Electronic Supplementary Material (ESI) for RSC Advances.


# Anisole hydrodeoxygenation over Ni-Co bimetallic catalyst: A combination of experimental, kinetic and DFT study

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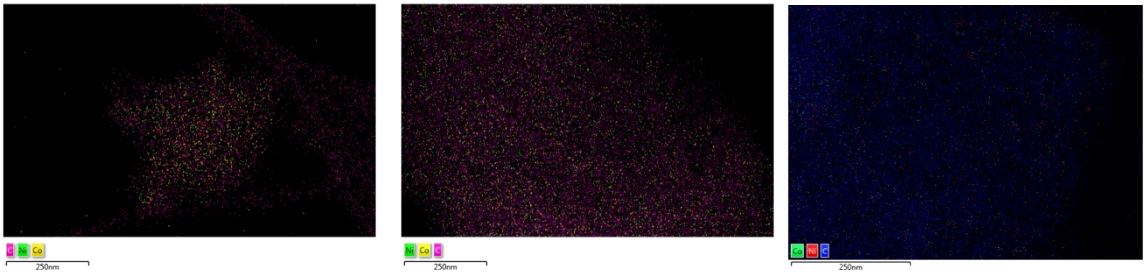


**Figure S1**: EDX mapping of $Ni_6Co_4$-AC, $Ni_5Co_5$-AC, and $Ni_4Co_6$-AC

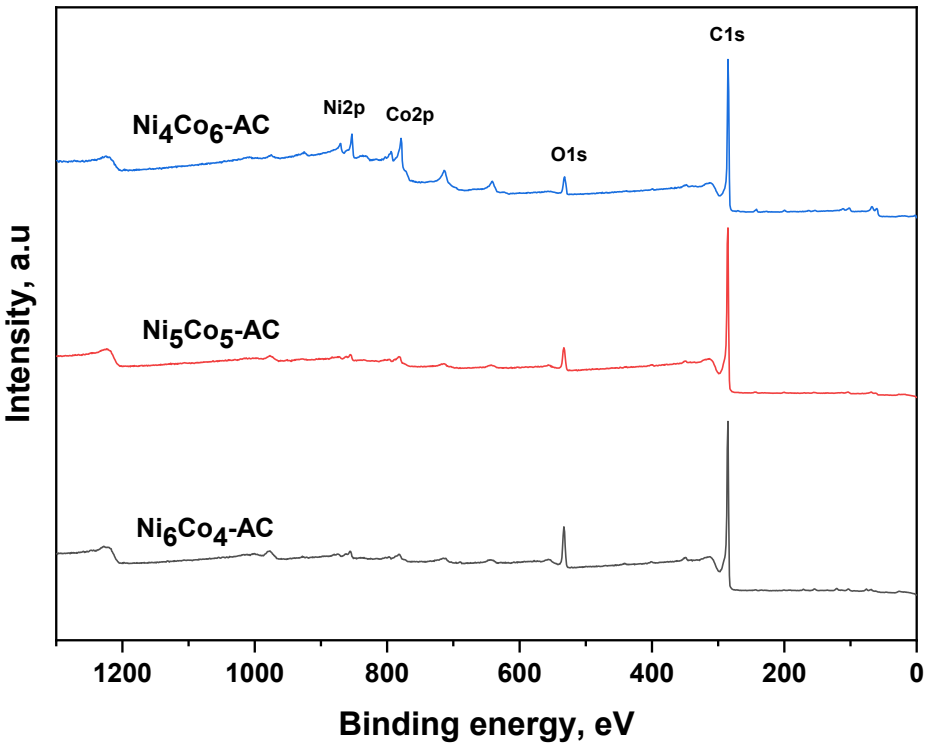



**Figure S2:** Survey scan of $Ni_6Co_4$-AC, $Ni_5Co_5$-AC, and $Ni_4Co_6$-AC

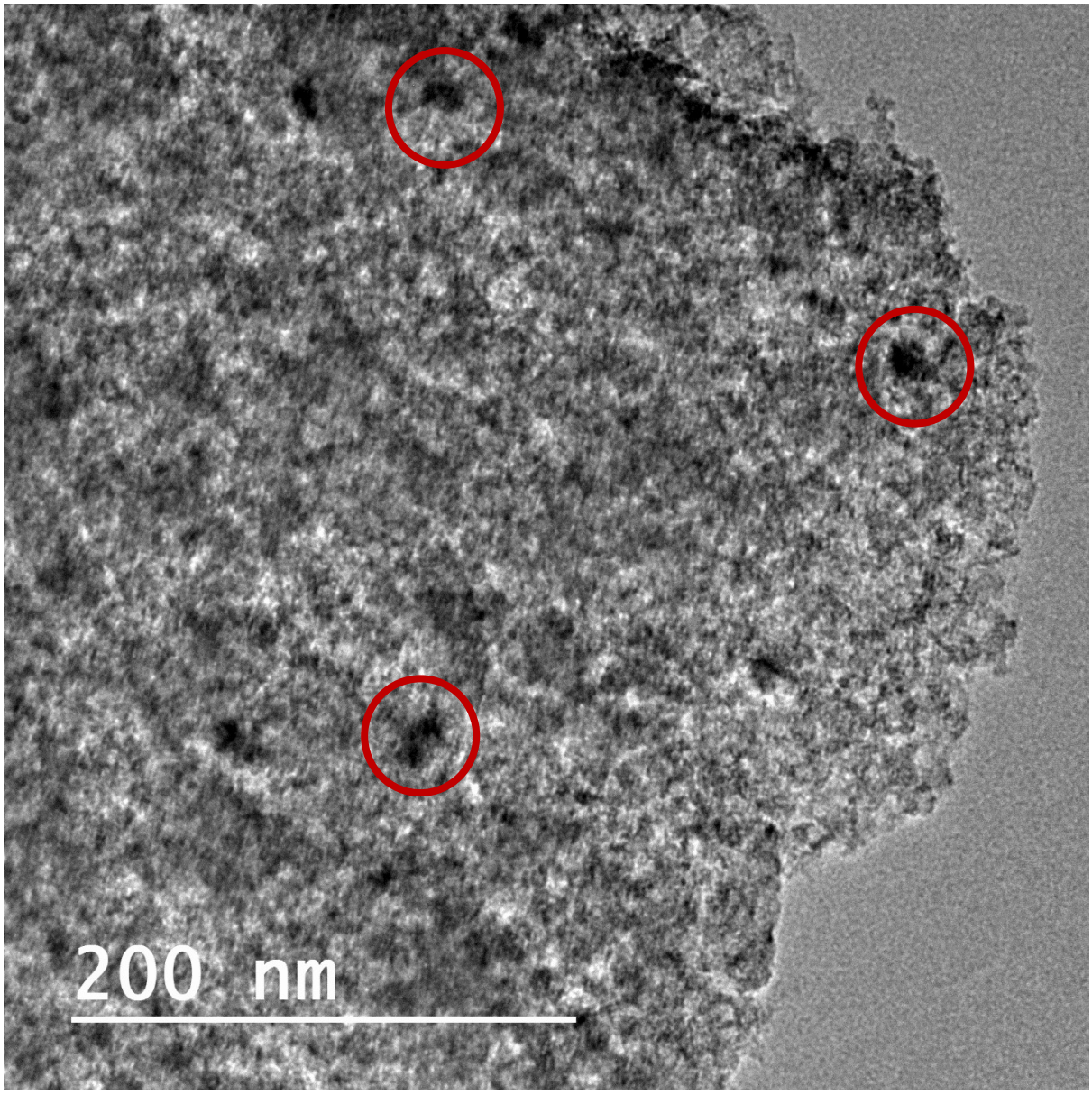
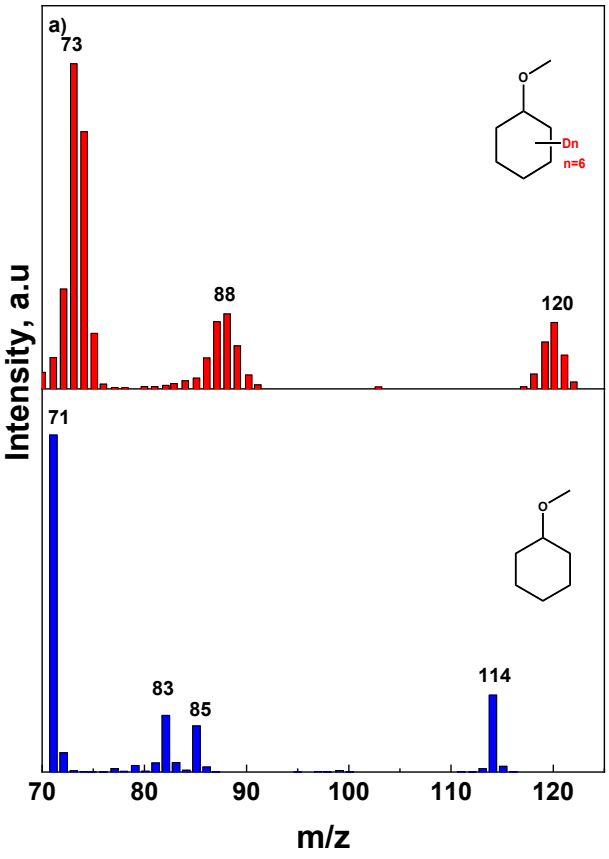



