

## Electronic Supporting Information (ESI)

# $\gamma$ -Al<sub>2-x</sub>M<sub>x</sub>O<sub>3±y</sub> (M = Ti<sup>4+</sup> through Ga<sup>3+</sup>): Potential *Pseudo-3D* Mesoporous Material with Tunable Acidity and Electronic Structure

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## ESI-1: Synthesis, Characterization and Catalytic activity measurement details

### (a) Preparation of metal ion precursor solutions in EDTA-ED-water mixture

All the metal compounds [ $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$ ,  $\text{TiCl}_3$  in HCl solution,  $\text{NH}_4\text{VO}_3$ ,  $\text{Cr}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Mn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Fe}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ ,  $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Ni}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ,  $\text{Cu}(\text{NO}_3)_2 \cdot 3\text{H}_2\text{O}$ ,  $\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ ], ethylene diamine tetraacetic acid (EDTA), ethylene diamine (ED), and tri-*n*-butyl amine (These chemicals are received from Wako chemicals, Sigma-Aldrich or Chameleon reagent) were used as such without any further purification. The concentration of each metal compound in EDTA-ED-water mixture was either 0.5 M (for Al, Ga, Mn, Fe, Co, Ni, Cu, Zn) or 0.25 M (for Ti, V, Cr) in terms of metal ion content.

The preparation of 0.50 M solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in EDTA-ED-water was carried out as follows: The precursors  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$ , EDTA and ED are in the molar ratio of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}:\text{EDTA}:\text{ED} = 0.1:0.1:0.3$  (1:1:3). First, EDTA (29.23 g, 0.1 mol) was mixed with about 125 ml water in a 250 mL beaker. To the EDTA-water mixture, 0.3 mol ED (18.03 g) was added with continuous stirring so that EDTA completely dissolves and a clear solution was obtained. About 0.1 mol of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  (37.51 g) was then added to the EDTA-ED-water solution with continuous stirring. A slight precipitation occurs initially. The resulting colloidal solution was then immediately heated by keeping in a water bath that has already maintained at 85-90°C. The solution was stirred using a glass rod during the heating process until the precipitate dissolves completely. A clear solution of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  was resulted in about 1 hour heating. The solution was then cooled, and made up to 200 mL in a standard flask. The concentration of  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  in EDTA-ED-water was 0.5 M.

