Facile Conversion of Levulinic acid to γ-Valerolactone using, high surface area magnetically separable Ni/NiO catalyst

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Supplementary Information

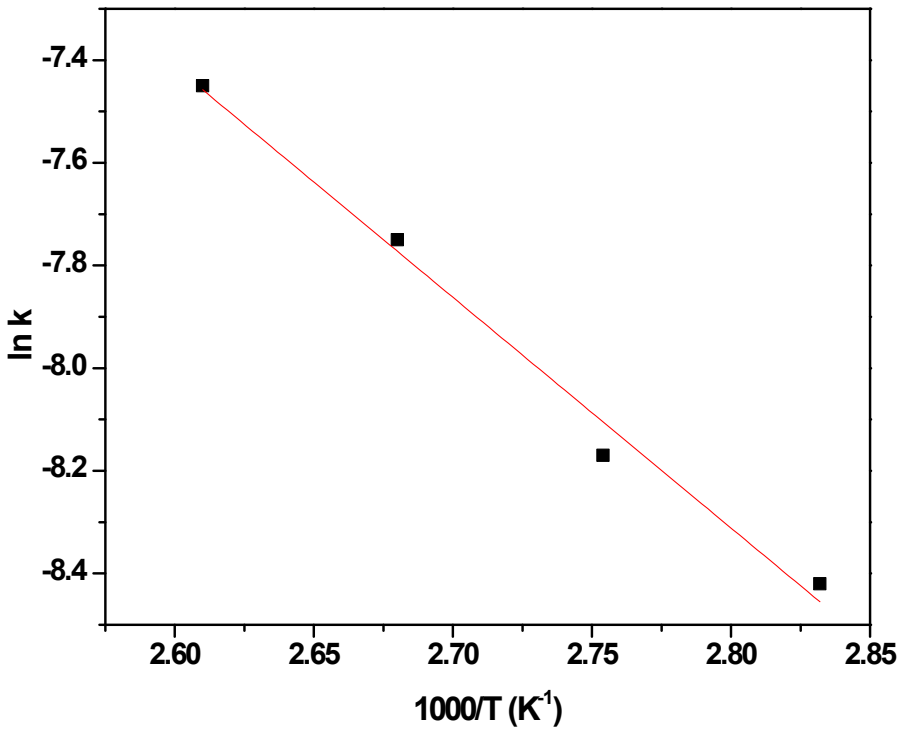

Fig. S1: Variation of ln k v/s 1000/T (K^{-1}) for the determination of activation energy.

