Supporting Information

Crucial Role of Oxygen Vacancies for the Efficient Hydrodeoxygenation of Lignin-based Phenolic Model Compounds with $Ni/Ti_{1-x}Zr_xO_2$

Hadi Ali, [ab] Neeraj Sharma[a], Sahil Kumar, [a] Joris W. Thybaut,[c] Jeroen Lauwaert,[d] Xiaolei Zhang,[e] Sushil Kumar Kansal [f] and Shunmugaval Saravanamurugan *[a]

[a] *Laboratory of Bioproduct Chemistry, BRIC - National Agri-Food and Biomanufacturing Institute (Formerly Center of Innovative and Applied Bioprocessing), Sector 81 (knowledge City), Mohali-140306, Punjab, India. E-mail: saravana@ciab.res.in*

[b] *Department of Chemistry, University of Ladakh, Kargil Campus, Ladakh-194105.*

[c] *Laboratory for Chemical Technology (LCT), Ghent University, Technologiepark 125, 9052, Ghent, Belgium.*

[d] *Industrial Catalysis and Adsorption Technology (INCAT), Ghent University, Valentin Vaerwyckweg 1, 9000, Ghent, Belgium.*

[e] *Department of Chemical and Process Engineering, University of Strathclyde.*

[f] *Dr. S. S. Bhatnagar University Institute of Chemical Engineering and Technology, Panjab University, Chandigarh-160014, India.*

Table S1. The data obtained from the O_2-TPD profile (Figure 5) of Ni-supported mono and mixed oxide catalysts

Catalysts	**O_2 (mmol/g)**		
	Peak I (<250 °C)	**Peak II (250−400 °C)**	**Peak III (>400 °C)**
Ni/ZrO_2	0.037	0.059	0.197
$Ni/Ti_{0.05}Zr_{0.95}$	0.054	0.092	0.139
$Ni/Ti_{0.25}Zr_{0.75}$	0.092	0.225	0.149
$Ni/Ti_{0.50}Zr_{0.50}$	0.088	0.340	0.186
$Ni/Ti_{0.25}Zr_{0.75}$	0.112	0.326	0.218
$Ni/Ti_{0.95}Zr_{0.05}$	0.109	0.221	0.305
Ni/TiO_2	0.037	0.097	0.158

