Supporting information

Degradation of Sulfur Mustard on KF/Al_2O_3 Supports: Insights into the Products and the Reactions Mechanisms

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General Experimental

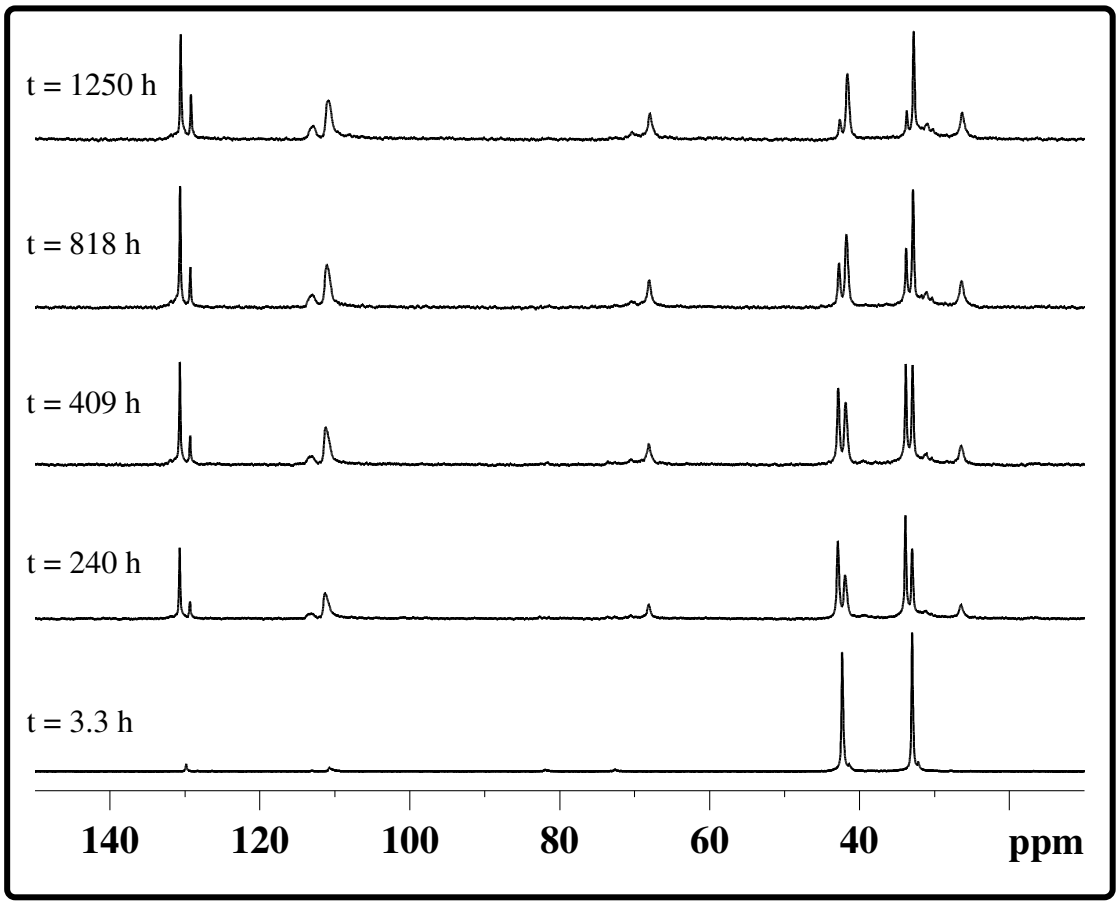
Materials. KF/Al_2O_3 reagents were prepared by impregnation of KF onto alumina from aqueous or alcoholic solutions.[2c] Cases in which the reaction was performed with a wetted solid supports, the appropriate amount of water was added to the powder prior to the reaction. ^{13}C-labeled HD (HD*) was prepared according to the literature procedure (Reiff, L. P.; Taber, D. F.; Yet, L. *Proceeding of the 1996 ERDEC Scientific Conference on Chemical* and *Biological Defense Research*, *19-22 November, 1996*. p. 799). In the course of the synthesis, the ^{13}C label was distributed evenly among carbons.

