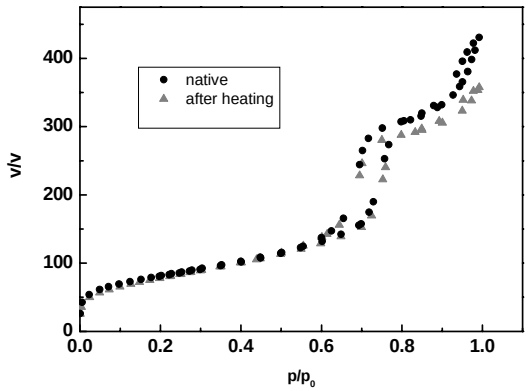
Supplementary information:

Heat treatment of SBA-15 Cu materials.

The SBA-15 Cu materials have been well characterized and are discussed fully in reference 28. However, the effect on the SBA-15 Cu surface due to thermal treatment was not a subject of discussion in that particular article. The N_2 adsorption isotherms of SBA-15 Cu 25% before and after thermal treatment corresponding to the LWC materials are compared here in Figure 1. The form of the N_2 isotherm corresponding to the SBA-15 Cu 25% after heating has not been altered with respect to the untreated one. The very similar aspects of the two N_2 isotherms indicate that no important change in pore structure or surface structure has occurred during heating. The decrease in the volume of adsorbed N_2 gas for the heated SBA-15 Cu material is assigned to the water lost which has occurred during the thermal process. Moreover, all SBA-15 Cu powders, even at the highest copper loading, became various colours of green indicating a change in the coordination sphere of copper and can indicate the formation of polynuclear copper complexes (M.M. Hassanien , I.M. Gabr , M.H. Abdel-Rhmanb, A.A. El-Asmy *Spectrochimica Acta Part A* 2008, **71**, 73–79). CuO in crystalline form is black and this indicates that CuO crystals are not present. It is likely however that with heating, some small oxidic Cu II clusters have formed as discussed by Bennici et al. (S. Bennici, A. Gervasini, N. Ravasio and F. Zaccheria, J .Phys. Chem. B 2003, 107, 5168). The small hysteresis found at very high relative pressures (0.8-1.0) corresponds to N_2 condensation occurring outside the pores which means that copper is not just on the pore surface but also on the exterior surface. Note that this phenomenon was not observed for lower copper loadings. Since the copper oxidic clusters are only present in the SBA-15 Cu materials with loadings higher than 20 % and the most drastic decrease in H_2 formation is observed from the non-modified SBA-15 to the SBA-15 Cu 15% (HWC) or 13%(LWC), their presence does not seem to have an important influence on H_2 formation.

Figure 1. N_2 adsorption isotherm of SBA-15 Cu 25% after LWC thermal treatment.



Presence of $Cu_2(OH)_3NO_3$ in the high copper loaded SBA-15 materials.

The SBA-15 powders containing 34% Cu II and which have undergone the less drastic thermal treatment (HWC) contain some $Cu^{II}_2(OH)_3NO_3$ species as evidenced by infrared spectroscopy. Characteristic peaks in the 3550 to 3450 cm^{-1} region, 1420 to 1320 cm^{-1} region and 1050 cm^{-1} region indicate the presence of stretching vibrations of O-H groups, O-NO_2 groups and N-O groups (of O-NO_2), respectively (Nyquist, R.; Kagel, R. In *Infrared Spectra of Inorganic Compounds*; Academic Press: New York, **1971**). When the SBA-15 copper powders are submitted to the more drastic thermal treatment (170°C for 4 days), the dehydroxylation of the hydroxide groups and loss of nitrate anion occur leaving CuO oxidic clusters. The copper salt decomposes between 220 and 300°C which is comparable to 170°C under vacuum (10^{-2} mbar)[6] giving CuO. As shown in Figure 5 (in the main article), the hydroxyl nitrate is not affected by the irradiation.

Figure 2: IR spectra of SBA-15 at 34% Cu^{II} having a high water content: before heating (black); after the thermal treatment (light gray) and after irradiation (gray) at 170 kGy. The stars indicate the infrared signature of nitrate groups (1418, 1353 and 1047 cm^{-1}).