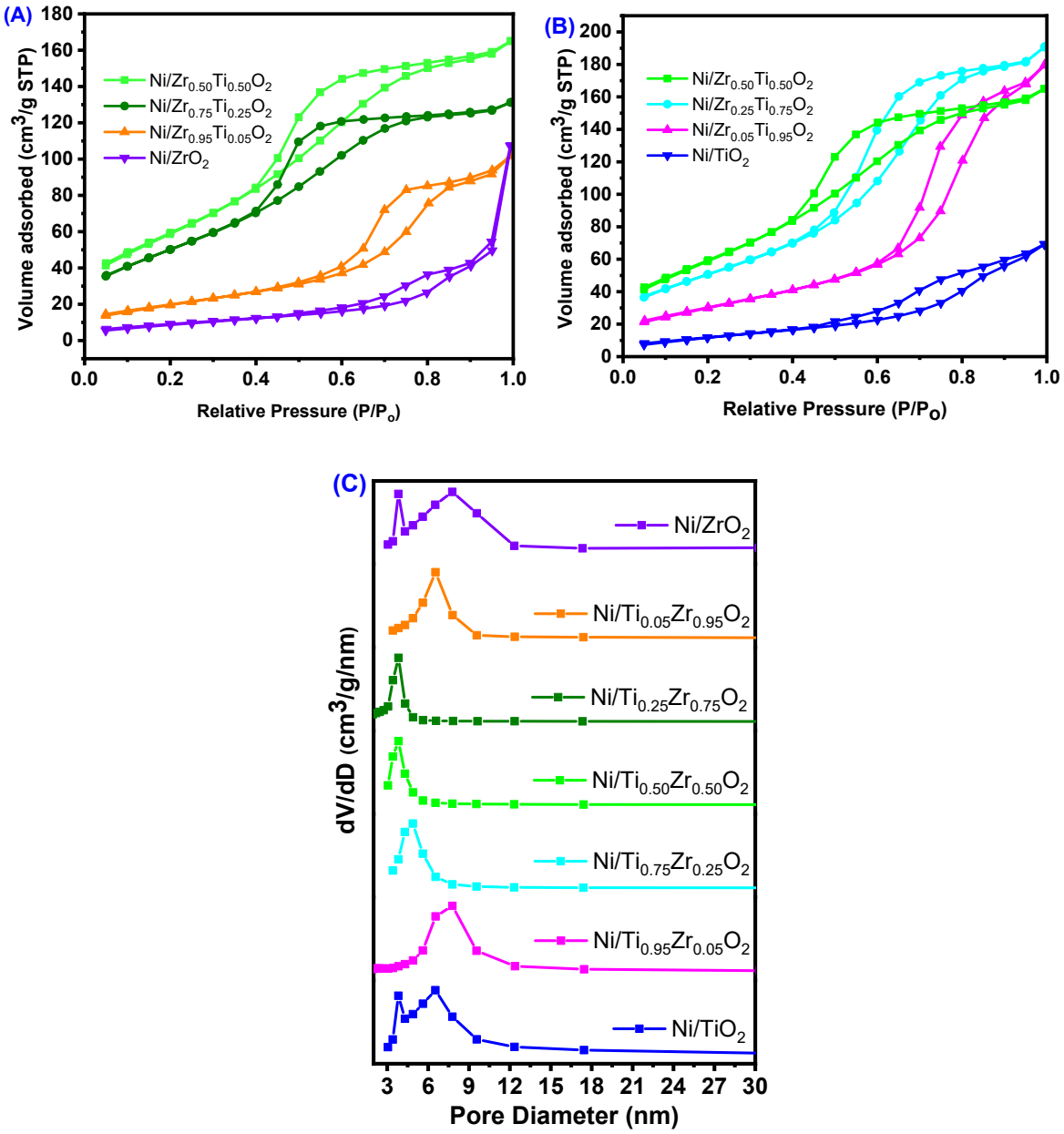


Figure S1: (A and B) Physisorption isotherm and (C) BJH pore size distribution of various Ni-supported mono and mixed oxide catalysts.