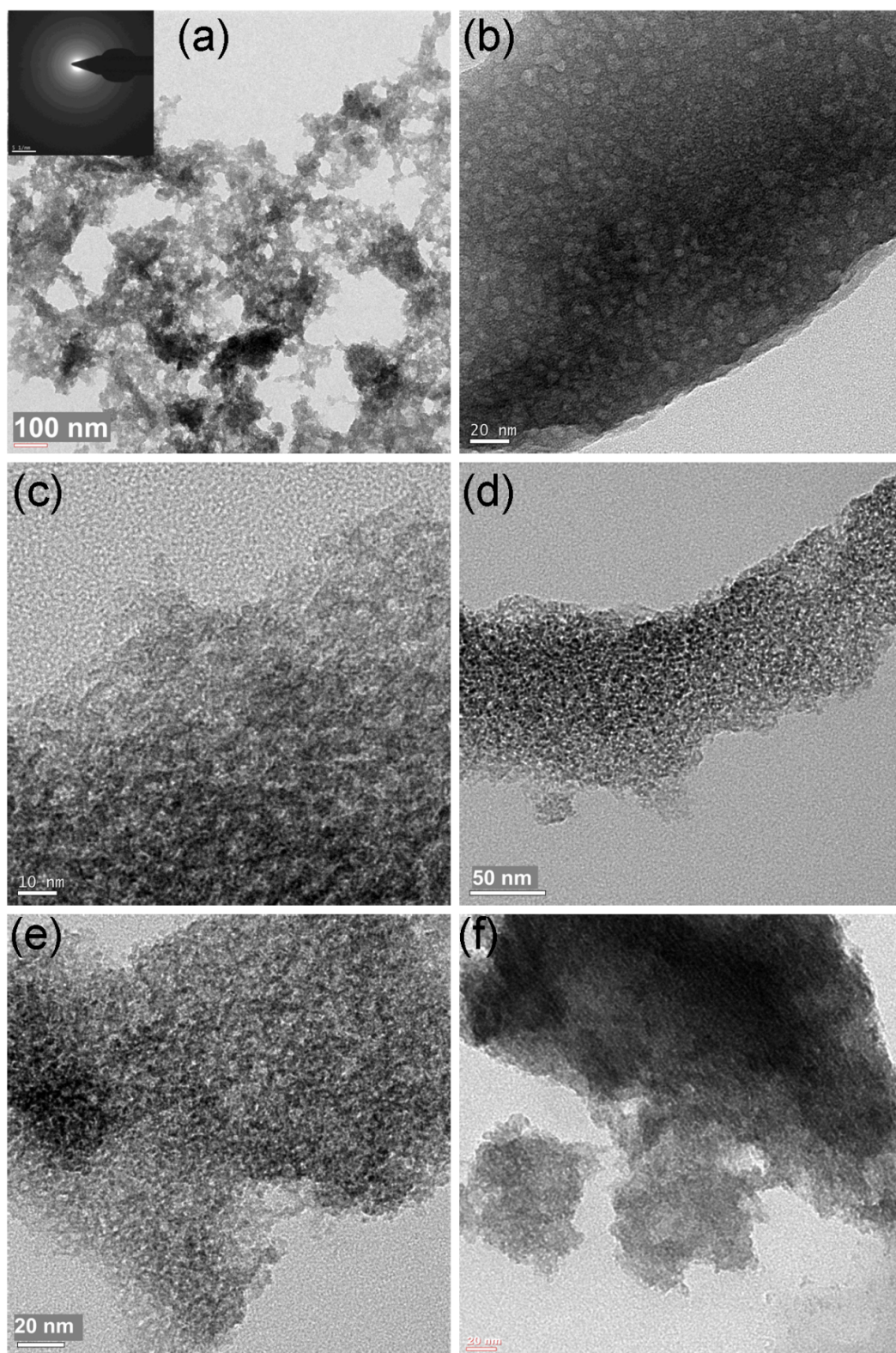
Similarly, 0.5 M gallium nitrate solution was made in EDTA-ED-water mixture with  $\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}:\text{EDTA}:\text{ED}$  at a mole ratio of 1: 1: 2. In an identical manner; 0.25 M (for Ti, V, Cr) or 0.5 M/l (for Mn, Fe, Co, Ni, Cu, Zn) transition metal ion solution was prepared with a mole ratio of metal compound:EDTA:ED = 1:1:2. Note that the order of mixing of various precursors for the preparation of each metal ion solution was similar to the case described for  $\text{Al}^{3+}$  ion. The dissolution of  $\text{Ga}(\text{NO}_3)_3 \cdot n\text{H}_2\text{O}$  was comparatively easier than  $\text{Al}(\text{NO}_3)_3 \cdot 9\text{H}_2\text{O}$  and it can be dissolved in EDTA-ED-water solution while gentle heating at temperature less than 80°C. There is no heating required for all other metal ion cases. If necessary, simple sonication is sufficient for dissolving V and Cr in EDTA-ED-water, whereas metal nitrates of Mn, Fe, Co, Ni, Cu and Zn can easily be dissolved in EDTA-ED-water at room temperature.