NMR. ^{13}C MAS NMR spectra were obtained at 125 MHz, on a 11.7 T (500 MHz) spectrometer, equipped with a 0.4 cm standard CP-MAS probe, using direct polarization (i.e., no cross polarization (CP) was used). Typical spinning rates were 5 kHz. Chemical shifts for ^{13}C were referenced to external TMS as 0.0 ppm. A sufficient repetition time of 15 seconds between the scans was applied in all the NMR measurements to ensure a complete relaxation of all the spins in the sample. The quantification of products was carried out by integration of the ^{13}C NMR signals of both the starting material and the products. For comparison purposes, spectra were recorded in identical conditions.

Chromatographic conditions: Separation was achieved by HPLC at 40 ^oC on a 150x2mm, synergy C18 column with 5μm particles. Gradient elution using H_2O with 0.02% MeOH, 0.1mM ammonium formate and 0.02% formic acid as eluent (A) and MeOH with 2mM ammonium formate as eluent (B), was performed at a flow rate of 0.3 ml/min as follows: 97% to 5% eluent A over 10 min, 6 min hold at 5%A and then back to 97% eluent A. The LC time was 16 min and the overall cycle time was 26 min.

MS conditions: Experiments were performed on a triple-quadrupole Quattro Ultima mass spectrometer interfaced to the HPLC system. The ESI source was operated at both negative and positive ion modes. The mass spectrometer was operated in full scan and daughter scan modes (in the range m/z 50 – 900 at a scanning cycle of 1s). Parameters used for ESI included capillary voltage of 3V, source temp of 120 ^oC, desolvation gas (N_2) temperature of 400 ^oC and cone voltage of 20V in ESI(+) or 50V in ESI(-). The source cone gas (N_2) flow rate was 120 L/h and the desolvation gas flow rate was 500 L/h. Syringe pump direct infusion at a flow rate of 10 l/min was used for daughter scan mode experiments. Argon was used as collision gas. The CID energy was in the range of 10–50 eV.

BET Analysis: The surface areas of the various powders were measured by the BET method using surface area analyzer.



