RSC Advances

Electronic Supplementary Information (ESI)

In-situ X-ray absorption spectroscopy study of CuO-NiO/CeO_2–ZrO_2 oxides: redox characterization and its effect in catalytic performance for partial oxidation of methane

Lucía M. Toscani[1,2], M. Genoveva Zimicz[3], Tereza S. Martins[4], Diego G. Lamas[5,6], Susana A. Larrondo[1,2]*

[1]UNIDEF, MINDEF, CONICET, Departamento de Investigaciones en Sólidos, CITEDEF, J.B. de La Salle 4397, 1603 Villa Martelli, Pcia. de Buenos Aires, Argentina.
[2]Instituto de Investigación e Ingeniería Ambiental, UNSAM, Campus Miguelete, 25 de Mayo y Francia, 1650 San Martín, Pcia. de Buenos Aires, Argentina.
[3]Department Instituto de Física del Sur (IFISUR), Departamento de Física, Universidad Nacional del Sur (UNS), CONICET, Av. Alem 1253, 8000 Bahía Blanca, Pcia. de Buenos Aires Argentina.
[4]Universidade Federal de São Paulo – UNIFESP. Departamento de Química, Instituto de Ciências Ambientais, Químicas e Farmacêuticas, Rua São Nicolau 210, 2nd floor, 09913-030, Diadema, São Paulo, Brazil.
[5]CONICET / Escuela de Ciencia y Tecnología, UNSAM, Campus Miguelete, 25 de Mayo y Francia, 1650 San Martín, Pcia. de Buenos Aires, Argentina.
[6]Departamento de Física de la Materia Condensada, Gerencia de Investigación y Aplicaciones, Centro Atómico Constituyentes, Comisión Nacional de Energía Atómica, Av. General Paz 1499, 1650 San Martín, Pcia. de Buenos Aires, Argentina.
*slarrondo@citedef.gob.ar

Element specific TPR profiles:

