Synthesis and catalytic properties of mesoporous, bifunctional, gallium-niobium mixed oxides.

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Supporting Information

Experimental Section

Materials. Gallium (III) nitrate hydrate (99.99 %, Strem Chemicals) and Niobium Chloride (99.99%, Sigma) were used as the inorganic precursors. Pluronic F127 (BASF) was used as structure directing agent (SDA). Ethanol (~99 % Sigma) was used as the organic solvent. Methyl oleate (85% Alfa Aesar) was employed as the probe molecule to determine the catalytic activity.

Synthesis of mixed mesoporous gallium-niobium oxide and mesoporous niobium oxide via SAHA. Mixed mesoporous gallium-niobium oxide phases were prepared under mild synthesis conditions by reacting alcoholic solutions of inorganic precursors with SDA solutions. In a typical synthesis, the inorganic precursors were uniformly mixed in ethanol. The solution was vigorously stirred at 40°C and 280 rpm until the precursors were dissolved completely. A homogeneous alcoholic solution of the structure directing agent F127 was prepared at 40°C. The SDA-alcohol solution was then added dropwise to the precursor solution under continuous stirring for about 30 min. During the entire process the temperature was kept constant at 40°C. This homogeneous gel was then transferred to a 45 ml Teflon lined stainless steel autoclave (Parr Instrument) and heated under autogenous pressure in a static condition in conventional oven at 180°C for 20 h. The resultant white solids were separated from the solution by centrifugation at 4000 rpm and 20 min, washed three times with deionized water and dried overnight at 60°C. The resultant powder was then calcined in air at 350°C for 10 h yielding mesoporous gallium-niobium mixed oxide phases. A similar method was employed for the synthesis of mesoporous niobium oxide. Typical synthesis compositions on molar basis were Precursor:Surfactant:Solvent:1:6.1x10^{-3}-350x10^{-3}:9, while the molar ratio of gallium to niobium varied between 0.2 to 6.6.

A reference mixed oxide (GaNb4A) sample was synthesized in the absence of the SDA by homogenously mixing the alcoholic solutions of inorganic precursors. This solution was then transferred to teflon lined stainless steel autoclave and heated under autogeneous pressure at 180ºC for 20h.

Catalysts Characterization. The morphology and crystal size of the mesophases were analyzed with a FE-SEM (FEI Nova 600) with an acceleration voltage of 6 kV. The XRD patterns were collected on Brukar D8 Discover diffractometer employing $Cu_{k\alpha}$-1.54Å as the source. N_2 adsorption BET surface areas were determined in a Micromeritics Tristar-3000 porosimeter. Before the surface area measurements, the samples were degassed at 300°C for 3 hrs. HRTEM images were collected on Technai F20 FEI TEM using a field emission gun, operating with an accelerating voltage of 200 kV.

Catalytic activity and Analysis of Reaction Products. The catalytic activity of the mesoporous mixed oxide was evaluated by reacting 0.2 g of the catalyst (activated in nitrogen overnight at 220°C) with 2 ml of the probe molecule (methyl oleate) in a standard batch autoclave (Parr Instruments) at 220°C and autogeneous pressures for 20 h. No solvents or carrier gases were used. At the end of the period, the reactor was cooled to room temperature. The catalyst was removed by filtration and the reaction products were analysed by GC-MS (HP 5890 Gas Chromatograph equipped with 5970 Mass Selective Detector; 30m X 0.32 mm column, HP-5 coated with 5% phenyl methyl poly siloxane stationary phase), and ^{1}H and ^{13}C NMR spectrometry (Varian 7600 AS 400 MHz).

