicellulose concentration. The results indicate that with 1 and 5 *wt*% substrate concentrations similar furfural yields (WO_3/SiO_2 (SG)=61±2%, Ga_2O_3/SiO_2 (SG)=56±1%) can be achieved however, with the increase in concentration to 10*wt*%, lower yields (WO_3/SiO_2 (SG)=45%, Ga_2O_3/SiO_2 (SG)=40%) were obtained. The lower yield of furfural can be due to the occurrence of side reactions since concentrated solution of furfural and xylose is present. The similar phenomenon is explained in case of fructose dehydration reaction to yield HMF.[6]
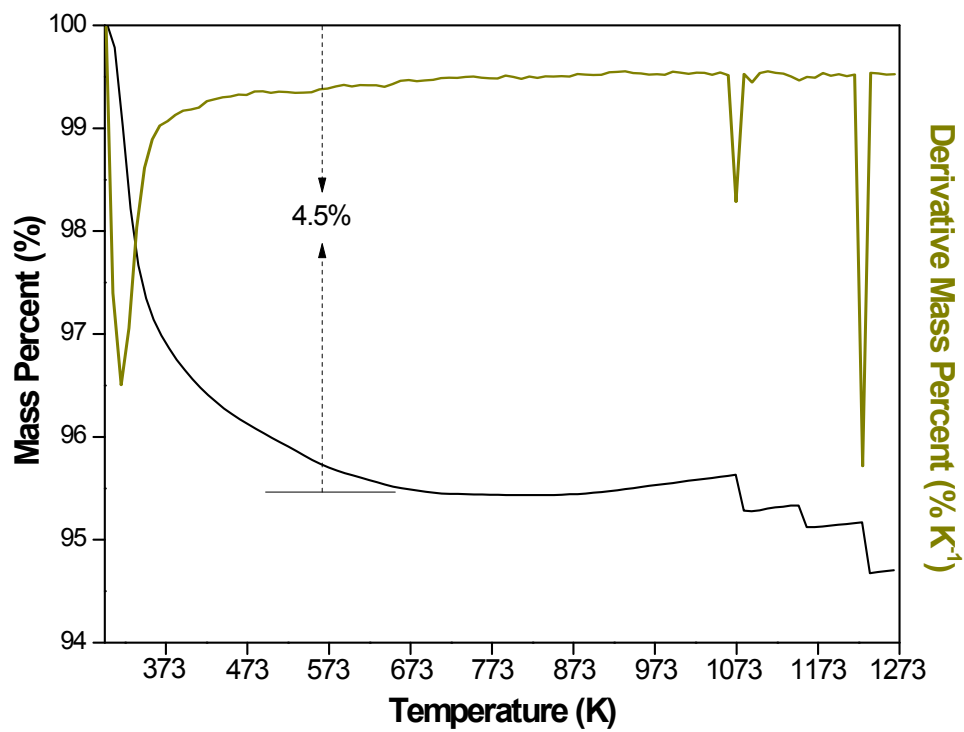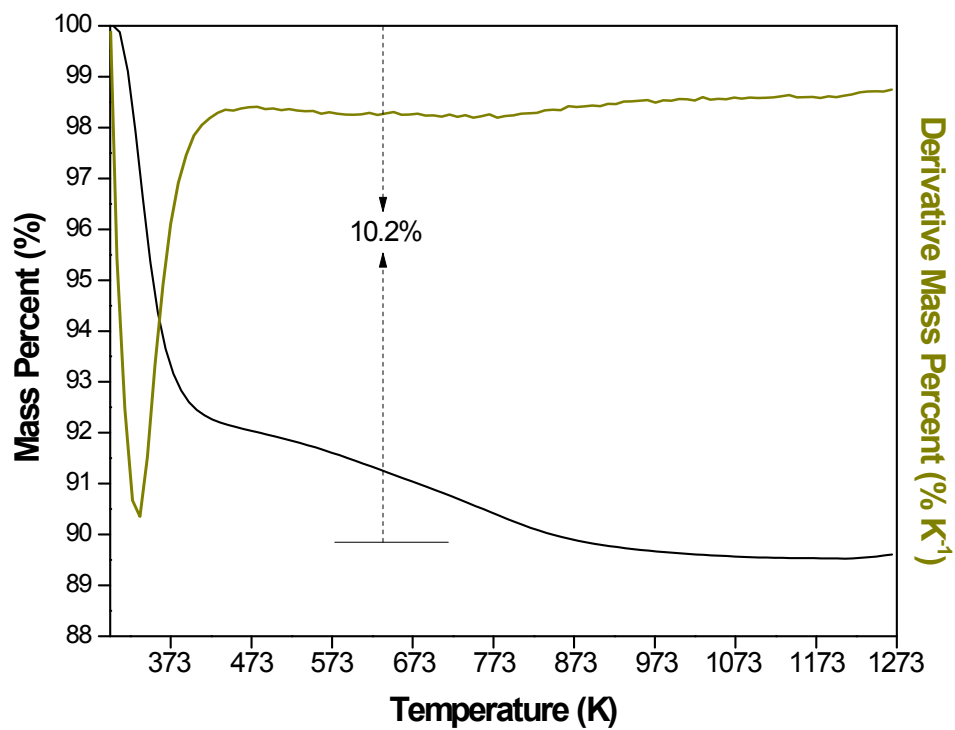
Fig. S4a TGA-DTG analysis for WO_3/SiO_2 (SG).