Only in the case of Ti, a modified procedure as given below was adopted to prepare the initial Ti-containing solution. Initially, a  $[\text{Ti}(\text{H}_2\text{O})(\text{EDTA})]$  complex was prepared by reacting sodium salt of EDTA and  $\text{TiCl}_3$  in HCl solution as previously reported [Sato, M.; Hara, H.; Nishide, T.; Sawada, Y. *J. Mater. Chem.* **1996**, *11*, 1767]. About 4.43 g of Ti complex  $\{[\text{Ti}(\text{H}_2\text{O})(\text{EDTA})]\}$  was then added to 20 ml EtOH and refluxed at  $90^\circ\text{C}$ . To this 3 ml tri n-butylamine was added and continued the reflux process. After 30 minutes, another 3 mL n-Bu<sub>3</sub>N was added and then kept for 3 hours at  $90^\circ\text{C}$ . A clear solution was obtained, which is the titanium source (at a concentration of 0.25 M) to prepare Al<sub>9</sub>GaTi oxide.

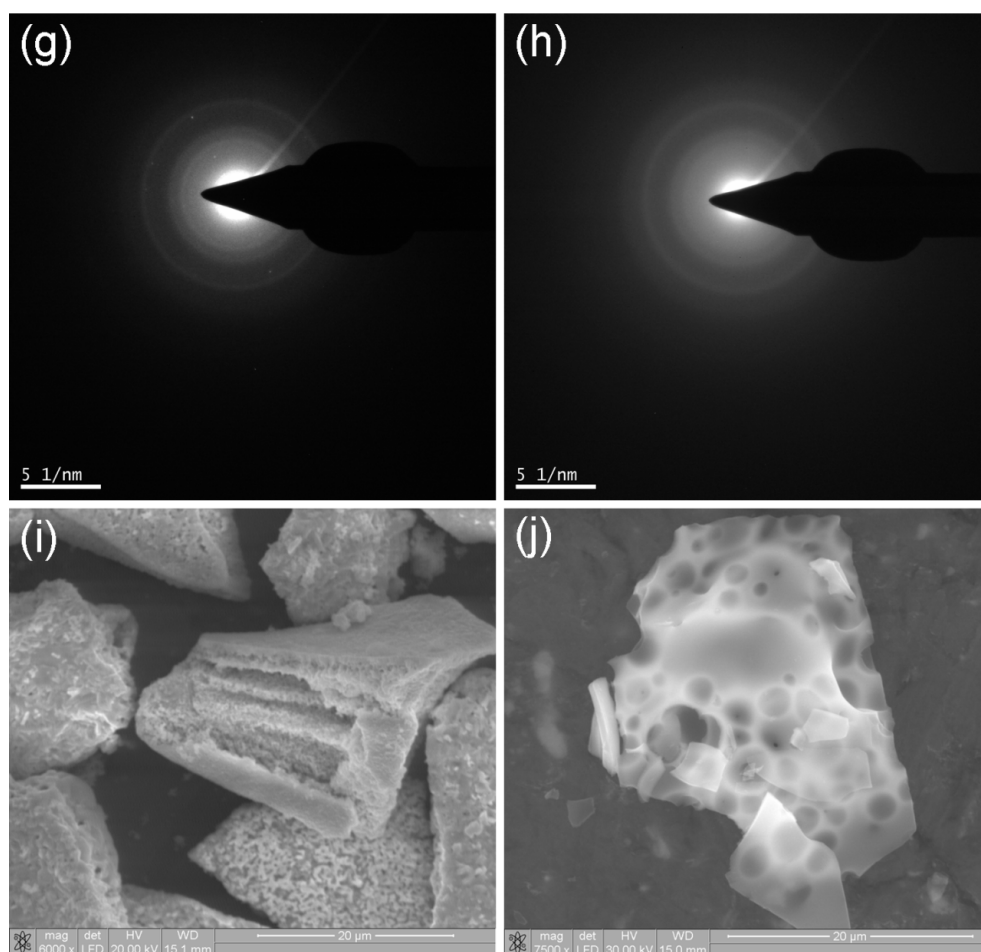
### **(b) Synthesis of mesoporous materials ( $\gamma\text{-Al}_2\text{O}_3$ , Al<sub>10</sub>Ga, and Al<sub>9</sub>GaTM)**