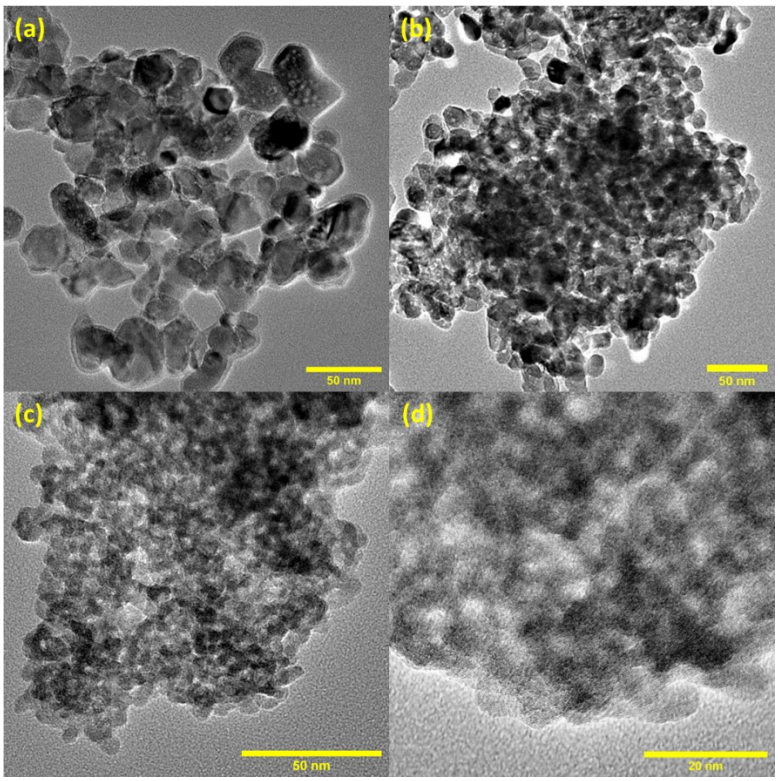
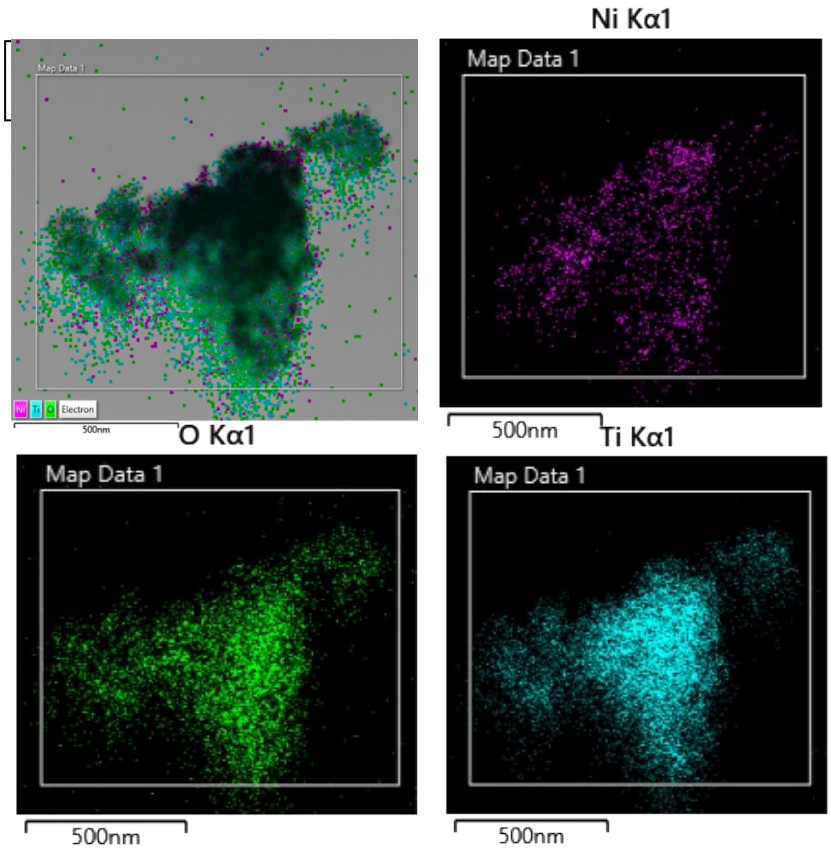
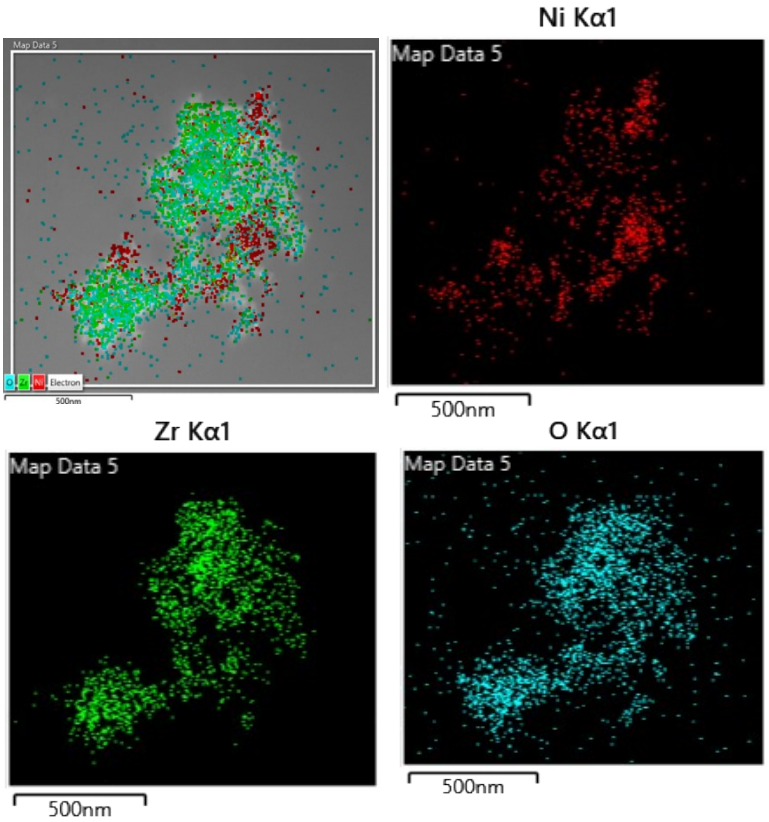


Figure S2. HRTEM images of (a) Ni/TiO_2, (b) Ni/ZrO_2 and (c-d) $Ni/Ti_{0.50}Zr_{0.50}O_2$ catalysts.




