Role of oxygenates and effect of operating conditions in the deactivation of a Ni/La_2O_3-αAl_2O_3catalyst during the steam reforming of bio-oil

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Electronic Supplementary Information

Evolution with time on stream of reaction indices

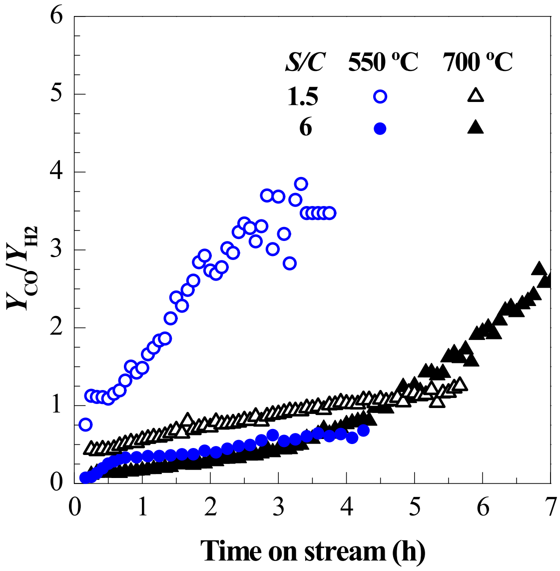

Fig. SI-1. Evolution with time on stream of the ratio of yields of CO and H_2 in mol%, for different values of temperature and *S/C* ratio. Space time, 0.19 $g_{catalyst}$ h $g_{bio\text{-}oil}^{-1}$.

XRD analysis

The assignment was carried out as follows:[1-3] Ni^0, 44.6° in plane (111), 52° in plane (200) and 76.5° in plane (220) (JCPDS 00-004-0850); LaAlO$_3$, 23.5°, 33.5°, 39.7°, 41.3°, 47.9°, 54.1°, 59.6°, 60.1° and 70.2° (JCPDS 01-085-1071); NiAl$_2$O$_4$, 31.3°, 36.9°, 44.6°, 59.6° and 60.1 ° (JCPDS 00-010-0339); Al$_2$O$_3$, 19.6°, 31.3°, 36.9°, 39.7°, 44.6°, 47.9°, 59.6°, 60.1°, 64.2° and 67.5°(JCPDS 01-086-1410); Al$_2$O$_3$ (corundum), 57.6°, 59.6°, 60.1° and 70.2° (JCPDS 01-075-0786). This assignment leads to an overlapping of several phases in the same 2θ positions, as observed in Fig. 3.

XPS spectroscopy

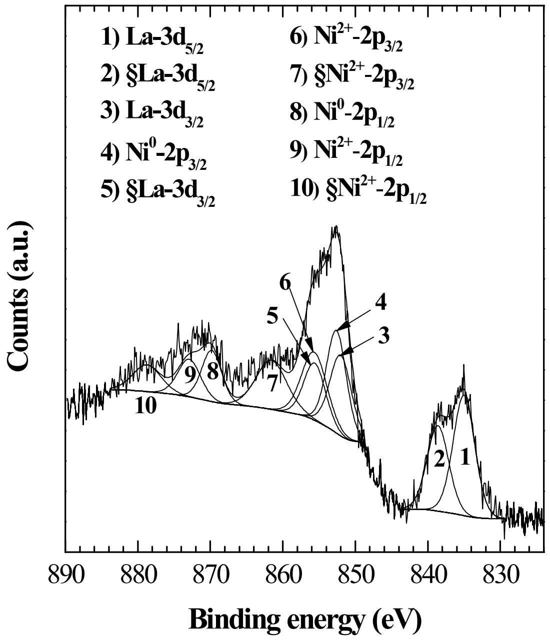

Fig. SI-2. La3d and Ni2p region in the XPS spectrum of the fresh reduced Ni/La$_2$O$_3$-αAl$_2$O$_3$ catalyst. §: satellite peak.

Table SI-1.

Assignment of phases in the XPS spectral region of 824-890 eV (Fig. SI-2).§: satellite peak.