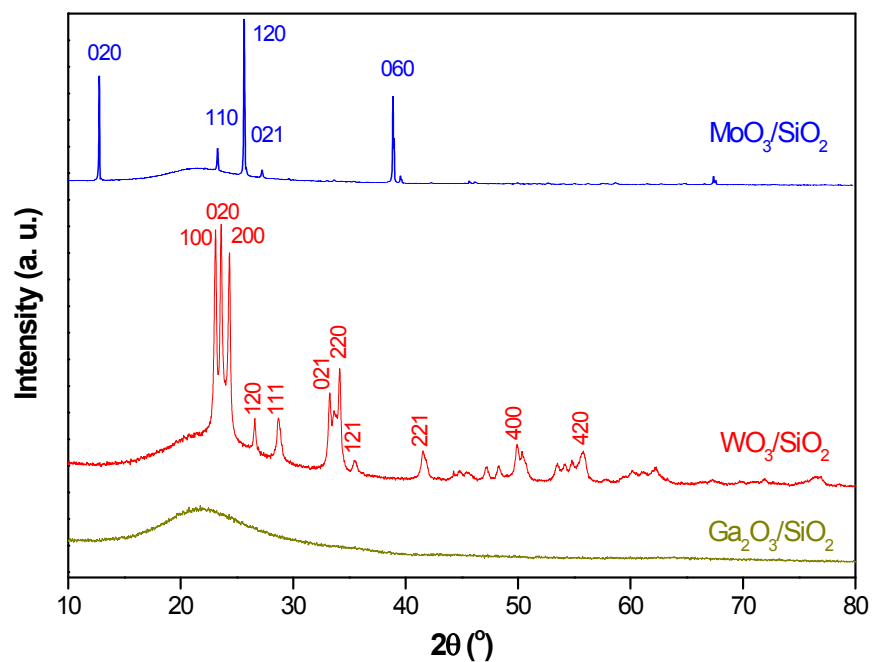**Fig. S4b** TGA-DTG analysis for Ga_2O_3/SiO_2 (SG).