Conversion of methyl oleate and selectivity to various products were calculated as follows:

Methyl oleate conversion (%wt) = ((C_{18} in feed-C_{18} in product)/C_{18} in feed) × 100

Selectivity for skeletal isomerisation products = ((skeletal isomers in product-skeletal isomers in feed)/C_{18} converted) ×100

Selectivity for (C_{14}+C_{16}) products = ((C_{14}+C_{16}) in product-(C_{14}+C_{16}) in feed)/C_{18} converted) × 100

Analysis of Reaction Products. The products consisted of branched methyl and ethyl isomers of methyl oleate, dehydrogenated dilolefinic product from methyl oleate (methyl linoleate), methyl palmitates, C_{16}:1 (from the dehydrogenation of methyl palmates, C_{16}:0, an impurity in the methyl oleate).

Product identification was done by a combination of gas chromatography, mass spectrometry and ^{1}H / ^{13}C NMR and IR spectroscopies. The gas chromatographic peaks corresponding to M^{+}296 and M^{+}294 peaks in the mass spectra were used to identify and quantify the concentrations of methyl oleate and linoleate, respectively. The concentration of the skeletal isomers was obtained from gas chromatography/mass spectrometry and also from the ratio of the intensities of the ^{1}H NMR peaks at 5.3-5.5 ppm (characteristic of internal olefinic C-H protons) and those at 1.92-2.08 ppm (characteristic of allylic protons), respectively. The concentration of oleic acid was estimated from gas chromatography, acid-base titration as well as changes in the ^{13}C NMR peaks of the carbonyl carbon (of the ester) at 174.3 ppm and the methyl carbon of the ester at 51.5 ppm. The quantification of the oleic acid concentration was also done using peaks in the 2.37-2.41 ppm region in the ^{1}H NMR spectra by procedures published elsewhere [15].