The synthesis procedure for mesoporous  $\gamma\text{-Al}_2\text{O}_3$  (*mγ*-Al), mesoporous Al<sub>10</sub>Ga, and mesoporous Al<sub>9</sub>GaTM (TM=Ti, V, Cr, Mn, Fe, Co, Ni, Cu, Zn) was similar to the case described for the synthesis of Al<sub>9</sub>GaFe in the experimental section of the communication. Briefly, in each case, the stoichiometric amount of the required metal ion precursor solution is pipetted, mixed well, aged at  $60^\circ\text{C}$  (for 30 – 36 hours), heated at  $200^\circ\text{C}$  (for 4 hours), and finally calcined at  $500^\circ\text{C}$  (for 4 hours).

The amount of precursor solution used for preparing various mesoporous materials are summarized as follows: For the preparation of Al<sub>9</sub>GaFe, Al precursor solution (0.5 M, 9 mL), Ga precursor solution (0.5 M, 1 mL) and Fe precursor solution (1 mL of 0.5 M) was used. For mesoporous alumina, Al precursor solution (0.5 M, 11 mL) alone was used, whereas for Al<sub>10</sub>Ga oxide system, 10 mL of 0.5 M Al precursor solution, and Ga precursor solution (0.5 M, 1 mL) was used. 9 mL of 0.5 M Al precursor solution, 1 mL 0.5 M Ga precursor solution, and 1 mL of 0.5 M transition metal precursor solution (Mn, Fe, Co, Ni, Cu, and Zn) or 2 mL of 0.25 M transition metal precursor solution (Ti, V, and Cr) leads to Al<sub>9</sub>GaTM oxide system. TM or Ga content can be varied by simply changing the volume of metal ion precursor solution. Lower concentrated solutions (0.25 M) was essential for Ti<sup>4+</sup>, V<sup>5+</sup>, Cr<sup>3+</sup> cases to achieve complete dissolution of metal ions (that is to get a clear metal ion solution), whereas in other cases complete dissolution of metal ions can be achieved even with higher concentration of 0.5 M (that is with less water).







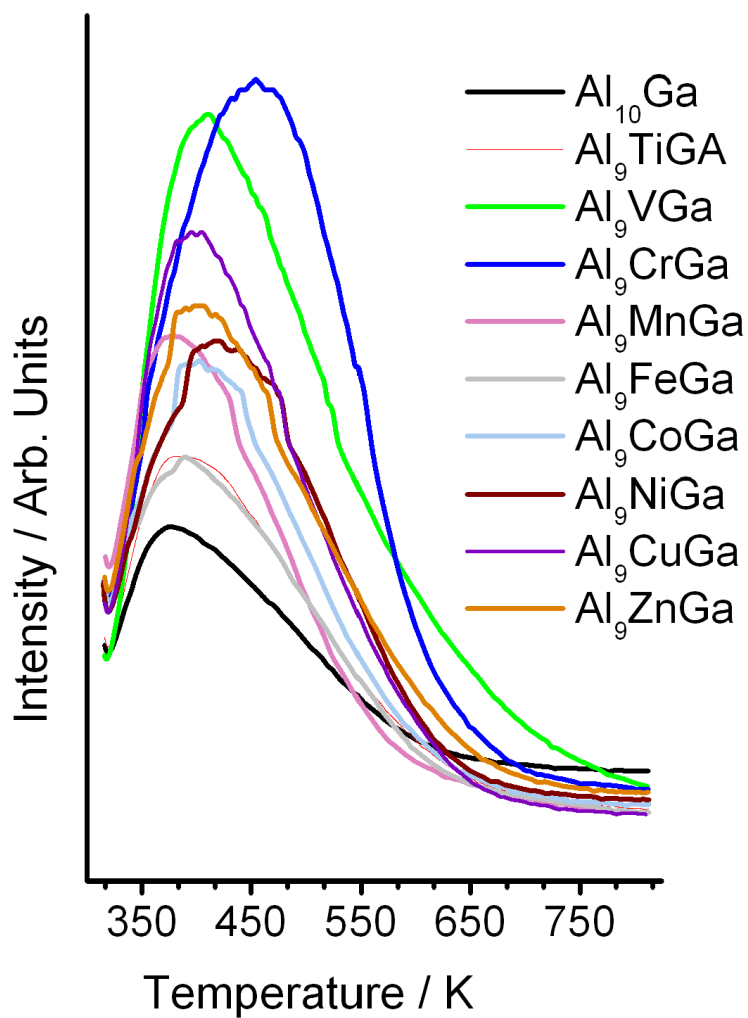
**Figure S1.** TEM images of (a)  $\text{Al}_9\text{Ga}_2$ , (b)  $\text{Al}_9\text{GaV}$ , (c)  $\text{Al}_9\text{GaFe}$ , (d)  $\text{Al}_9\text{GaCo}$ , (e)  $\text{Al}_9\text{GaCu}$ , and (f)  $\text{Al}_9\text{GaZn}$ . Selected area electron diffraction (SAED) patterns of (g)  $\text{Al}_9\text{GaZn}$ , and (h)  $\text{Al}_9\text{GaCr}$ . SEM images of (i)  $\text{Al}_9\text{GaFe}$  and (j)  $\text{Al}_9\text{GaCr}$ .