**Figure S3:** Agglorimation of Ni-Co in spent catalyst.


a)
73
88
120
71
83
85
114
Intensity, a.u
m/z
70
80
90
100
110
120
O
Dn
n=6

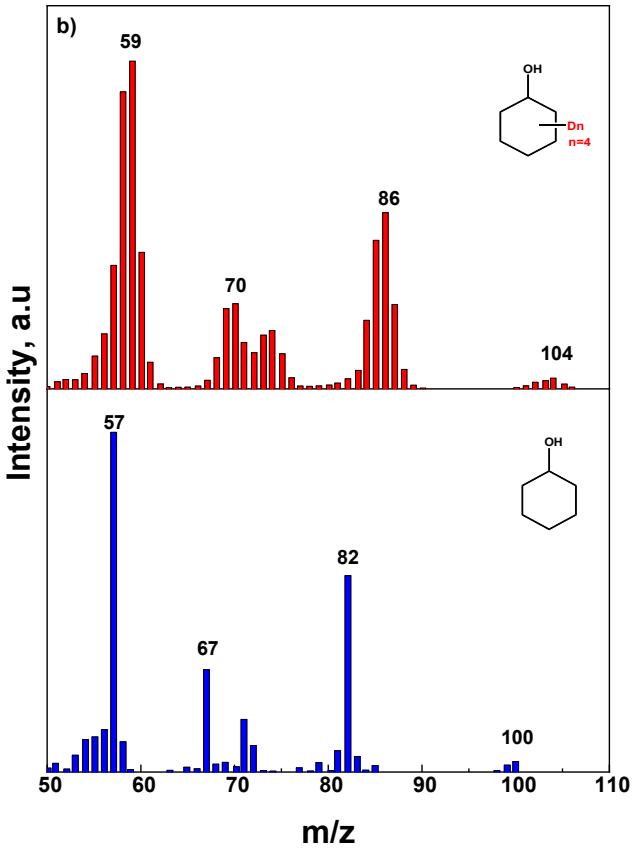



**Figure S4:** MS ion chromatogram of products of anisole HDO over $Ni_5Co_5$-AC in $D_20$; Reaction condition - Catalyst- 100mg, T-180$^o$C, P- 5 MPa, Time - 4 h and $D_2O$-5 ml.

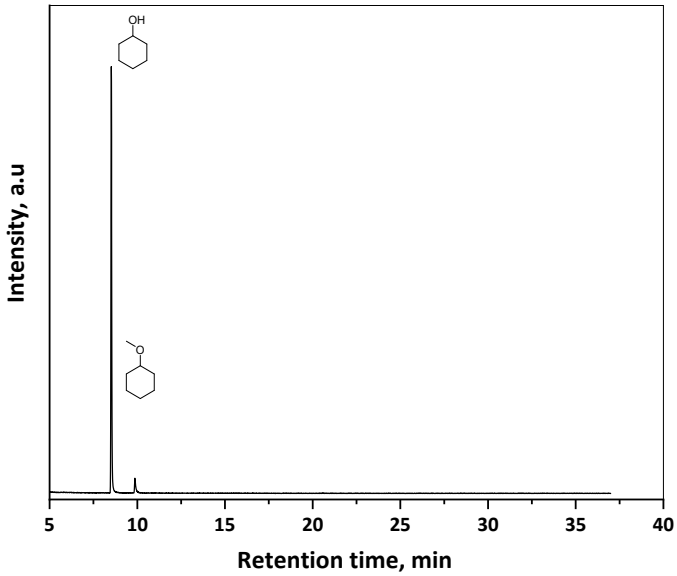



**Figure S5:** GC chromatogram of anisole hydrodeoxygenation over $Ni_5Co_5$-AC; Reaction condition: Catalyst- 100mg, T-180$^o$C, P- 5 MPa, Time - 4 h and Water-5 ml.