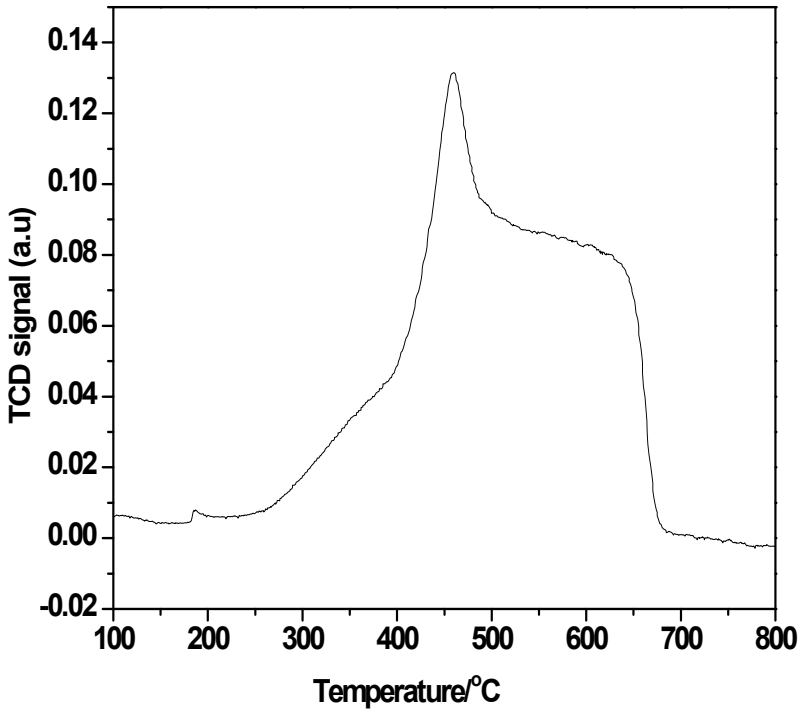

Fig. S2a: Ammonia TPD profile of Ni/NiO catalyst

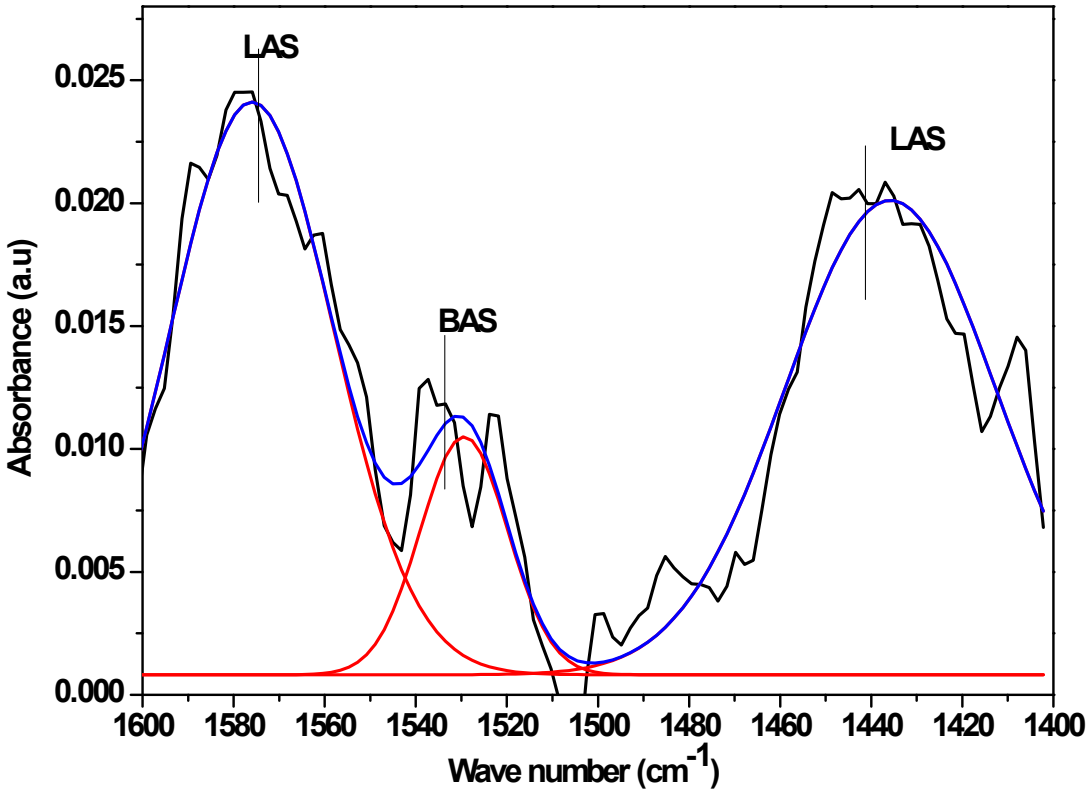

Fig. S2b: Pyridine adsorbed FTIR spectrum of Ni/NiO catalyst