**Table S1.** Atom percent of representative Al<sub>9</sub>GaTM determined by EDX

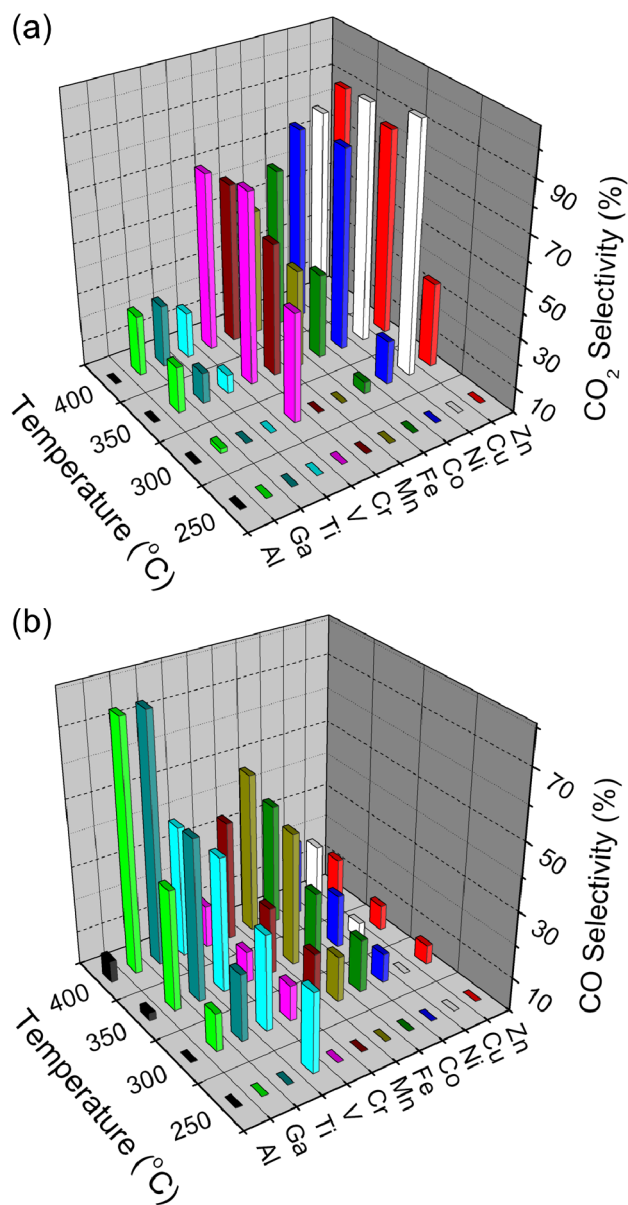
Material	Al, %	O, %	Ga, %	Ni, %	Fe, %
Al <sub>9</sub> GaNi	31.96 ± 0.14	61.04 ± 0.2	3.25 ± 0.08	3.73 ± 0.08	---
Al <sub>9</sub> GaFe	32.12 ± 0.14	60.9 ± 0.2	3.31 ± 0.08	---	3.65 ± 0.08