Ni Kα1
Map Data 5
500nm
Zr Kα1
Map Data 5
500nm
O Kα1
Map Data 5
500nm

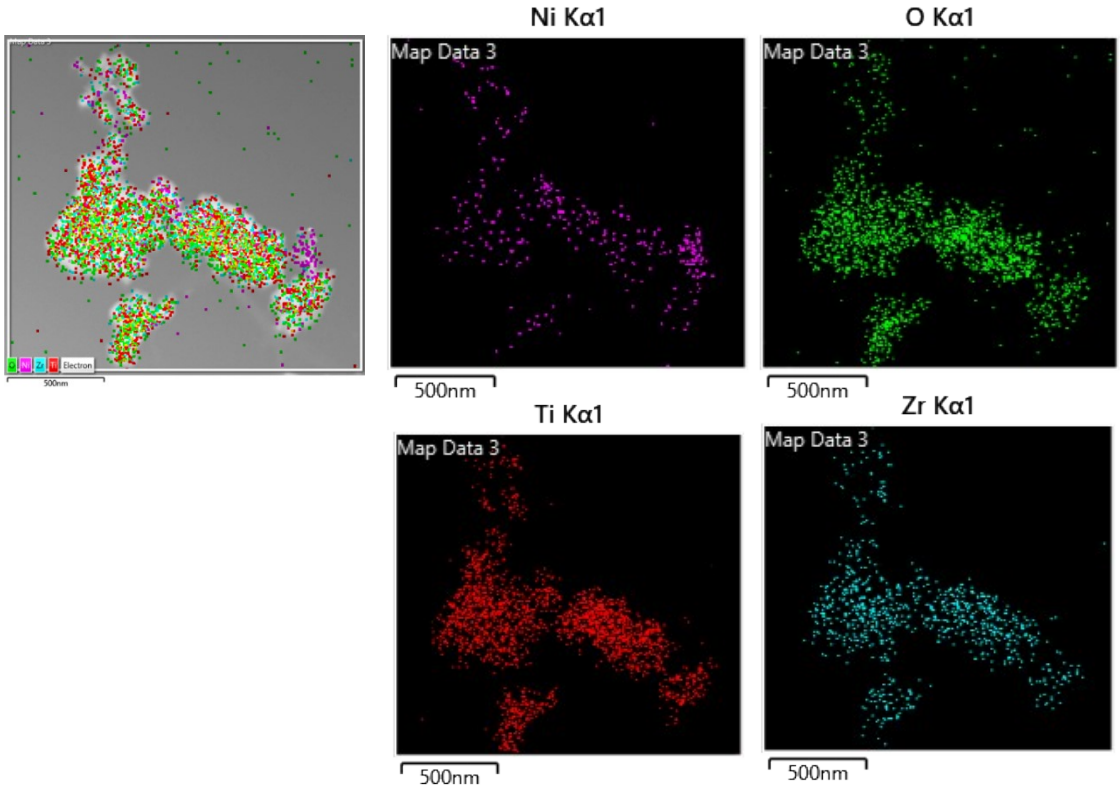

Ni Kα1
Map Data 3
500nm
O Kα1
Map Data 3
500nm
Ti Kα1
Map Data 3
500nm
Zr Kα1
Map Data 3
500nm

Figure S3. EDS elemental mapping images of a) Ni/TiO_2, b) Ni/ZrO_2, and c) $Ni/Ti_{0.50}Zr_{0.50}O_2$.