Assigment	Binding energy (eV)
$La3d_{5/2}$	835.3 ± 0.6 eV
§$La3d_{5/2}$	838.9 ± 0.6 eV
$La3d_{3/2}$	852.3 ± 0.6 eV
§$La3d_{3/2}$	855.9 ± 0.6 eV
Ni^0-$2p_{3/2}$	852.6 ± 0.0 eV
Ni^0-$2p_{1/2}$	869.8 ± 0.0 eV
Ni^{2+}-$2p_{3/2}$	856.1 ± 0.6 eV
§Ni^{2+}-$2p_{3/2}$	862.4 ± 0.7 eV
Ni^{2+}-$2p_{1/2}$	874.2 ± 0.8 eV
§Ni^{2+}-$2p_{1/2}$	880.2 ± 0.8 eV

EDX spectroscopy

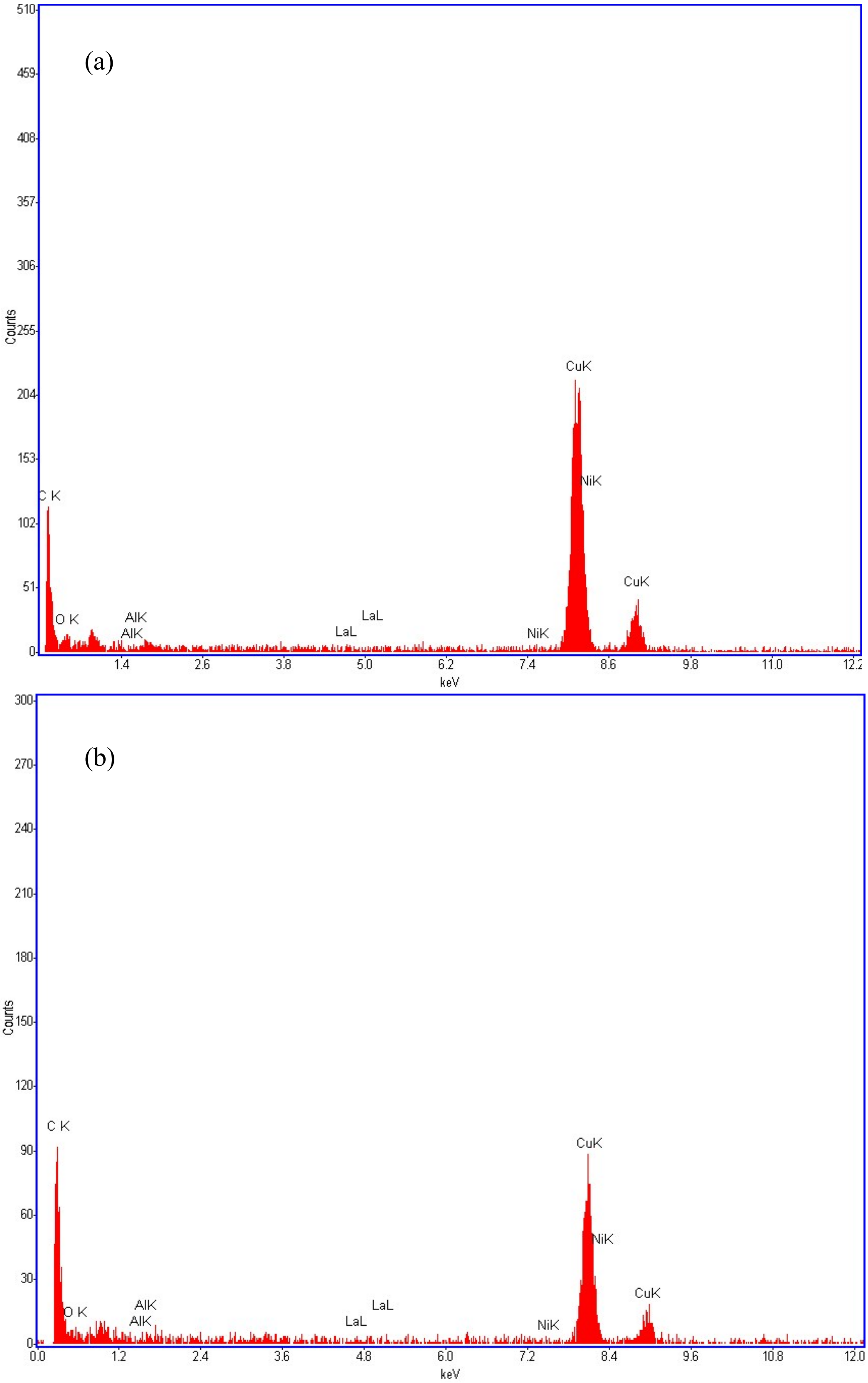

Fig. SI-3. EDX spectra of the catalyst deactivated at 550 ºC and *S/C* = 6, analyzed at different zones ((a) and (b)) in their TEM microscopic analysis (Figs. 6a,b).

