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**Figure S1:** Shifting of XRD peaks of doped oxides as compared to their undoped analogues.



**Figure S2.** (a) STEM image of Ti-In2O3. EDX elemental mapping of the selected region (b) showing the presence of (c) In and (d) Ti.



**Figure S3.** Diffuse reflectance UV-Vis analysis of Ti-In2O3 and undoped In2O3.



**Figure S4:** XRD analysis of H2 pretreated In-TiO2 at reduction temperature as observed in H2 TPR analysis (Figure 3a, main manuscript). The pretreatment was done at respective temperatures for 30 min under 5% H2/Ar mixture.



**Figure S5:** UV-Vis analysis for TiO2 before and after treating under H2 atmosphere at 350 °C.



**Figure S6.** (a) CO2 TPD experiment and (b) DRIFTS analysis during CO2 TPD after treating catalysts at 300 °C under H2 atmosphere.



**Figure S7.** In situ DRIFTS analysis of In-TiO2 catalyst. Reaction condition: 350 °C, 0.1 MPa, H2:CO2 = 3:1. No intermediate was identified. The dotted lines shows expected position of formate (HCOO\*) and carboxyl intermediate (COOH\*) reported in literature.1

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**Figure S8.** CO production during the oxidation of reduced In2O3 using CO2.

**Table S1:** Physical properties of doped In2O3 and TiO2 along with the undoped oxides.

|  |  |  |  |
| --- | --- | --- | --- |
| **Catalyst** | **Dopant** | **Crystallite size (nm)** | **Surface area (m2 g-1)** |
| In-TiO2 | In | 12 | 74 |
| TiO2 | NA | 15 | 49 |
| Ti-In2O3 | Ti | 24 | 26 |
| In2O3 | NA | 16 | 27 |

**Table S2:** Comparison of catalytic activity of In-TiO2 catalyst with highly selective catalysts under similar reaction conditions reported in literature.

|  |  |  |  |  |  |  |  |
| --- | --- | --- | --- | --- | --- | --- | --- |
| **Catalyst** | **T****(°C)** | **P****(MPa)** | **H2:CO2** | **SV****(mL h-1 gcat-1)** | **STY (CO)****(μmol g-1 s-1)** | **S(CO)****(%)** | **Ref** |
| In-TiO2 | 300 | 3 | 3:1 | 30,000 | 6.9 | >99 | This work |
| In-TiO2 | 350 | 3 | 3:1 | 30,00060,000 | 1822 | >99>99 | This Work |
| CoZrOx (10) | 340 | 3 | 4:1 | 60,000 | 8.6 | 97 | 2 |
| Cu/CeO­2-hs | 350 | 0.1 | 3:1 | 300,000 | ca. 55a | 100 | 3 |
| Cu/CeO2 | 400 | 0.1 | 1:1 | 30,000 | 9.5b | 100 | 4 |
| Cu-Fe/CeO2 | 450 | 0.1 | 1:1 | 2400 | 3.86 | 100 | 5 |
| 8Cu/CeO2-δ | 340 | 0.1 | 4:1 | 60,000 | 18c | 100 | 6 |
| Cu/CeO2-NR | 350 | 0.1 | 5:1 | 150,000 | 38.9d | 100 | 7 |
| Cu-CeO2 | 300 | 0.1 | 3:1 | 1120 | 1.6 | 100 | 8 |
| Ni/TiO2 | 360 | 0.1 | 3:1 | 15,000 | 1.6 | 100 | 9 |
| Ni3-Fe9/ZrO2 | 400 | 0.1 | 2:1 | 9000 | 6.4 | 96 | 10 |
| CuAl2O4 | 350 | 0.1 | 2:1 | 15,000 | 2.1 | 100 | 11 |
| NiMgOx (SAC)e | 300 | 3 | 4:1 | 60,000 | 0.2 | 100 | 12 |
| 5% Ir/CeO2 | 300 | 1 | 4:1 | 11,400 | 2.0 | >99 | 13 |
| Pt-Co/TiO2 | 300 | - | 2:1 | 36,000 | 11.4 | 99 | 14 |
| Pt/mullite | 340 | 0.1 | 1:1 | 27,000 | 12.5 | 96 | 15 |
| Ru/Al2O3 | 350 | 0.1 | 3:1 | 72,000 | 21.6 | 98 | 16 |
| Au/TiO2 | 300 | 0.1 | 9:1 | 20,000 | 7.4 | >99 | 17 |
| NiAlIn2 | 350 | 0.1 | 4:1 | 30,000 | 14.8 | >99 | 18 |
| H-SiO2@Ru@SiO2-30 | 350 | 0.1 | 1:1 | 80,000 | 4.0 | >99 | 19 |
| Cubic In2O3 | 350 | 0.1 | 2:1 | 18,000 | 3.17 | 100 | 20 |
| In2O3-CeO2 | 350 | 0.1 | 1:1 | 48,000 | 3.72 | 100 | 21 |

a Cu/CeO­2-hs: poor catalyst stability, lost 27% of activity during the stability check for 30 h.

b Cu/CeO2: poor catalyst stability, lost 25% of activity during the stability check for 24 h.

c 8Cu/CeO2-δ: reaction carried out for 2 h.

d Cu/CeO2-NR: reaction carried out for 2 h.

eSAC = Single atom catalyst

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