Fig. S5 XRD patterns for silica supported tungsten, molybdenum and gallium oxide catalysts synthesized by wet-impregnation (WI) method.
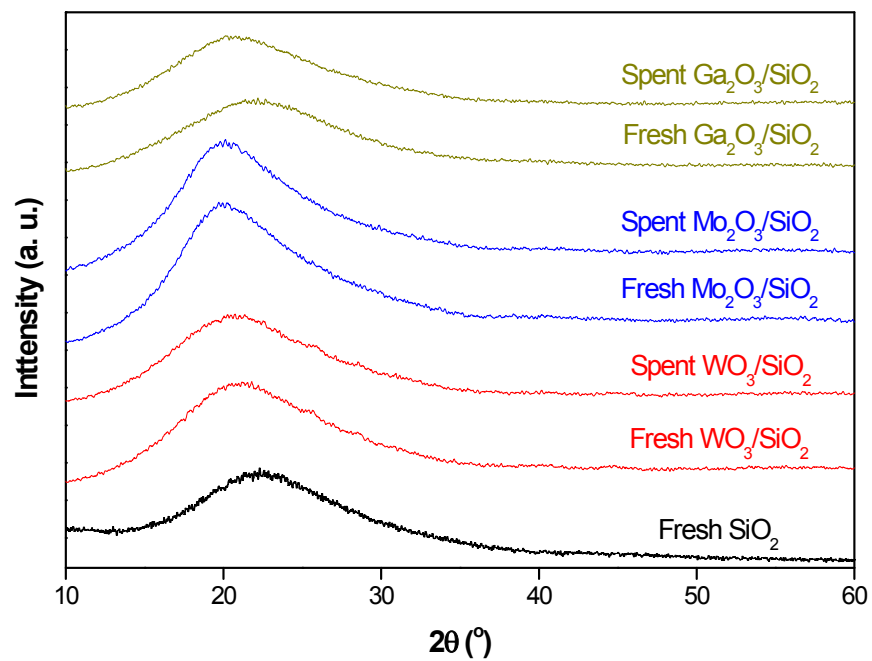

Fig. S6 XRD patterns for silica supported tungsten, molybdenum and gallium oxide catalysts synthesized by sol-gel (SG) method.
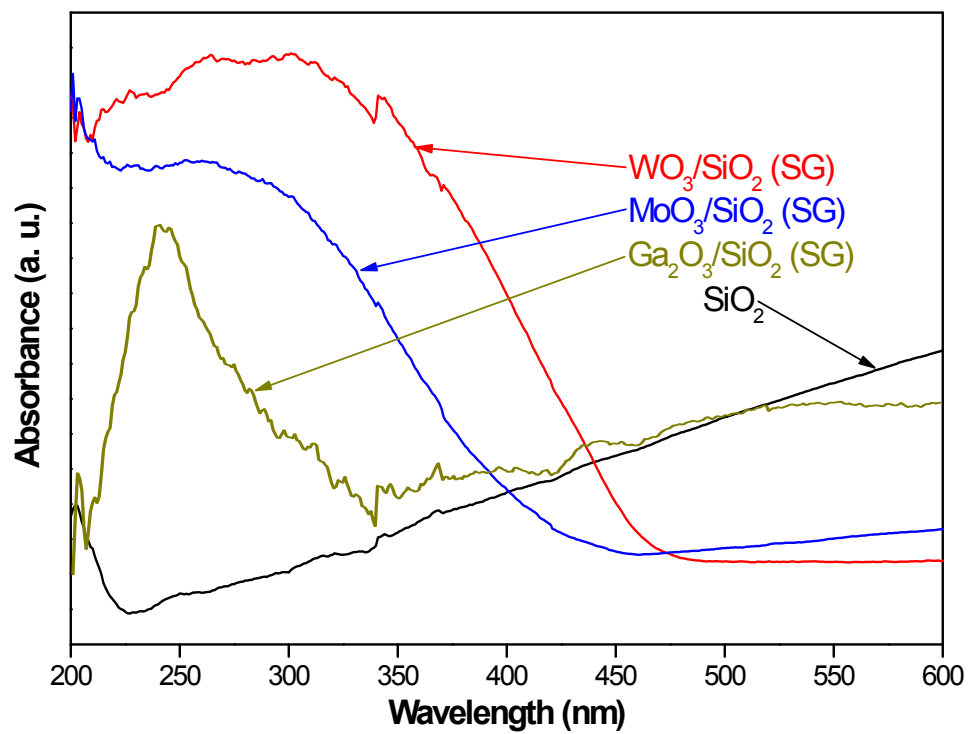
Fig. S7 UV-Vis analysis of sol-gel (SG) synthesized silica supported tungsten, molybdenum and gallium oxide catalyst along with fumed silica.