SEM microscopy

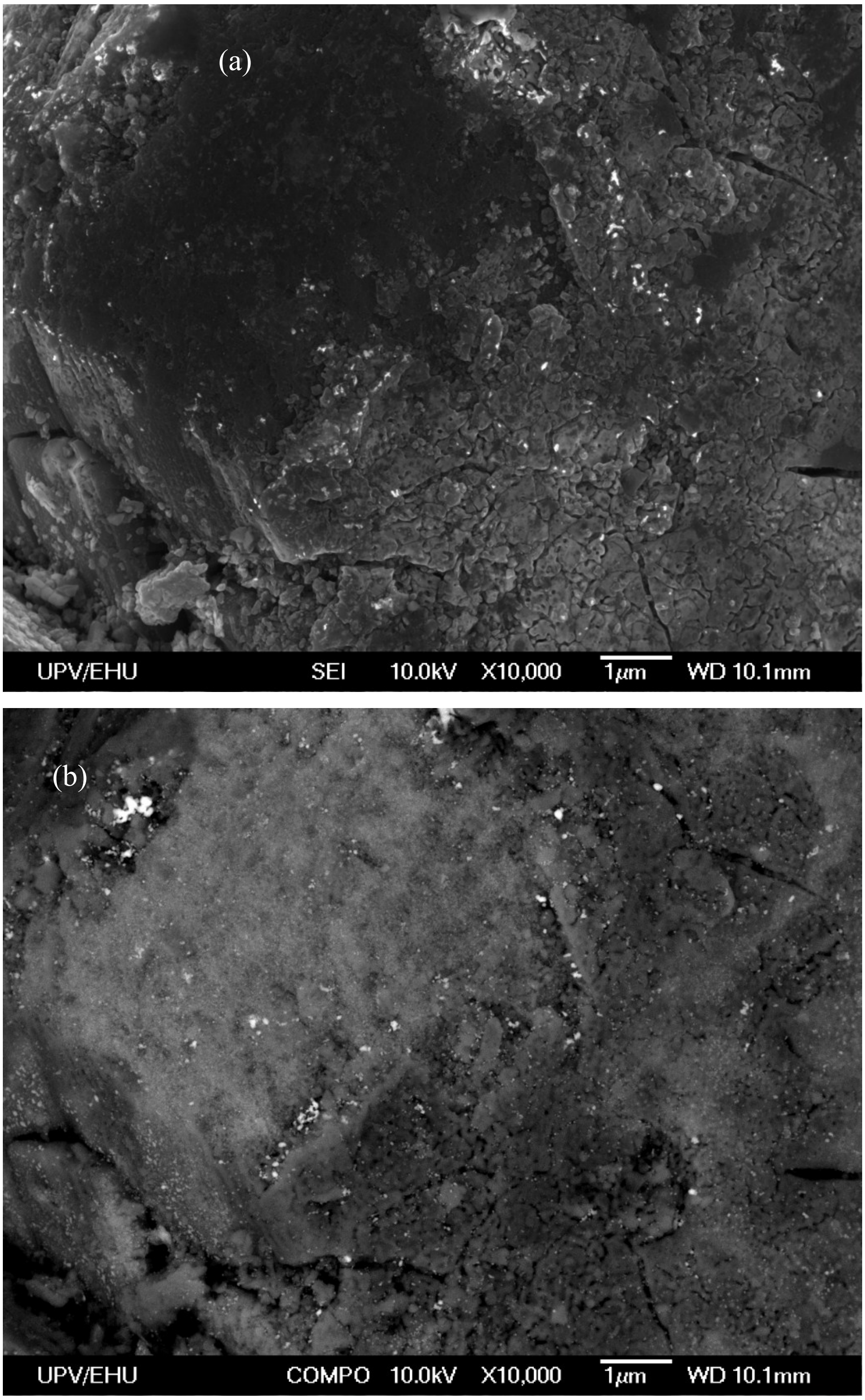

Fig. SI-4. SEM image (a) and its corresponding backscattered electron image (b) of the catalyst deactivated at 550 ºC and *S/C* = 6.