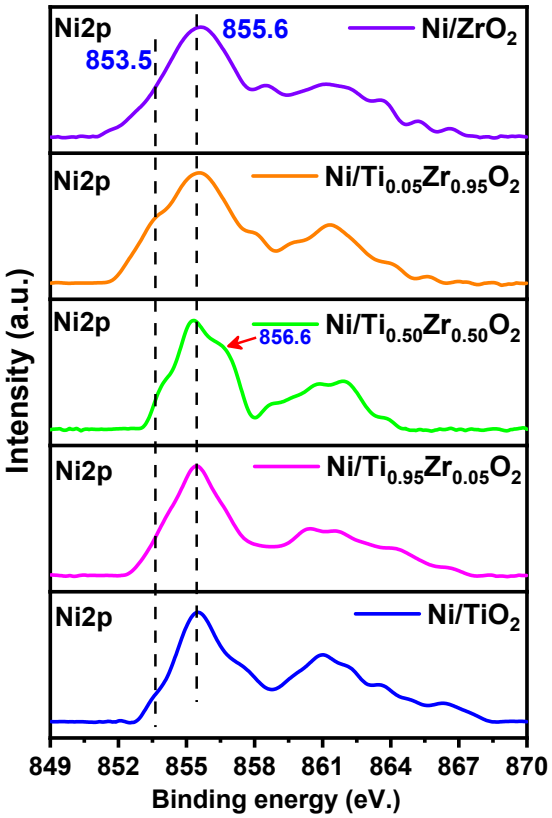


Figure S4. XPS spectra of Ni2p of various Ni-supported mono and mixed metal oxide catalysts.

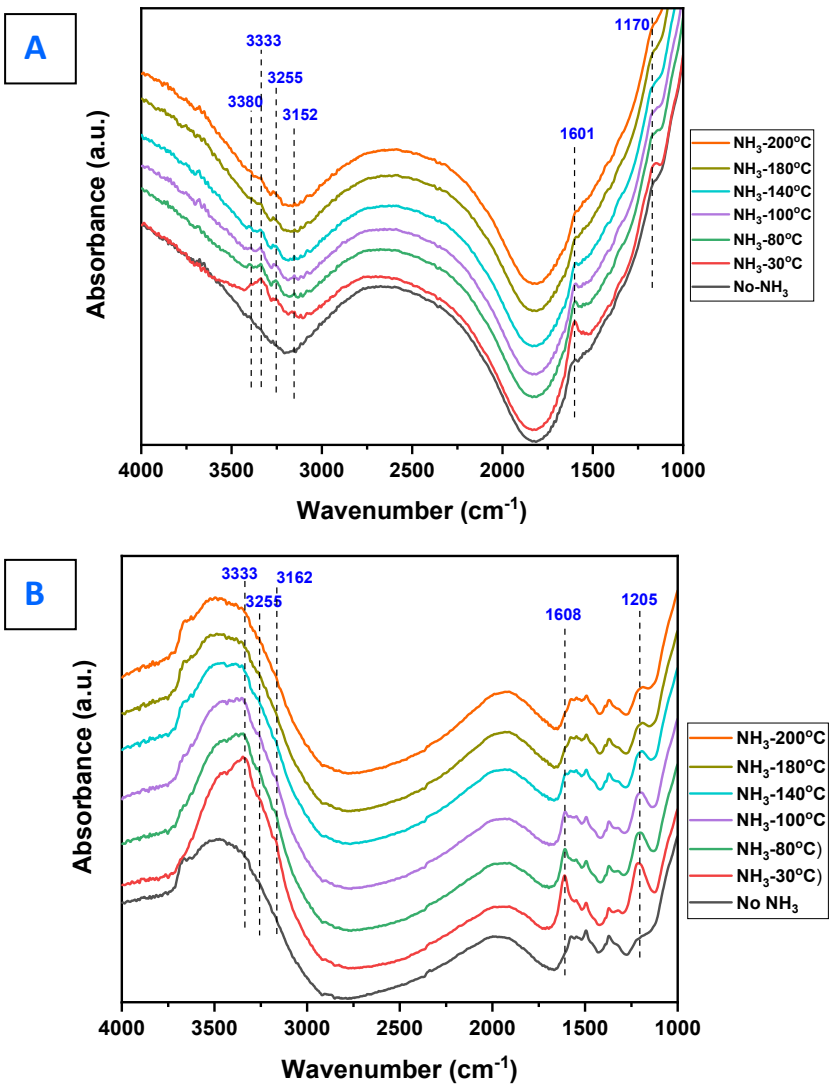


Figure S5. In-situ DRIFT spectra of NH_3 desorbed at various temperature (A) Ni/TiO_2 and (B) Ni/ZrO_2 catalyst.