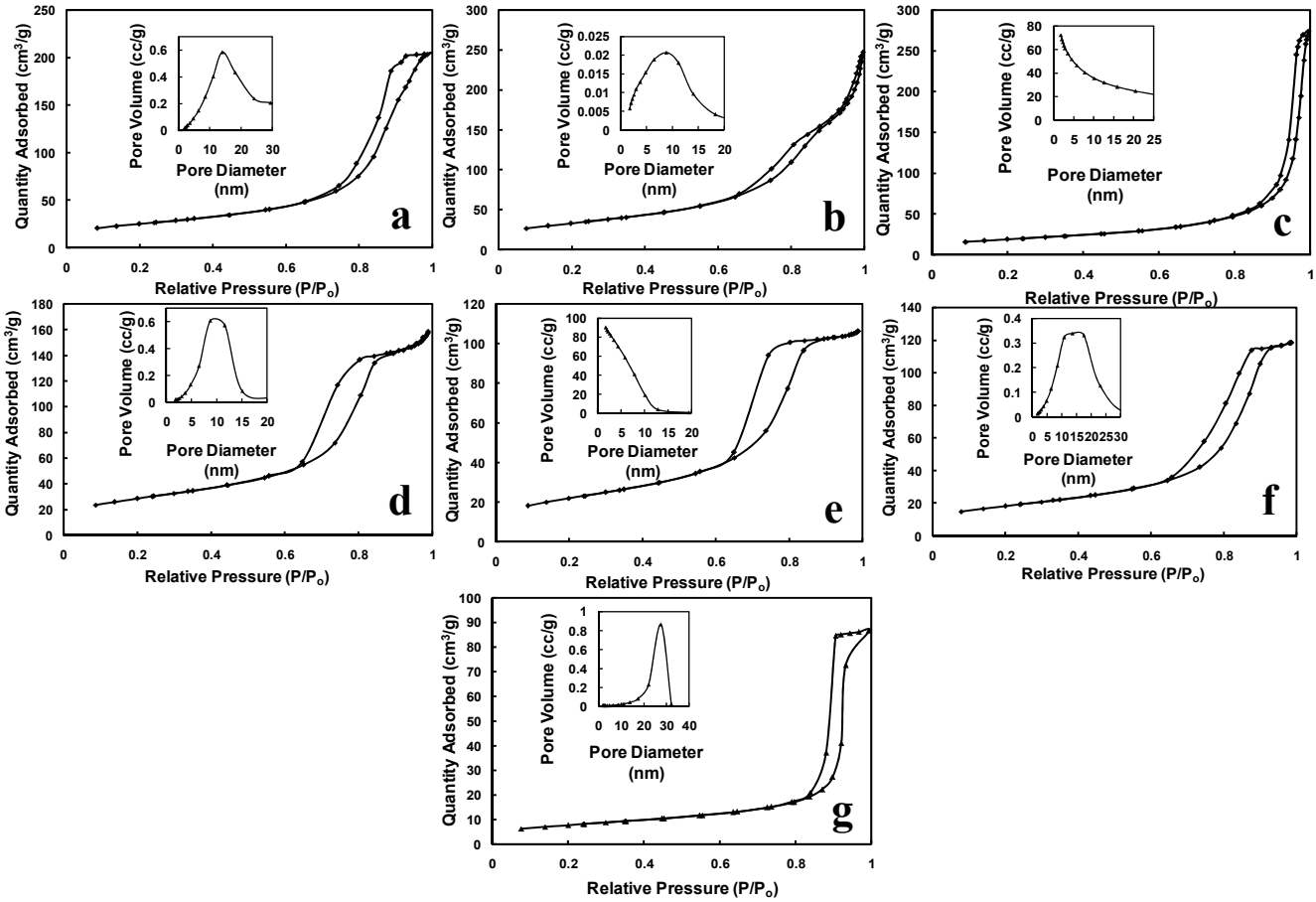

Figure S1. N_2 adsorption-desorption isotherms and BJH pore size distribution from adsorption branch of the mesoporous a) Ga_2O_3, b)-f) Ga-Nb mixed oxides, and h) Nb_2O_5 synthesized by SAHA employing F127 as SDA and calcined at 600˚C.

Table S1. General synthesis conditions and textural properties and average particle size of mesoporous gallium oxide, gallium-niobium mixed oxides and niobium oxide phases synthesized by SAHA calcined at 600ºC.

Sample ID	Composition Ga/Nb molar ratio	S. S. A. (m^2/g)	Average Pore Size (nm)	Pore Volume (cm^3/g)
Ga_2O_3	-	89	11.7	0.31
GaNb1	2.80	116	11.8	0.35
GaNb2	0.84	67	23.4	0.40
GaNb3	0.14	101	8.2	0.25
GaNb4	0.08	77	7.3	0.16
GaNb5	0.03	65	11.1	0.21
Nb_2O_5	-	27	18.2	0.13