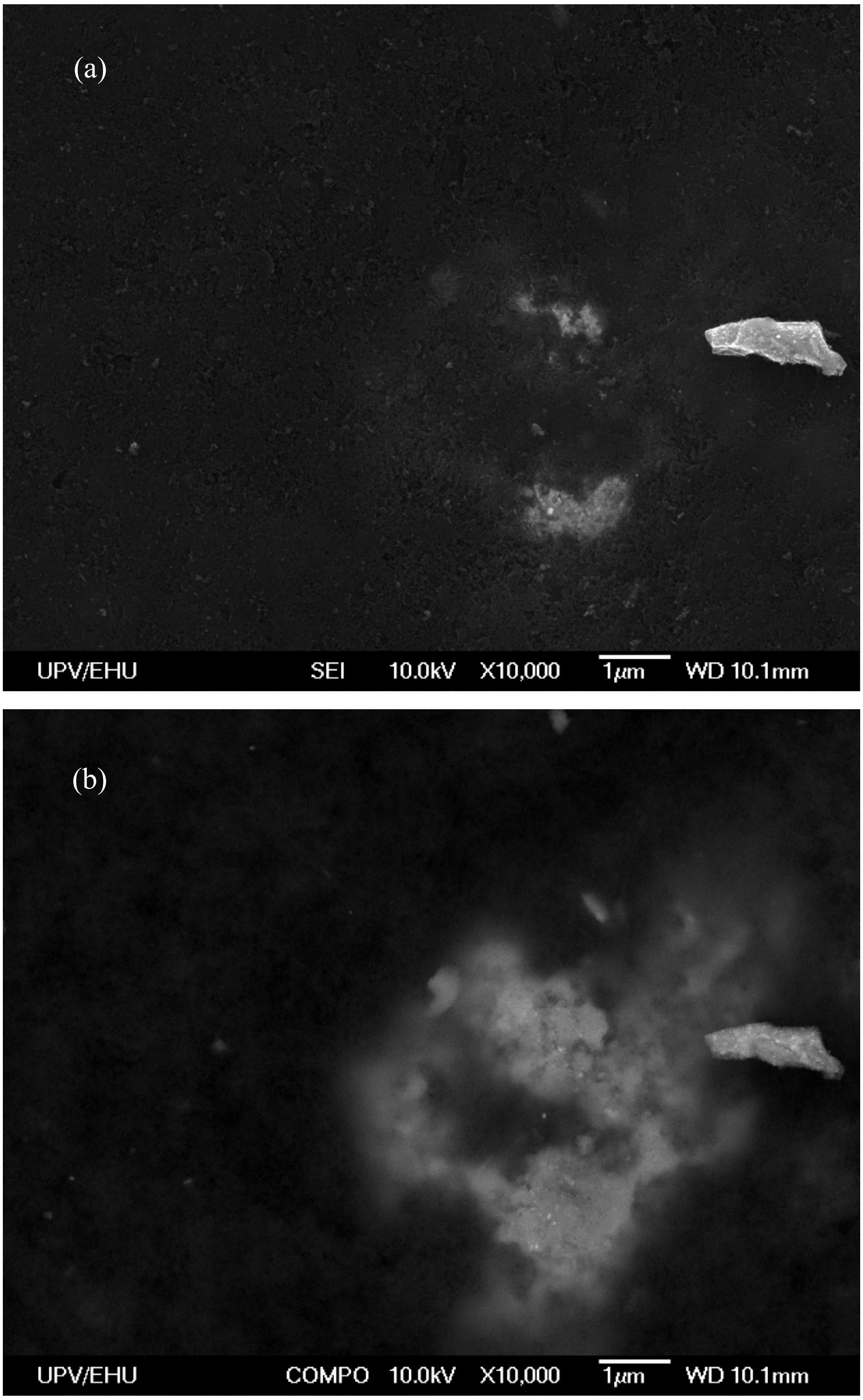

Fig. SI-5. SEM image (a) and its corresponding backscattered electron image (b) of the catalyst deactivated at 700 ºC and *S/C* = 6.