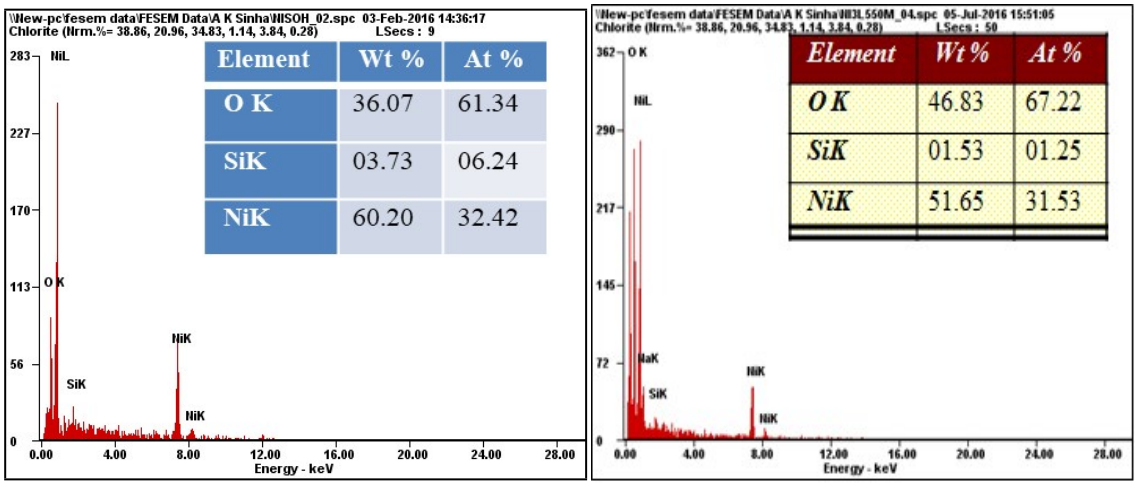

Fig. S3: SEM-EDAX spectra of unleached (a) leached (b) Ni/NiO catalyst

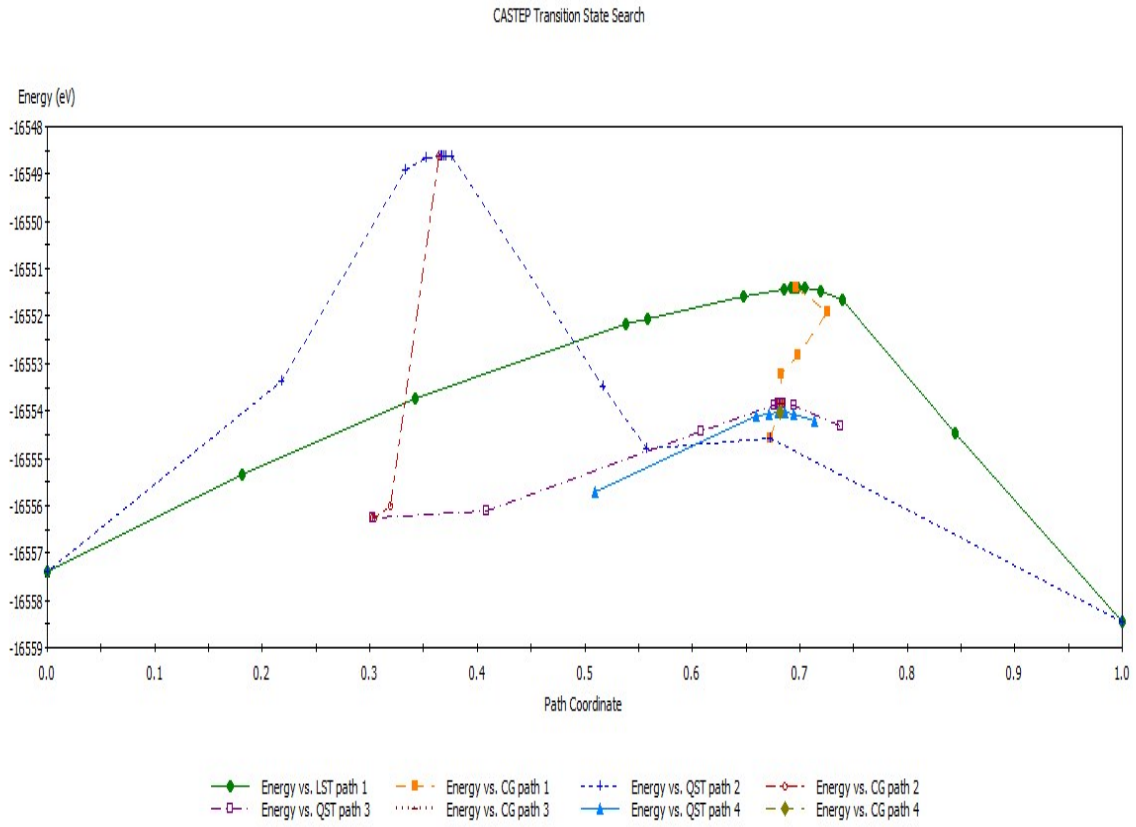

Fig. S4: Transition state energy profile on NiO(Ni) surface vs. different paths.