XRD analysis of ZrO$_2$ supported metal oxide catalysts

The below figure shows the XRD patterns for bulk structures of pure ZrO$_2$ and ZrO$_2$ supported metal oxides (SG). Pure ZrO$_2$ calcined at 773 K shows peaks for both the phases, monoclinic and tetragonal. The similar observation is noted in the literature.[7] The incorporation of molybdenum in ZrO$_2$ shows characteristic peaks for orthorhombic MoO$_3$ species with change in the ZrO$_2$ peak pattern. This is obvious since calcination at higher temperature (823 K) modifies tetragonal phase into monoclinic phase in ZrO$_2$.[7] Moreover, it is also reported that peak due to Zr(MoO$_4$)$_2$ species can be observed around same 2θ value (30.2°) where peak due to tetragonal phase of ZrO$_2$ is observed. However, in our case we rule out this possibility since we prepared the catalysts with 10wt% Mo loading and literature describe formation of Zr(MoO$_4$)$_2$ at very high Mo loading (37wt%). XRD pattern for WO$_3$/ZrO$_2$ catalyst shows typical peaks for orthorhombic WO$_3$ phase with tetragonal phase (major) in ZrO$_2$. The similar observation was reported in the literature for WO$_3$/ZrO$_2$.[8] Absence of metal oxide peaks in Ga$_2$O$_3$/ZrO$_2$ might be due to very high dispersion and ZrO$_2$ mostly remain in tetragonal phase since calcination was done at 573 K.[8]
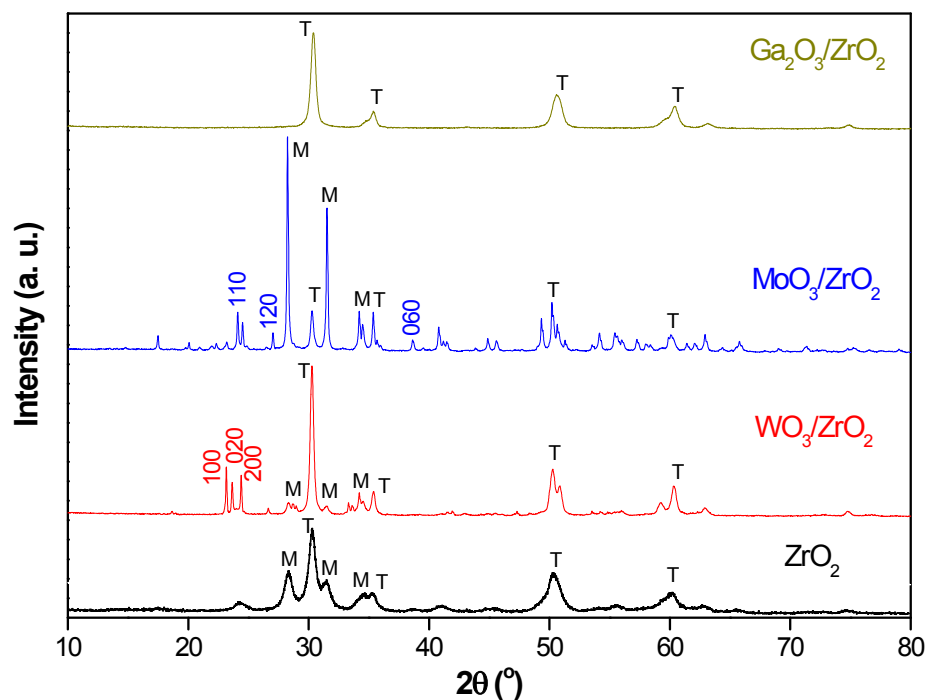