Raman spectroscopy

The Raman spectra were deconvoluted into four Lorentzian peaks (G, D1, D3 and D4), as observed in Fig. SI-6, ascribed to: (i) G band (1575-1600 cm^{-1}), characteristic of graphitic layers,[4, 5] that is to say, stretching vibrations of *sp*^{2} bonds in aromatic clusters;[6] (ii) D1 band (1350-1380 cm^{-1}), corresponding to the *sp*^{2} bond vibrations close to the edges in the graphitic layers;[5] (iii) D3 band (1450-1510 cm^{-1}) assigned to amorphous coke in turbostratic fashion due to bond vibrations close to the edges in highly disordered graphitic layers;[5] (iv) D4 band (~1200 cm^{-1}), assigned to *sp*^{2}-*sp*^{3} bond vibrations in disordered graphitic layers, with aliphatic chains.[5]

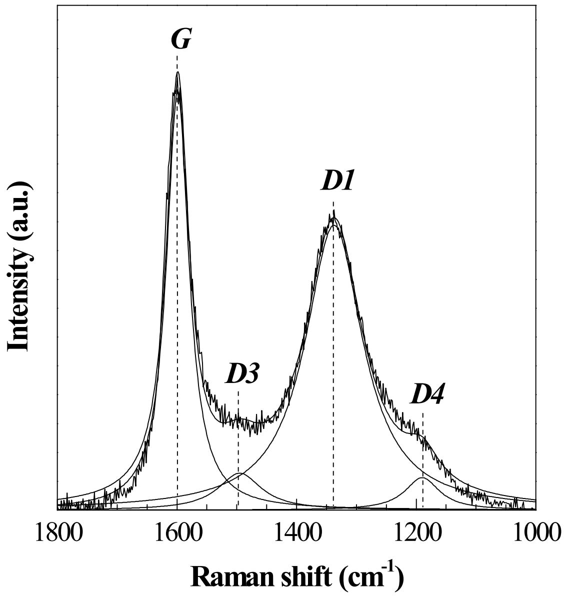

Fig. SI-6. Raman spectra (1000-1800 cm^{-1} region) of the coked Ni/La$_2$O$_3$-αAl$_2$O$_3$ catalyst deactivated in the steam reforming of bio-oil. Operating conditions: 700 ºC, *S/C* = 6, space time = 0.19 g$_{\text{catalyst}}$ h g$_{\text{bio-oil}}$$^{-1}$.

FTIR spectroscopy

The most representative bands of the FTIR were assigned to the following functional groups in the deposited coke:[4, 6-12]stretching vibrations in C−O bonds, such as in ethoxy groups and/or alcohols, 1050 cm^{-1}; rocking vibrations in $-CH_3$ groups in aliphatics and/or C−O bonds in phenols and/or ethers, 1150-1160 cm^{-1}; C−O bonds in acetate groups, phenolic esters and/or ethers $C=C-O-C_{aliphatic}$ and/or $C_{aromatic}-O-C_{aliphatic}$, 1240-1260 cm^{-1}; symmetric stretching vibrations of O=C−O bonds in acetate groups, 1420-1430 cm^{-1}; bending vibrations in $-CH_2$ and $-CH_3$ aliphatic groups, alkylaromatic compounds and/or symmetric bending vibrations of O=C−O in acetate groups, 1460 cm^{-1}; asymmetric stretching vibrations of O=C−O in groups such as carbonates, 1530 cm^{-1}; polycondensed aromatics ('coke band') and/or asymmetric stretching vibrations of O=C−O bonds in acetate groups, 1580 cm^{-1}; dienes, 1610 cm^{-1}; C=O groups in ketones and/or aldehydes, 1680-1700 cm^{-1}; C−H in $-CH_2$ aliphatic groups, 2855 cm^{-1}; C−H in $-CH_3$ aliphatic groups, 2870 cm^{-1}; C−H in −CH and $-CH_2$ aliphatic groups, 2920 cm^{-1}; C−H in $-CH_3$ aliphatic groups, 2960 cm^{-1}. This assignment reveals a high heterogeneity of functional groups in coke and thus difficulty to univocally assign IR bands to particular species.