Ce L3-edge

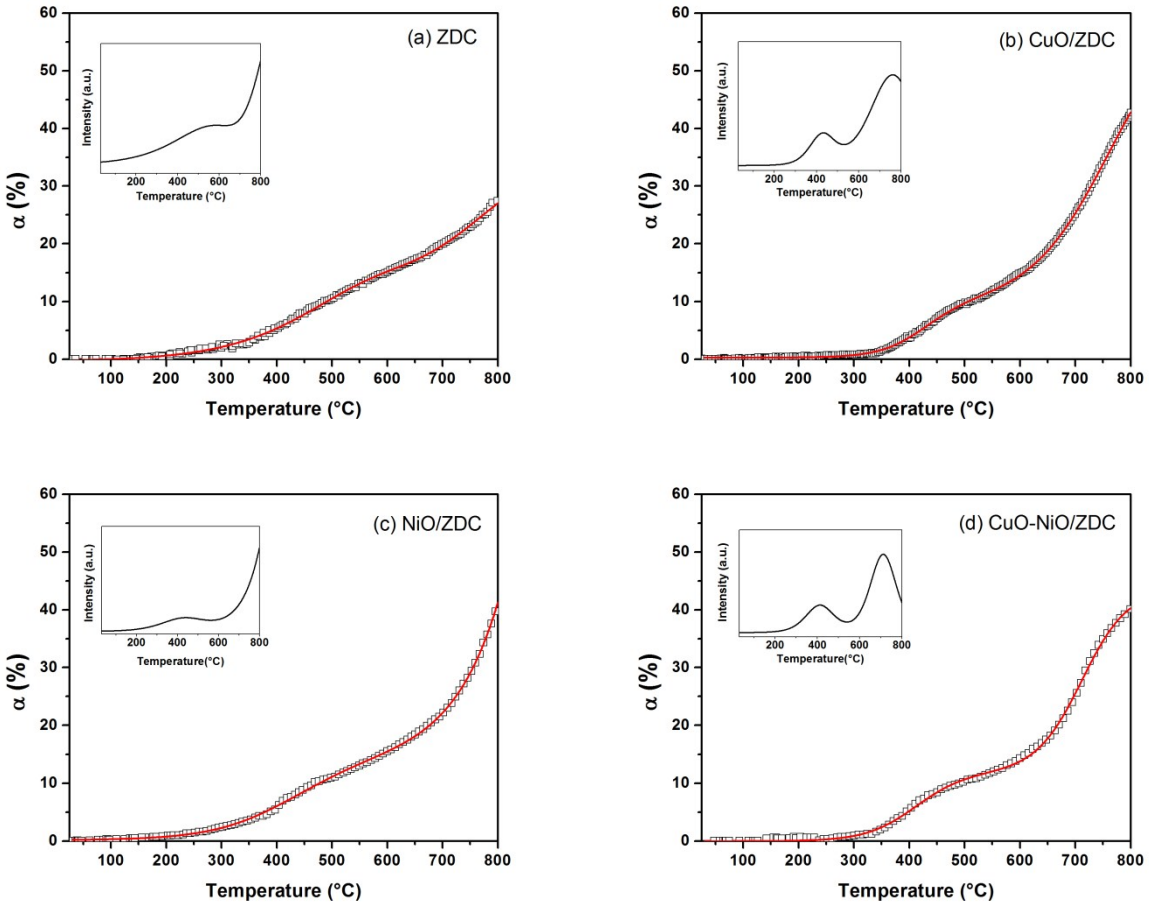

Figure S1: Degree of Ce reduction [$\alpha=Ce^{3+}/(Ce^{4+}+Ce^{3+})$] calculated for samples (a) ZDC, (b) CuO/ZDC, (c) NiO/ZDC and (d) CuO-NiO/ZDC during the course of in-situ XANES TPR experiments in 5 mol % H_2/He atmosphere (square symbols). The red solid line corresponds to the fitting of the reduction profile with two Boltzmann sigmoid functions. In the inset: simulated Ce-TPR profiles obtained from differentiation of the reduction profiles.

Ni K-edge

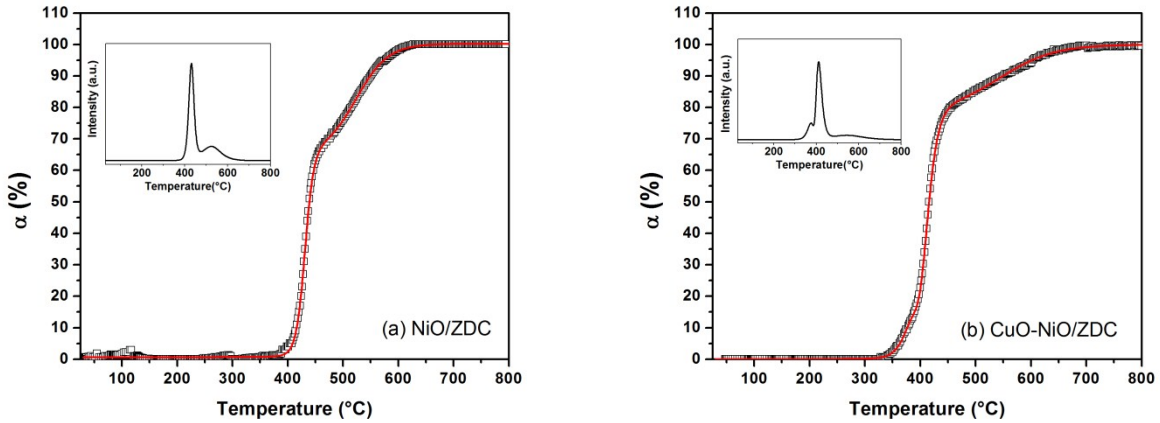

Figure S2: Degree of Ni reduction [$\alpha=Ni^0/(Ni^{2+}+Ni^0)$] calculated for samples (a) NiO/ZDC and (b) CuO-NiO/ZDC during the course of in-situ XANES TPR experiments in 5 mol % H_2/He atmosphere (square symbols). The red solid line corresponds to the fitting of the reduction profile with two step functions in the case of NiO/ZDC and three step functions in the case of CuO-NiO/ZDC. In the inset: simulated Ni-TPR profiles obtained from differentiation of the reduction profiles.

Cu K-edge

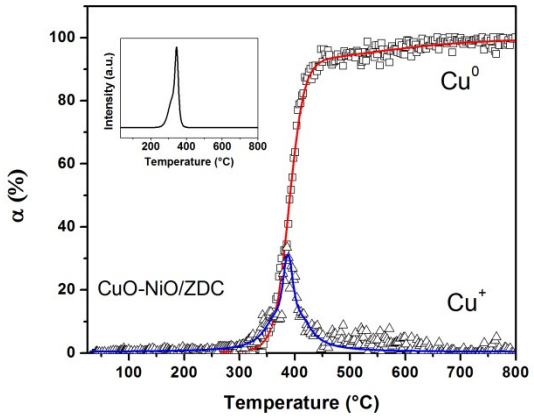

Figure S3: Degree of Cu^{2+} reduction [$\alpha_1=Cu^0/(Cu^{2+}+Cu^{+}+Cu^0)$] and degree of Cu^{+} reduction [$\alpha_2=Cu^{+}/(Cu^{2+}+Cu^{+}+Cu^0)$] calculated for sample CuO-NiO/ZDC during the course of in-situ XANES TPR experiments in 5 mol % H_2/He atmosphere (square symbols). The red solid line corresponds to the fitting of the Cu^{2+} to Cu^0 reduction profile with two step functions. The blue solid line corresponds to the fitting of the Cu+ to Cu0 reduction profile with a pseudo-voigt curve. In the inset: simulated Cu-TPR profile obtained from the addition of both profiles and subsequent differentiation.