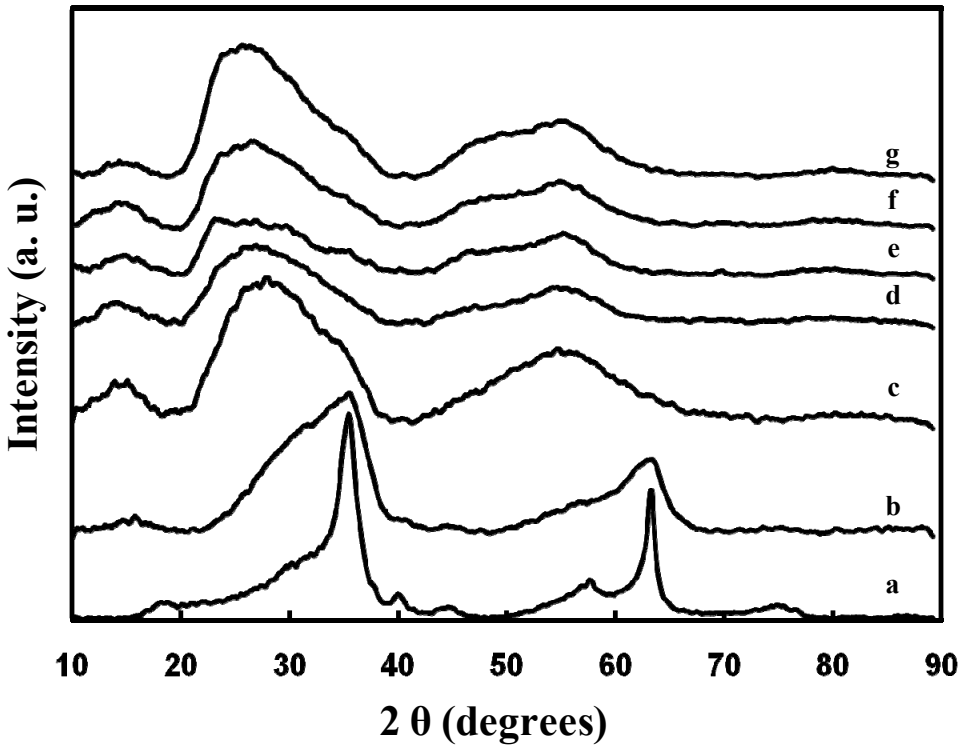

Figure S2. High-angle XRD patterns of a) mesoporous Ga_2O_3, b)-f) mixed GaNb (1-5) oxides, and g) mesoporous Nb_2O_5 calcied at 350˚C.

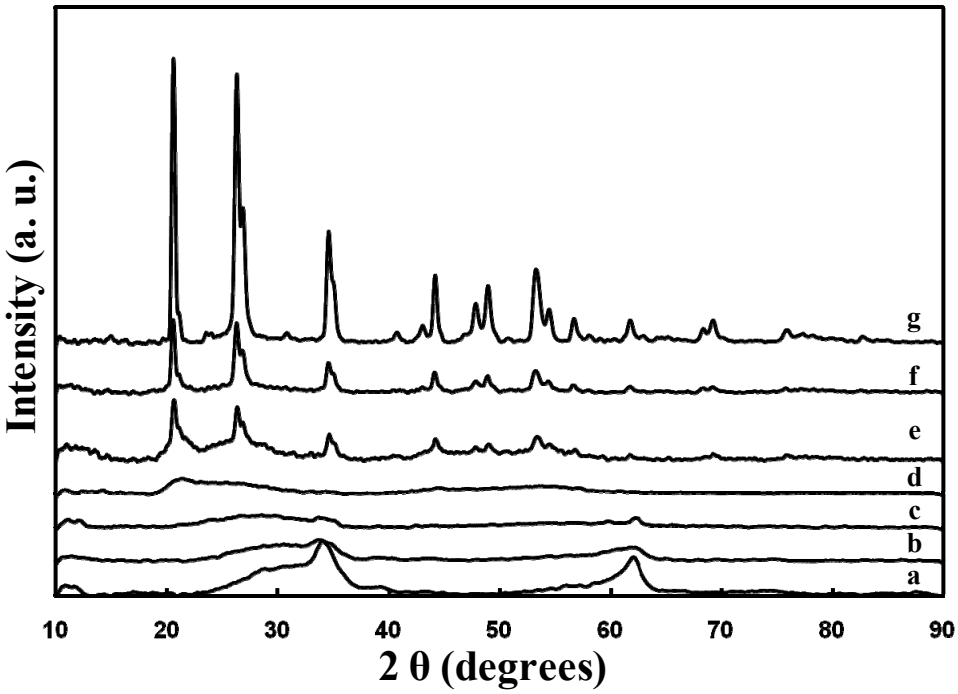

Figure S3. High-angle XRD patterns of mesoporous a) Ga_2O_3, b)-f) Ga-Nb mixed oxides, and g) Nb_2O_5 phases synthesized by SAHA employing F127 as SDA calcined at 600˚C.