**Table S2.** Surface area of mesoporous Al-Ga-Cr ternary oxide materials

No.	Material	Surface area, m <sup>2</sup> g <sup>-1</sup>
1	Al <sub>9</sub> Cr	383
2	Al <sub>9</sub> Ga <sub>0.25</sub> Cr	396
3	Al <sub>9</sub> Ga <sub>0.5</sub> Cr	401
4	Al <sub>9</sub> GaCr	374
5	Al <sub>9</sub> Ga <sub>2</sub> Cr	322
6	Al <sub>9</sub> Ga <sub>4</sub> Cr	290

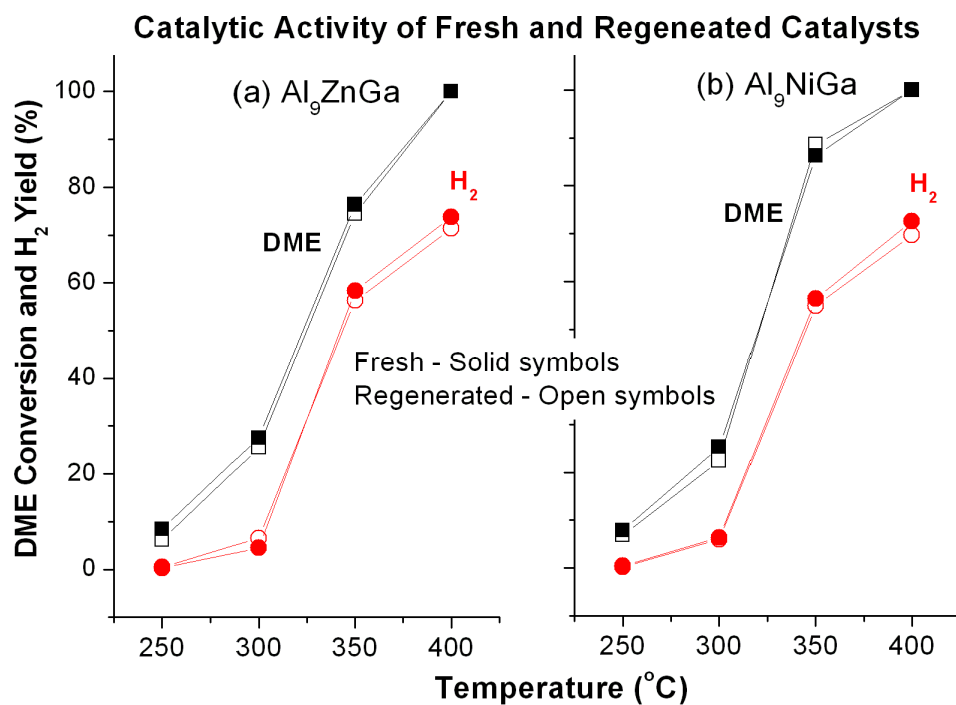


**Figure S2.** Acidity of mesoporous  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and mesoporous metal ion incorporated  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> samples calcined at 500°C. Acidity was measured through temperature programmed desorption (TPD) of ammonia.