Fig. S8 XRD patterns for zirconia supported tungsten, molybdenum and gallium oxide catalysts synthesized by sol-gel (SG) technique. 'M' indicates monoclinic ZrO$_2$ phase and 'T' indicates tetragonal ZrO$_2$ phase.
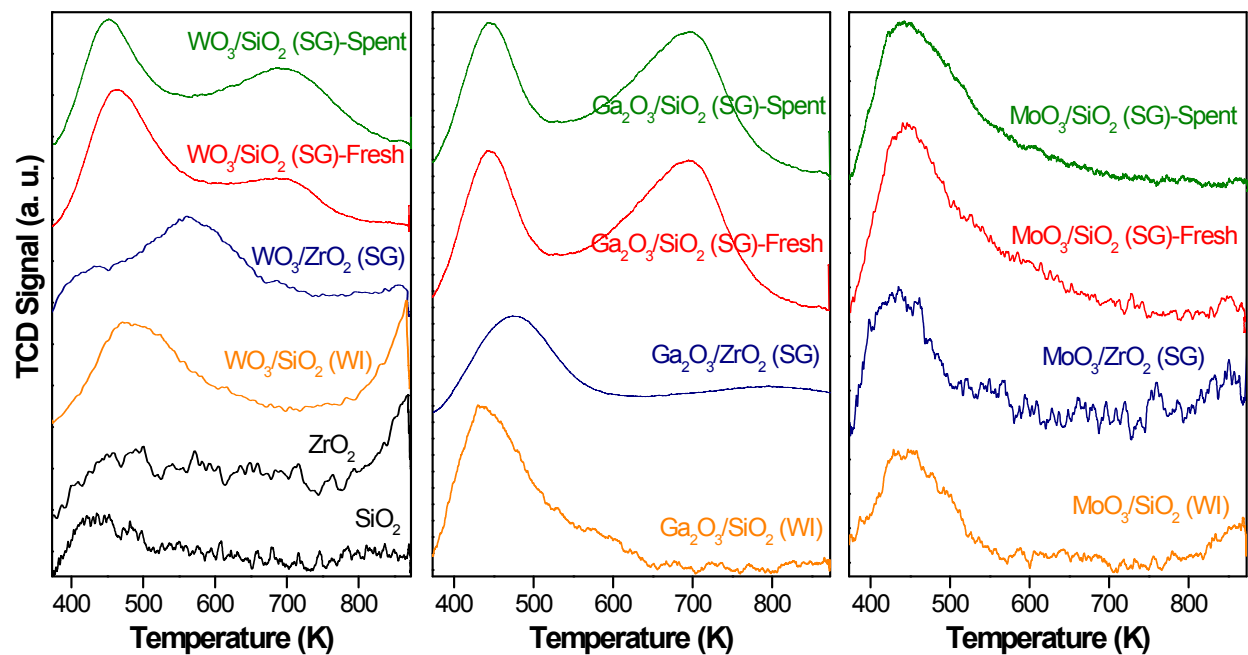
Fig. S9 TPD-NH$_3$ profile for all synthesized supported metal oxide.

Hammett acidity calculation for sol-gel synthesized supported metal oxide catalysts

Determination of Hammett acidity was carried out with a basic indicator, *p*-nitro aniline (*p*-NA) according to previous report.[9] With the increase in acid scale in sample, the absorbance of the un-protonated form of basic indicator decreased, whereas the protonated form of indicator could not be observed because of its small molar absorptivity. In a typical procedure, 0.0025 g of catalyst was added to 10 mL standard *p*-NA solution in water (10 ppm, $pK_a = 0.99$). Stirred the mixture for 0.5 h and filtered the solution through 0.22 μm syringe filter. Absorbance of filtrate was checked with UV-Vis spectrophotometer in the range of 200-600 nm. A maximum absorbance for all the samples was observed at 380 nm. Hammett acidity (H_0) of samples was calculated according to the following equation.