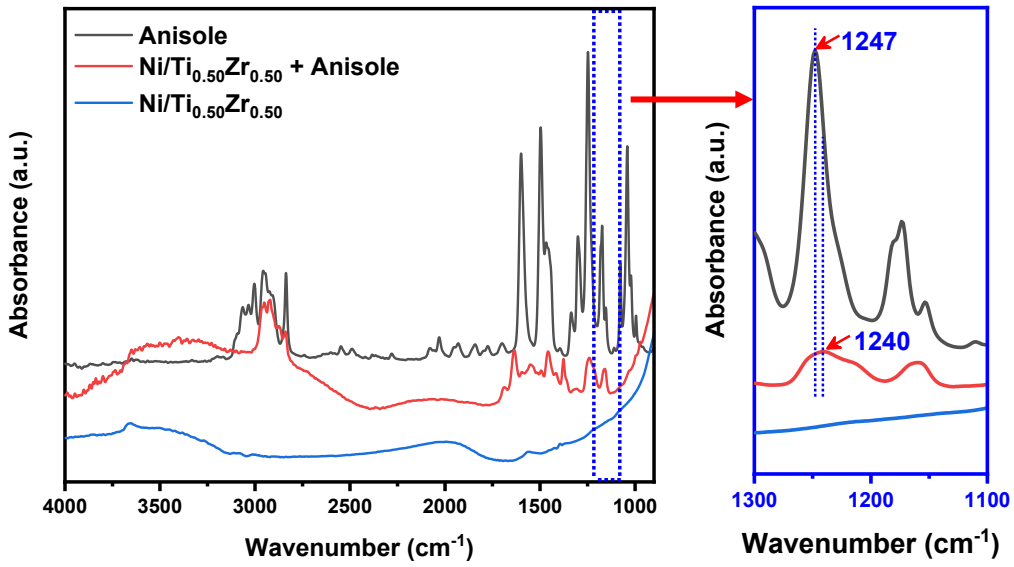


Figure S6. Catalytic activity of $Ni/Ti_{0.50}Zr_{0.50}O_2$ and previous studies related to Ni-based catalysts for HDO of anisole

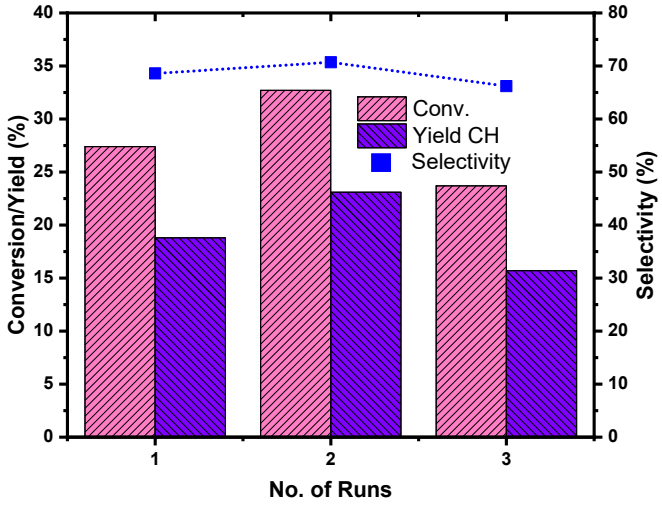


Figure S7. The recyclability of the $Ni/Ti_{0.50}Zr_{0.50}O_2$ catalyst for anisole HDO. (Reaction conditions: $m_{cat:anisole}$ = 1:2, 20 g decane, 230 °C, 15 min, 30 bar H_2,450rpm.)

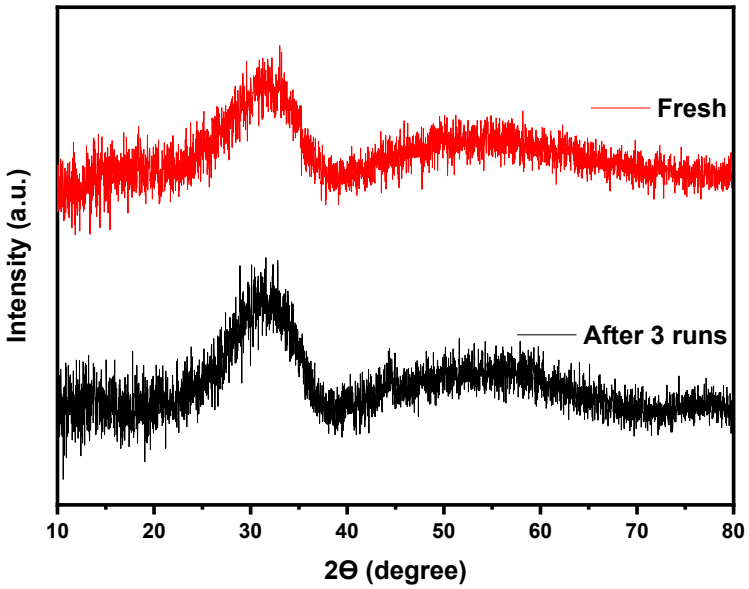


Figure S8. XRD pattern of fresh and 3rd use of Ni/ $Ti_{0.50}Zr_{0.50}O_2$ catalysts