**Table S1:** BET analysis of NiCo-AC done by $N_2$ adsorption-desorption isotherm.

| Catalyst | $S_{BET,}$ $m^2.g^{-1}$ | $V_{p,}$ $cm^3.g^{-1}$ |
|---|---|---|
| AC | 938 | 0.67 |
| $Ni_{10}Co_0$-AC | 791 | 0.15 |
| $Ni_8Co_2$-AC | 772 | 0.16 |
| $Ni_6Co_4$-AC | 797 | 0.18 |
| $Ni_5Co_5$-AC | 788 | 0.17 |
| $Ni_4Co_6$-AC | 784 | 0.14 |
| $Ni_2Co_8$-AC | 782 | 0.16 |
| $Ni_0Co_{10}$-AC | 791 | 0.20 |

**Table S2:** Effect of solvent on anisole hydrodeoxygenation.

| Solvent | Conversion, % | Methoxy Cyclohexane, % | Cyclohexanol, % |
|---|---|---|---|
| Methanol | 2 | 48 | 52 |
| Ethanol | 5 | 56 | 44 |
| Iso-propanol | 13 | 72 | 28 |
| Iso-butanol | 9 | 54 | 46 |
| Water | 100 | 5 | 95 |
| Iso-propanol | 100 | 88.2 | 11.8 |
| **Reaction conditions:** Catalyst - $Ni_5Co_5$-AC, T- 180 $^oC$, Anisole - 0.5 mmol, P - 5 MPa, Time - 4h | | | |

**Table S3:** Reuse study of catalyst for anisole hydrodeoxygenation.

| Cycle | Conversion, % | Methoxy Cyclohexane, % | Cyclohexanol, % |
|---|---|---|---|
| **1** | 100 | 5 | 95 |
| **2** | 98.5 | 8 | 92.0 |
| **3** | 78.6 | 18.3 | 81.7 |
| **4** | 62 | 27.5 | 72.5 |
| **Reaction conditions:** Catalyst - $Ni_5Co_5$-AC, T- 180 $^oC$, Anisole - 0.5 mmol, P - 5 MPa, Time - 4h | | | |

| Time, min | Conversion, % | Methoxy Cyclohexane, % | Cyclohexanol, % |
|---|---|---|---|
| 5 | 1.5 | 100 | 0 |
| 10 | 6.5 | 39 | 61 |
| 15 | 15 | 26 | 74 |
| 20 | 21 | 25 | 75 |
| 25 | 44 | 17 | 83 |
| 30 | 66 | 18 | 82 |
| 45 | 71 | 16 | 84 |
| 60 | 79 | 13 | 87 |
| 120 | 87 | 11 | 89 |
| 180 | 90 | 7.5 | 92.5 |
| 240 | 100 | 5 | 95 |
| **Rxn conditions:** Catalyst - $Ni_5Co_5$-AC, T- 180 $^oC$, Anisole - 0.5 mmol, P - 5 MPa | | | |

**Table S4:** Impact of reaction time on anisole HDO and cyclohexanol selectivity.

According to the initial rate method, the rate of reaction can be given as

$$\text{Rate} = \frac{-dc_{anisole}}{dt} = \frac{C_2 - C_1}{t_2 - t_1} = \frac{dc_{cychohexanol}}{dt} = K.\ C^{n}_{cyclohexanol} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(1)$$

Where K and n represent the rate constant and order of the reaction, respectively and n≠1.

$R_{0.5}$ and $R_1$ calculated by the initial rate equation.

$$R_{0.5} = \left[\frac{C_2 - C_1}{t_2 - t_1}\right]_{0.5\ mmol} = 0.294 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(2)$$

$$R_1 = \left[\frac{C_2 - C_1}{t_2 - t_1}\right]_{1\ mmol} = 0.662 \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(3)$$

Rate expression for 0.5 mmol

$$R_{0.5} = k.\ C^{n}_{cyclohexanol} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(4)$$

Rate expression for 1 mmol

$$R_1 = k.\ C^{n}_{cyclohexanol} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(5)$$

Dividing equation 5 by 4

$$\frac{0.662}{0.294} = \left[\frac{1}{0.5}\right]^{n} \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots(6)$$

$2.25 = 2^n$

Taking log of equation 6

$\log 2.25 = n \log 2$

$n = 1.125$

Hence the order of the reaction is 1.125 and close to 1. The rate constant (K) was calculated by equation 5, and it was $1.1x10^{-2}.sec^{-1}$.