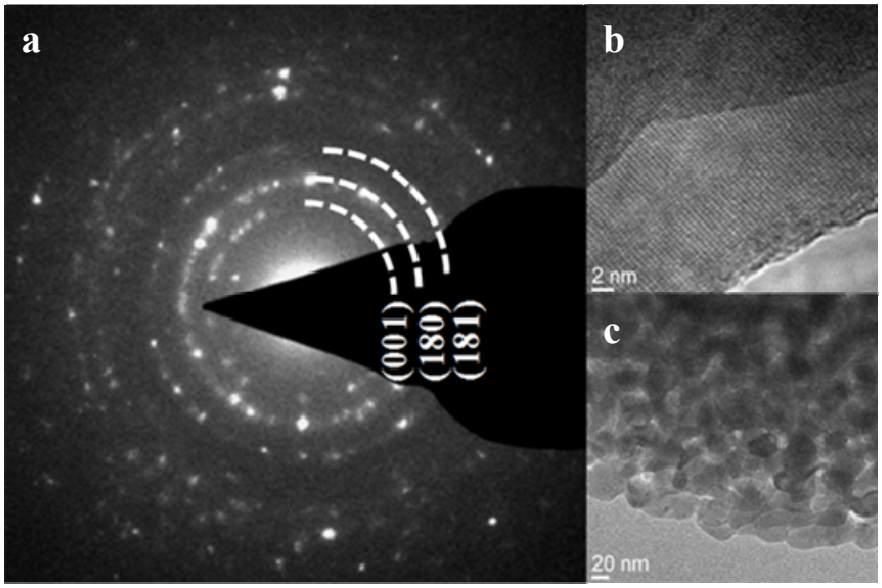

Figure S4. a) SAED pattern of mesoporous Nb_2O_5 synthesized by SAHA calcined at 600˚C, b) Magnified image of the crystals displaying the lattice fringes and c) HRTEM image of the crystals on the surface of the oxide.