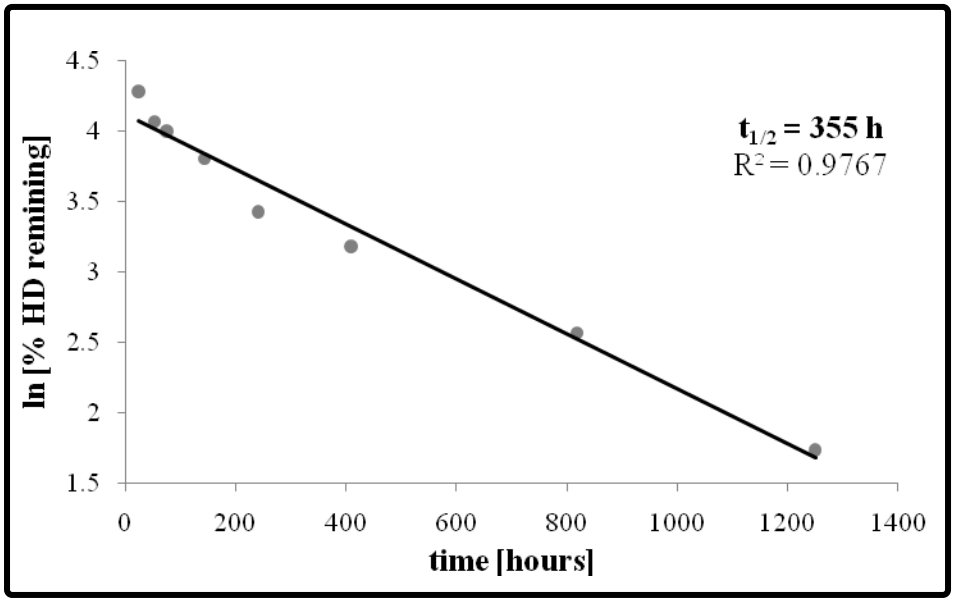
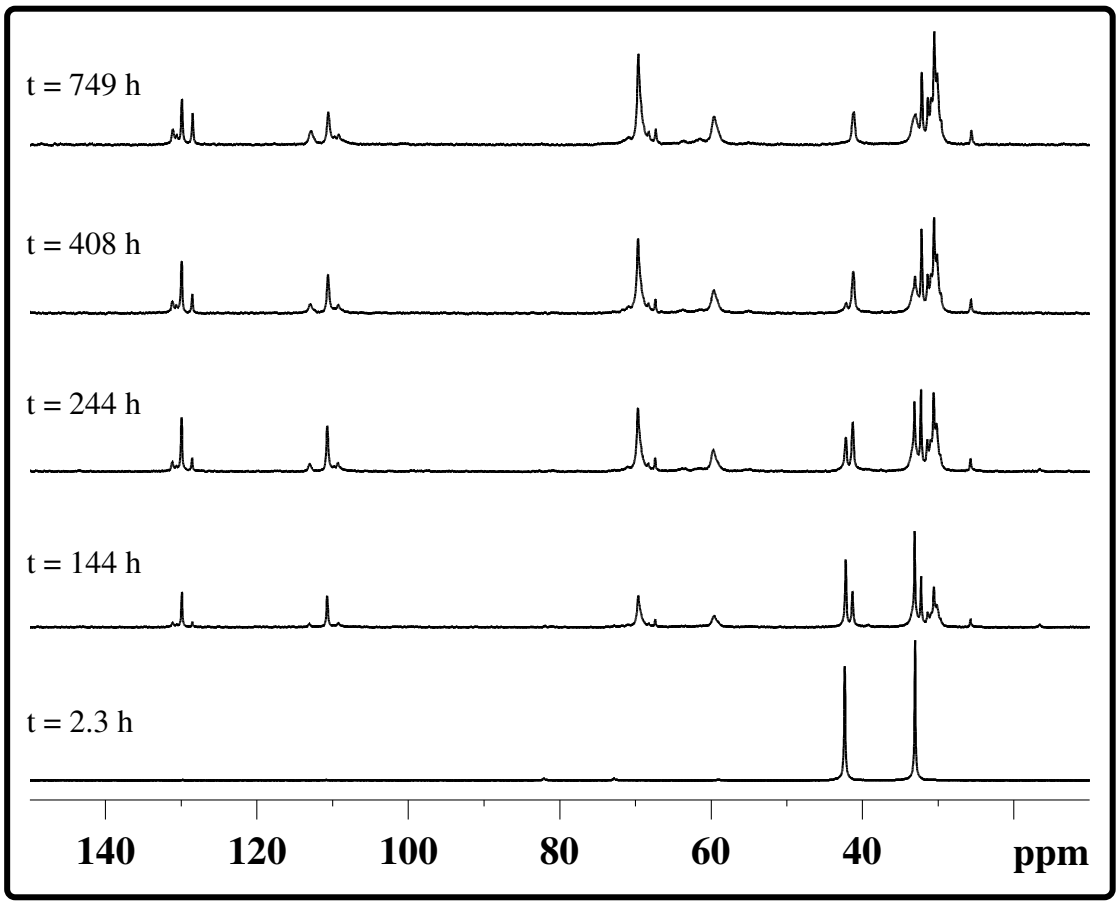


Figure S3. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5% wt) on dry KF/Al_2O_3 (20, H_2O, 160) and its degradation profile onto this sorbent.