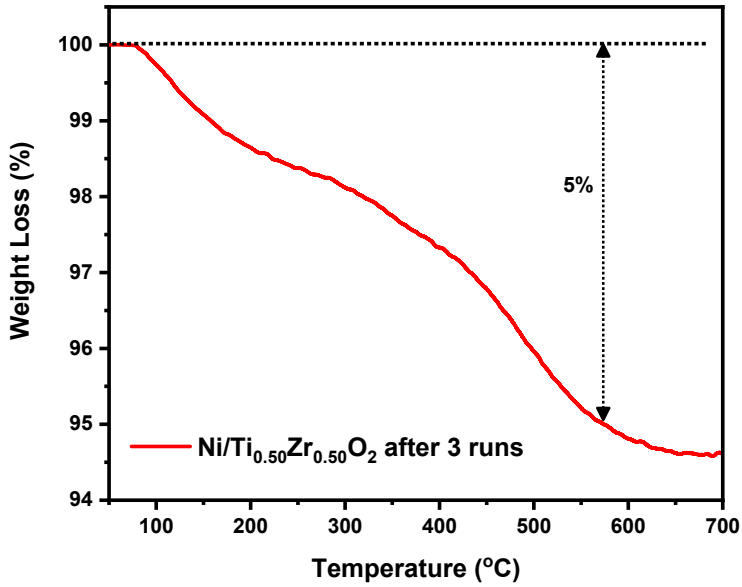


Figure S9. TGA analysis of the spent catalyst

Table S2. Catalytic activity of **3wt%Ni/$Ti_{0.50}Zr_{0.50}O_2$** and previous studies related to Ni-based catalysts for HDO of anisole

Entry	Catalysts	Reaction conditions	Conv. (%)	Selec. DeO (%)	Reference
1	**3wt%Ni/$Ti_{0.50}Zr_{0.50}O_2$**	**230 °C, 30 bar H_2, 3 h**	**>99**	**94%**	**This work**
2	30wt% Ni/Al_2O_3-ZrO_2	230 °C, 10 bar H_2, 3 h	100	77.6	[1]
3	5wt% Ni/TiO_2-ZrO_2	300 °C, 40bar H_2, 4h	60	~87	[2]
4	10wt% Ni/SiO_2	300 °C, 50 bar H_2, 16 h	>99	80.4	[3]
5	$Ni_2P/Ti_{0.98}Ce_{0.02}O_2$	300 °C, 7 bar H_2, 0.2 h	29.2	79.2	[4]
6	3wt% Ni/Nb_2O_5	240 °C, 20bar H_2, 1 h	90	91.0	[5]
7	90wt% Ni/Nb_2O_5	240 °C, 30bar H_2, 4h	>99	100	[6]
8	90wt%Ni /SiO2	280 °C, 60bar H_2, 0.75h	100	40	[7]
9	10wt%Ni/SBA-15	280°C, 35bar H_2, 6h	100	100	[8]
10	5wt%Ni/HSZ	200°C, 68bar H_2, 2.3 h	98	84	[9]
11	4.6% hie-Ni/ZSM-5	200 °C, 60 bar H_2, 2h decalin	100	88.1	[10]
12	4.96% Ni/Al-MCM-41(90)	280 °C, 48 bar H_2, 6h	96.5	97.6	[11]
13	60wt% Ni 5wt%Cu 30wt%Si	320 °C, 60bar H_2, 2.5h	~85	100	[12]
14	Ni_1Mo_3N/C	260 °C, 4 h, 10 bar H_2,	99.9	97.8	[13]
15	Ni/C-H_3[P-$(Mo_3O_{10})_4$]*13H_2O	240°C, 10 bar H_2, 3 h	100	100	[14]
16	Ni/C	230 °C, 10bar H_2, 2 h, water	15	57.4 (benzene)	[15]
17	Ni@C-500	230°C, 10 bar N_2, 2 h	15.4	57.4 (benzene)	[16]
18	NiPt/S	280 °C, 73 bar H_2, 6 h	98.5	72	[17]

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