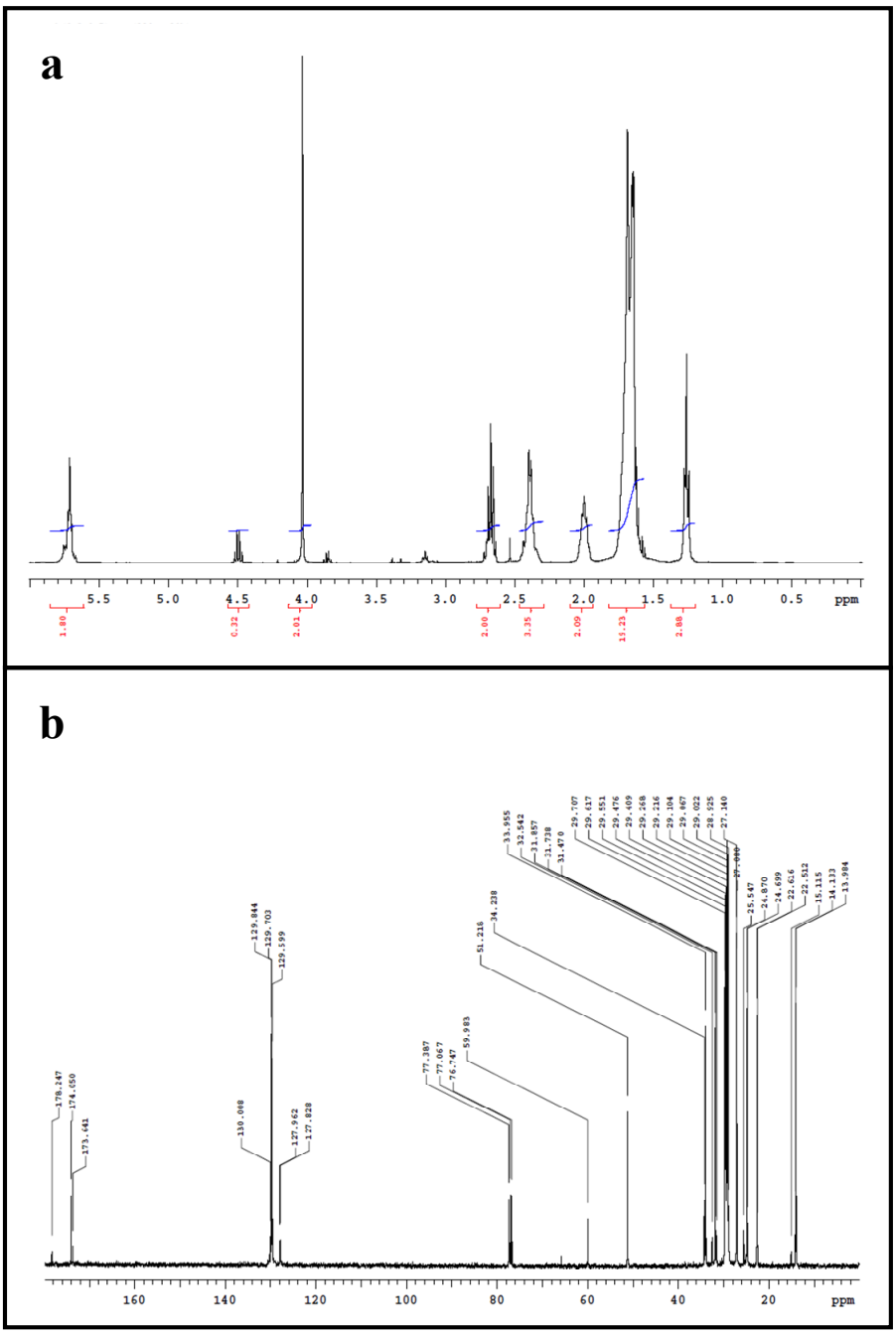

Figure S5. a) ^{1}H and b) ^{13}C NMR spectrums for the isomerisation products obtained using GaNb4 catalyst.

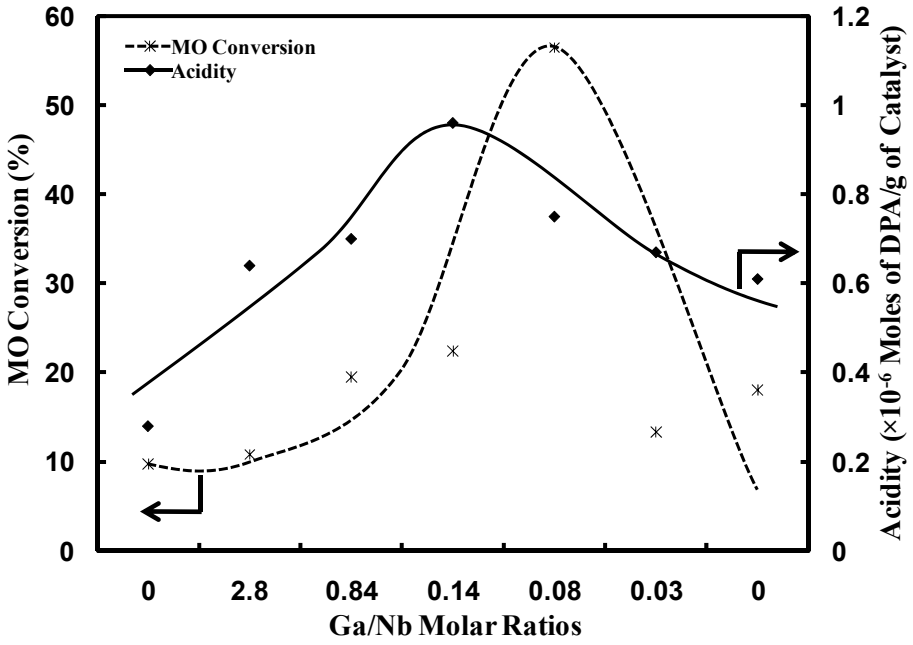

Figure S6. Plot of Composition of GaNb against Methyl oleate conversion and Acidity of the catalyst.