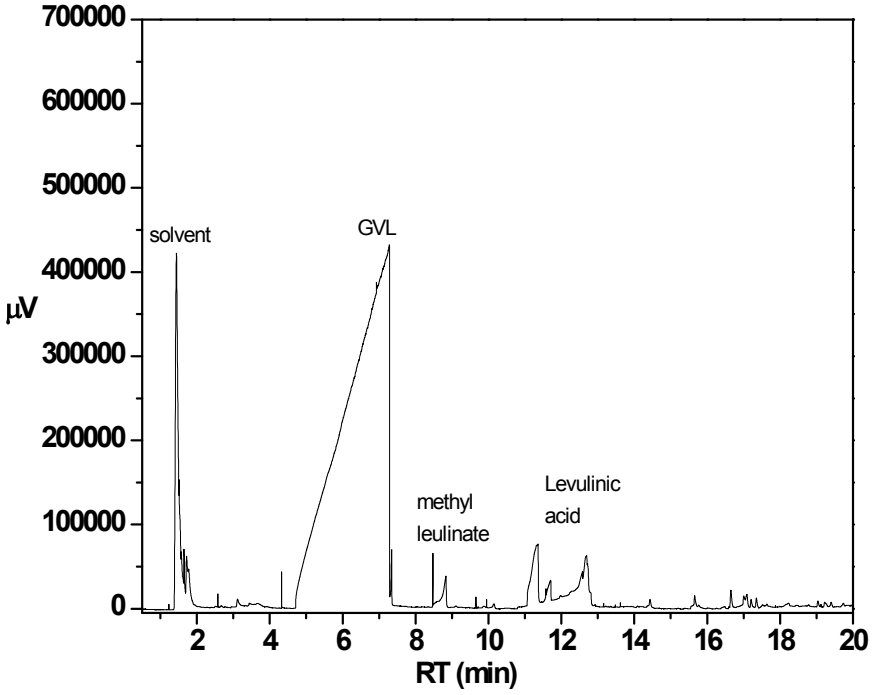

Figure S5: Gas chromatograms of the product mixture after the conversion of LA to GVL over Ni/NiO catalyst.

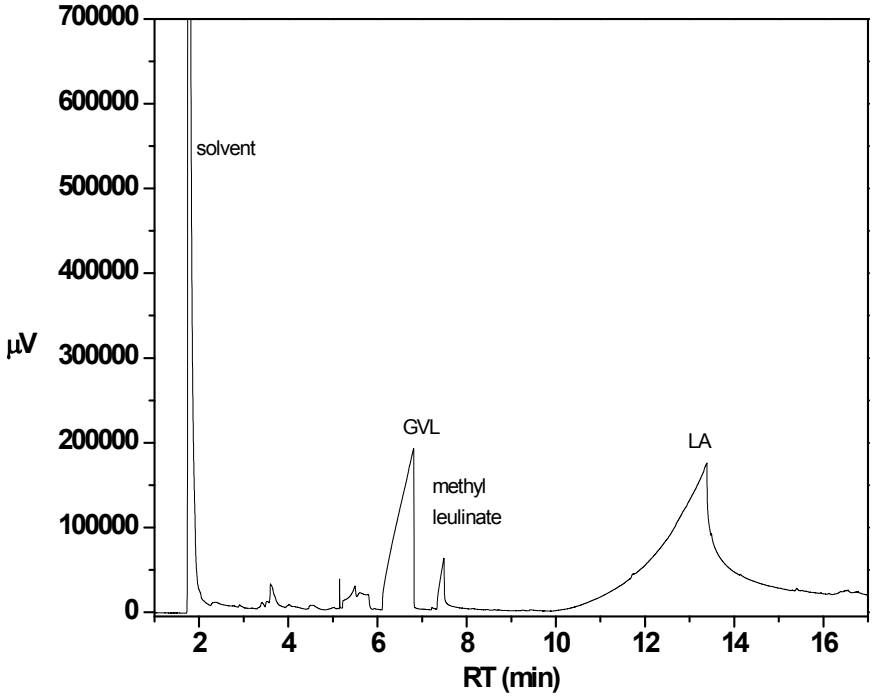

Figure S6: Gas chromatograms of the product mixture after the conversion of LA to GVL over Ni/Al_2O_3 catalyst.