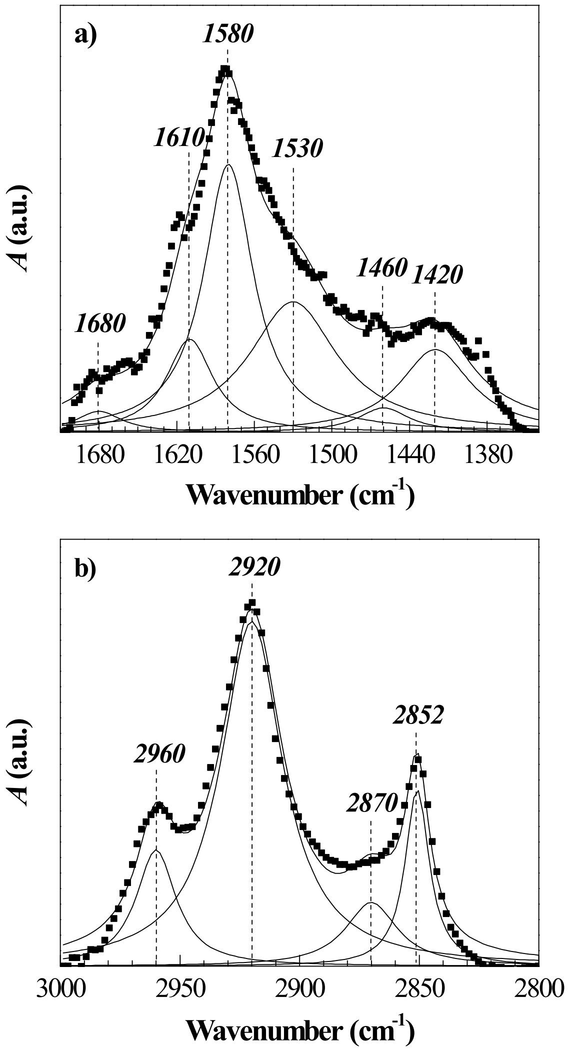

Fig. SI-7. Infrared spectra of the Ni/La_2O_3-αAl_2O_3 catalyst deactivated in the steam reforming of bio-oil, at 700 ºC and *S/C* = 6. 1340-1710 cm^{-1} region (a); 2800-3000 cm^{-1} region (b).

References

1. K. F. M. Elias, A. F. Lucrédio and E. M. Assaf, *Int. J. Hydrogen Energy*, 2013, **38**, 4407-4417.
2. A. Remiro, B. Valle, A. T. Aguayo, J. Bilbao and A. G. Gayubo, *Fuel Process. Technol.*, 2013, **115**, 222-232.
3. B. Valle, B. Aramburu, A. Remiro, J. Bilbao and A. G. Gayubo, *Appl. Catal. B: Environ.*, 2014, **147**, 402-410.
4. J. Robertson, *Mater. Sci. Eng., R*, 2002, **37**, 129-281.
5. A. Sadezky, H. Muckenhuber, H. Grothe, R. Niessner and U. Pöschl, *Carbon*, 2005, **43**, 1731-1742.
6. P. Castaño, G. Elordi, M. Olazar, A. T. Aguayo, B. Pawelec and J. Bilbao, *Appl. Catal. B: Environ.*, 2011, **104**, 91-100.
7. B. Stuart, *Infrared spectroscopy: fundamentals and applications*, John Wiley & Sons, New York, 2004.
8. Ë. Pretsch, P. Bühlmann and M. Badertscher, *Structure determination of organic compounds: tables of spectral data*, Springer, Berlin, 4th edn., 2009.
9. M. Ibáñez, B. Valle, J. Bilbao, A. G. Gayubo and P. Castaño, *Catal. Today*, 2012, **195**, 106-113.
10. L. V. Mattos, G. Jacobs, B. H. Davis and F. B. Noronha, *Chem. Rev.*, 2012, **112**, 4094-4123.
11. W. Xu, Z. Liu, A. C. Johnston-Peck, S. D. Senanayake, G. Zhou, D. Stacchiola, E. A. Stach and J. A. Rodriguez, *ACS Catal.*, 2013, **3**, 975-984.
12. A. Ochoa, B. Aramburu, M. Ibáñez, B. Valle, J. Bilbao, A. G. Gayubo and P. Castaño, *ChemSusChem*, 2014, **7**, 2597-2608.