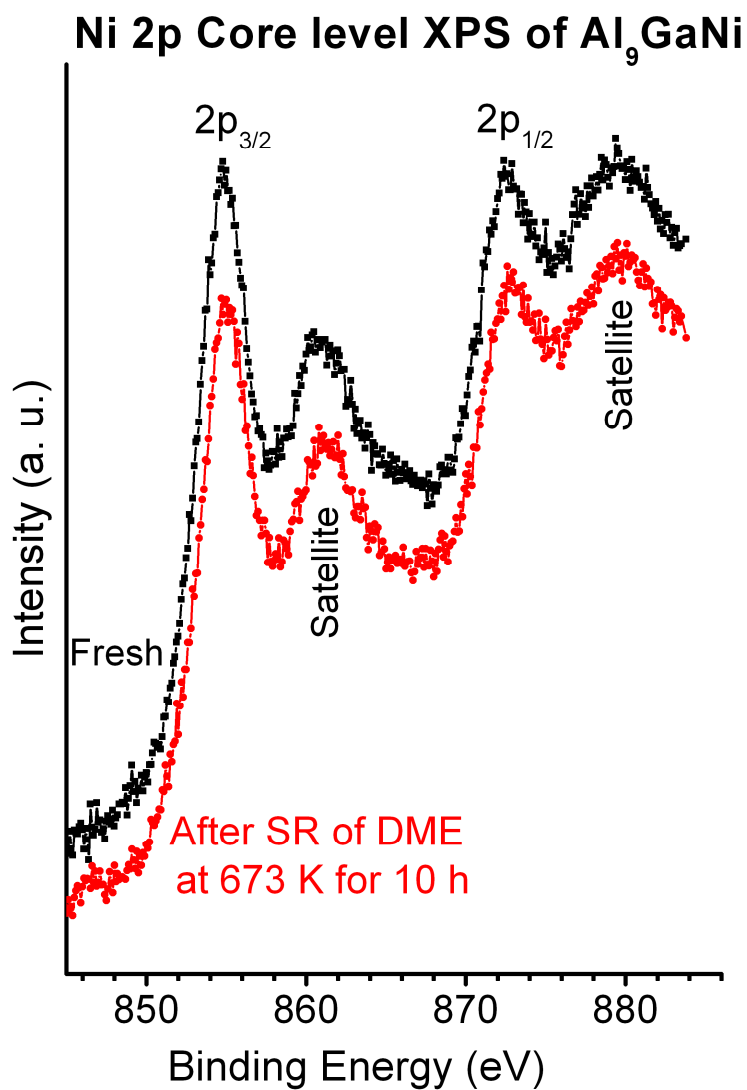


**Figure S3.** Selectivity of (a) CO<sub>2</sub> and (b) CO at 250 – 400°C on various mesoporous samples. Selectivity was calculated among the carbonaceous products. The label Al and Ga in the figure indicate  $\gamma$ -Al<sub>2</sub>O<sub>3</sub> and Al<sub>10</sub>Ga, respectively, whereas the label transition metal (TM) corresponds to Al<sub>9</sub>GaTM. Note an approximately opposite change in selectivity of the above products from Ga, Ti to Cu, Zn at 300°C and 350°C.





**Figure S4.** DME conversion and H<sub>2</sub> yield measured for the fresh and regenerated catalysts are shown for (a) Al<sub>9</sub>GaZn, and (b) Al<sub>9</sub>GaNi. The 10 h SRDME studied catalysts (spent catalysts) after air calcination at 500°C represent the regenerated catalyst. Within the experimental limits of uncertainty, the results are reproduced very well highlighting the stability of the materials under reaction conditions.



**Figure S5.** Ni 2p core level XPS spectra of Al<sub>9</sub>GaNi obtained before reaction and after SRDME reaction at 400°C for 10 h. Note the similar spectra indicating the non-leaching of Ni<sup>2+</sup> from the lattice.