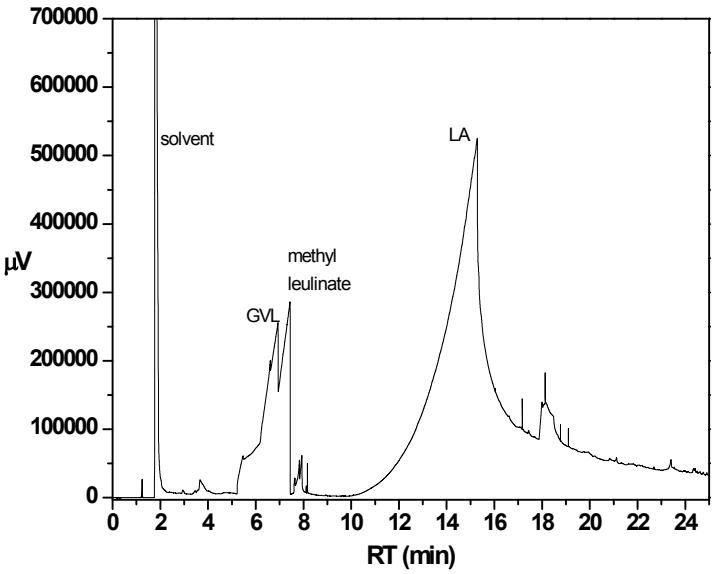

Figure S7: Gas chromatograms of the product mixture after the conversion of LA to GVL over Raney Ni catalyst.

Entry	catalyst	Composition	
		Ni/Si (ICP-AES)	Ni/Si (TEM-EDAX)
1	Fresh leached Ni/NiO	51	36
2	Fresh unleached Ni/NiO	30	24
3	Spent Ni/NiO	50	35

Table S1. The composition of fresh leached, unleached Ni/NiO and Ni/NiO spent catalyst from ICP-AES and TEM.

Catalyst	$S_{BET(m^2/g)}$	Pore vol. (ml/g)	Pore dia. (nm)	Crystal size (nm)##	Metal Dispersion	
					H_2-chemisorp.	XRD and TEM[#]
Ni/NiO	250	0.40	8	7	18	15
Raney Ni[32]	56	0.15	7	5	5	-
Ni/Al_2O_3	110	0.43	6	-	-	-

Table S2: Surface area, pore volume, mean pore diameter of different catalysts

##Crystal size was determined by the Scherrer equation from Ni (111) plane in XRD patterns

The mean particle diameter of the nickel particles and dispersion calculated from XRD[33]

Entry #	Catalyst conc. (%)	Conversion (%)	Selectivity(GVL)	Selectivity (ML)
1	2	63	76	24
2	10	99	94	6
3	20	99	93	6

Table S3: Catalytic Hydrogenation of levulinic acid at 120 ^{o}C and 40 bar at three different catalyst concentrations (Reaction time: 4h; Solvent: Methanol).

We performed the catalytic reaction at three different catalyst concentrations, viz., 2wt%, 10wt% and 20wt% relative to the amount of the substrate. The results are shown in Table 1 for the 110 ^{o}C and 40 bar H_2 pressure. The results show that the optimum concentration of the reaction is 10wt%. We performed the remaining catalytic reactions at this concentration.

Entry #	Catalyst	Total Conversion (%)	Selectivity (GVL)	Selectivity (ML)
1	Fresh Ni/NiO	99	94	8
2	Used (1)	96	93	7
3	Used (2)	95	92	6
4	Used (3)	94	92	6

Table S4: Reusability study of the Ni/NiO catalyst. Conditions are 120 ^{o}C and 40 bar.