$H_0 = pK(I)_{aq} + \log_{10} ([I] / [IH^+])$

In this equation, $pK(I)_{aq}$ stands for the pK_a value of standard indicator aqueous solution, [I] stands for percentage of un-protonated indicator and [IH$^+$] stands for percentage for protonated indicator. Calculations of H_0 were shown in below table.

Table S2 Determination of Hammett acidity in supported metal oxide catalysts

Catalyst[#]	A_{max}	[I]%	[IH$^+$]%	H_0
Blank	1.105	100	0	-
Fresh WO$_3$/SiO$_2$	0.918	83.1	16.9	1.68
Spent WO$_3$/SiO$_2$	0.911	82.4	17.6	1.66
Fresh MoO$_3$/SiO$_2$	1.027	92.9	7.1	2.11
Spent MoO$_3$/SiO$_2$	1.033	93.5	6.5	2.15
Fresh Ga2O$_3$/SiO$_2$	0.990	89.6	10.4	1.92
Spent Ga2O$_3$/SiO$_2$	0.995	90.0	10.0	1.95

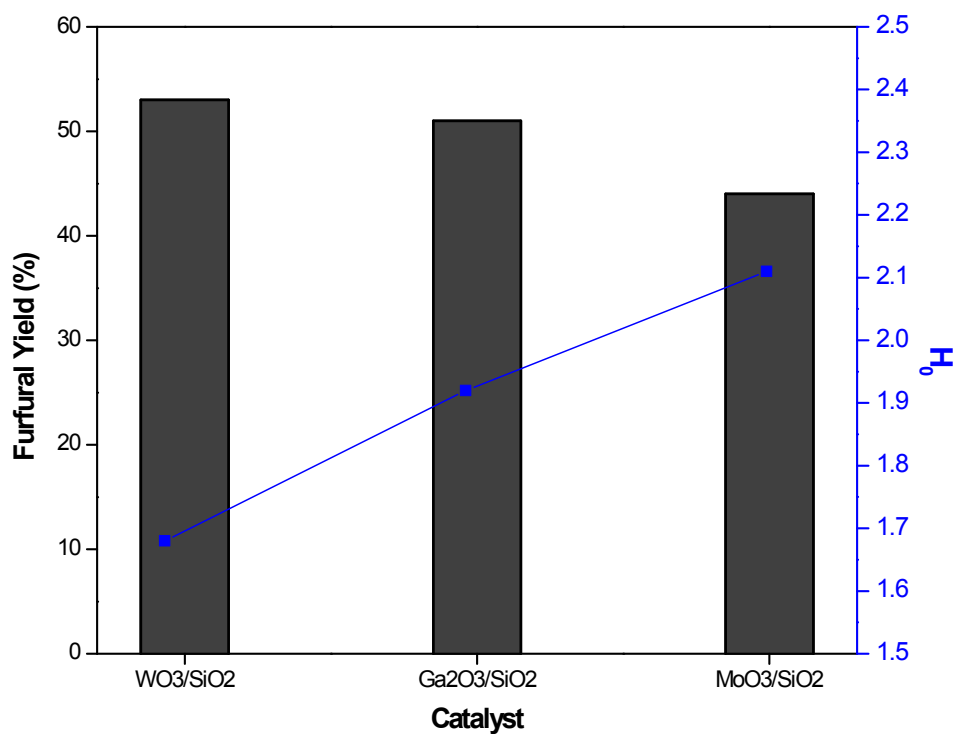[#]catalysts synthesized by sol-gel (SG) method.

Fig. S10 Correlation between furfural formation activity and acid strength of silica supported tungsten, molybdenum and gallium oxide catalysts synthesized by sol-gel (SG) method.

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