Entry #	Temperature (^oC)	Pressure (bar)	Conversion (%)	Selectivity of γ-valerolactone
1	120	40	93	100
2	140	40	94	100
3	170	40	94	100
4	200	40	95	100

Table S5. Catalytic Hydrogenation of levulinic acid under solvent-free conditions. Reaction time -4 h.

Table S5 shows the solventless selective hydrogenation of levulinic acid to produce γ-valerolactone with 100% selectivity and 93% conversion of levulinic acid into GLV at 120 ^oC under 40 bar H_2 pressure. It is observed that on increasing temperature from 120 to 200 ^oC at 40 bar H_2 pressure, the conversion increases from 93% to 95%.

Entry #	Temperature (^{o}C)	Pressure (bar)	Total Conversion	Selectivity (GVL)	Selectivity (ML)
1	80	10	82	60	40
2	80	20	88	78	22
3	80	30	91	84	16
4	80	40	92	90	10
5	90	10	85	62	38
6	90	20	88	82	18
7	90	30	93	85	15
8	90	40	95	91	09
9	100	10	87	58	42
10	100	20	.90	75	25
11	100	30	94	83	17
12	100	40	97	90	10
13	120	10	88	57	43
14	120	20	93	76	24
15	120	30	98	87	23
16	120	40	99	94	08

Table S6: Catalytic Hydrogenation of levulinic acid under different conditions with 10 wt% catalyst concentration (Reaction time: 4h; Solvent: Methanol).

Study of the reaction parameters

The parameters of the reaction, the order of the reaction and activation energy were calculated. For the conversion data presented for temperatures between 80-120 ^{o}C, there is a continuous increase in GVL yield with H_2 pressure at the expense of ML (Table S6). We can conclude, therefore, that the conversion of LA to GVL is the dominant pathway. We have, consequently, reported the kinetics study of this reaction pathway.

Order of reaction for H_2

The order of the reaction for H_2 has been studied at five different temperatures (80-120 ^{o}C) (Table S6). For all these four temperatures, four pressures of H_2 gas have been used (10, 20, 30 and 40 bar) and the order has been calculated from the place. In our case, the concentration of H_2 was calculated to between 0.31-1.36 M. The order of the reaction is calculated as 0.47±0.06.

Entry	Conc. of LA (M)	Conversion (%)	Selectivity of GVL (%)
1	1.52	99	92
2	2.87	99	94
3	4.64	99	94

Table S7. Variation in the conversion of LA and selectivity of GVL with the concentration of LA. The reaction has been performed at 110 ^{o}C and 40 bar in methanol solvent.

Order of reaction for LA

Three different amounts of LA were used at the best reaction conditions, i.e., 110^{o}C and 40 bar pressure. The results are tabulated in Table S7. The volume of the solvent was adjusted in each case so that the net volume of the reaction mixture was 20 ml. The concentrations of LA in methanol in these three reaction mixtures were 1.52 M, 2.87 M and 4.64 M. The results indicate a conversion that is nearly independent of the LA concentration. The calculated order was 0.04±0.01.

Entry #	Catalyst	Total Conversion (%)	Selectivity (GVL)	Selectivity (ML)
1	Fresh Ni/Al_2O_3	89	90	10
2	Used (1)	45	78	22
3	Used (2)	40	70	30
4	Used (3)	35	70	30

Table S8: Reusability study of the Ni/Al_2O_3 catalyst. Conditions are 110 ^{o}C and 40 bar. (Reaction time: 4h, 10wt% catalyst, LA 5 ml, methanol 15 ml).

Entry #	Catalyst	Total Conversion (%)	Selectivity (GVL)	Selectivity (ML)
1	Raney Ni	90	87	13
2	Used (1)	50	80	20
3	Used (2)	35	75	25
4	Used (3)	35	75	25

Table S9: Reusability study of the Raney Ni catalyst. Conditions are 110 ^{o}C and 40 bar. (Reaction time: 4h, 10wt% catalyst, LA 5 ml, methanol 15 ml).