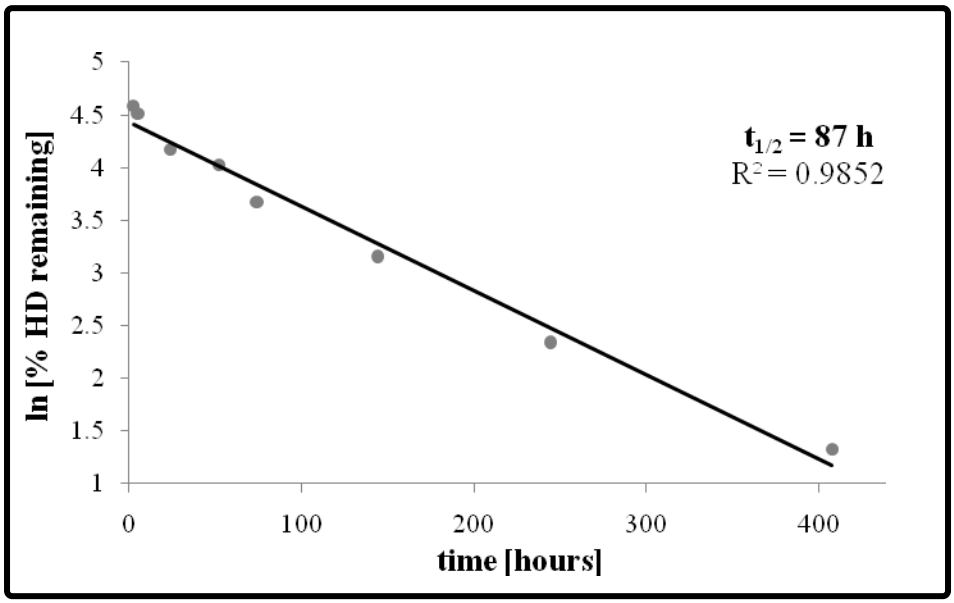
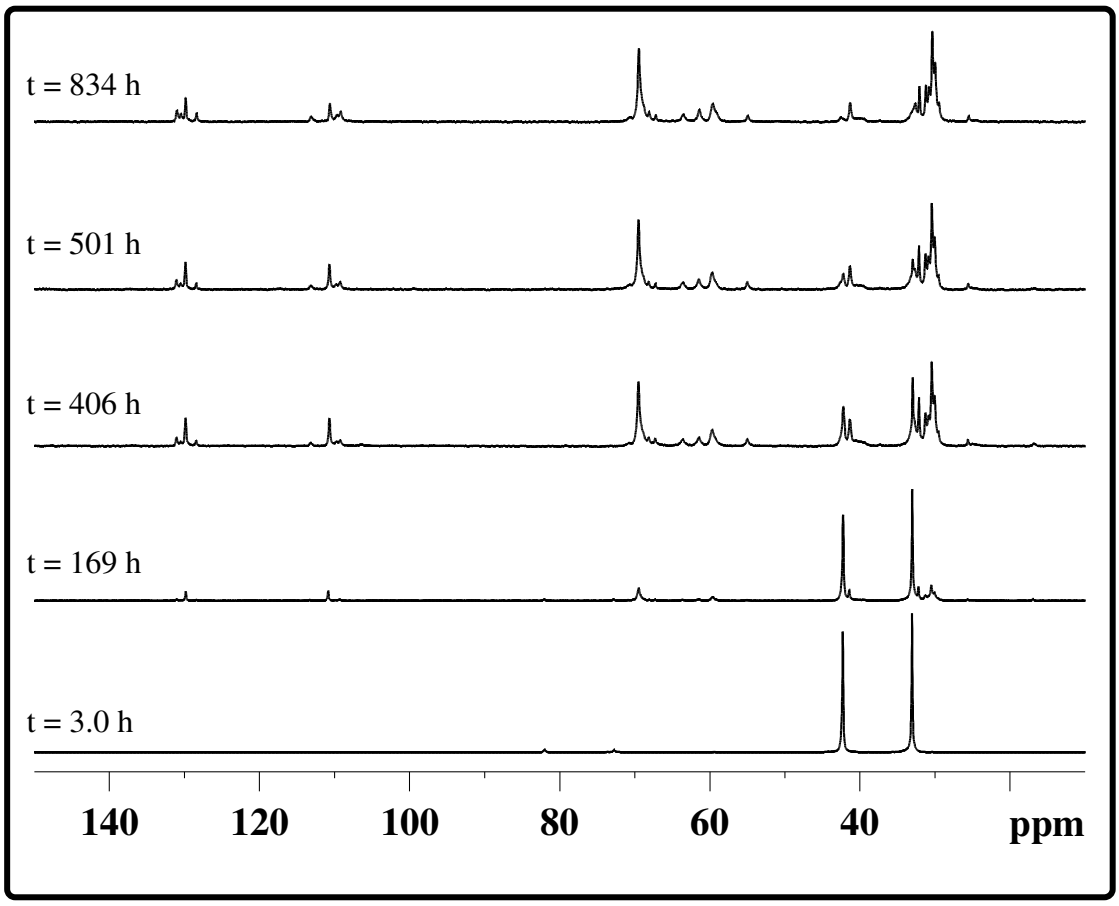


Figure S4. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5% wt) on KF/Al_2O_3 (20, H_2O, 160) using H_2O (5%) as an additive and its degradation profile onto this sorbent.



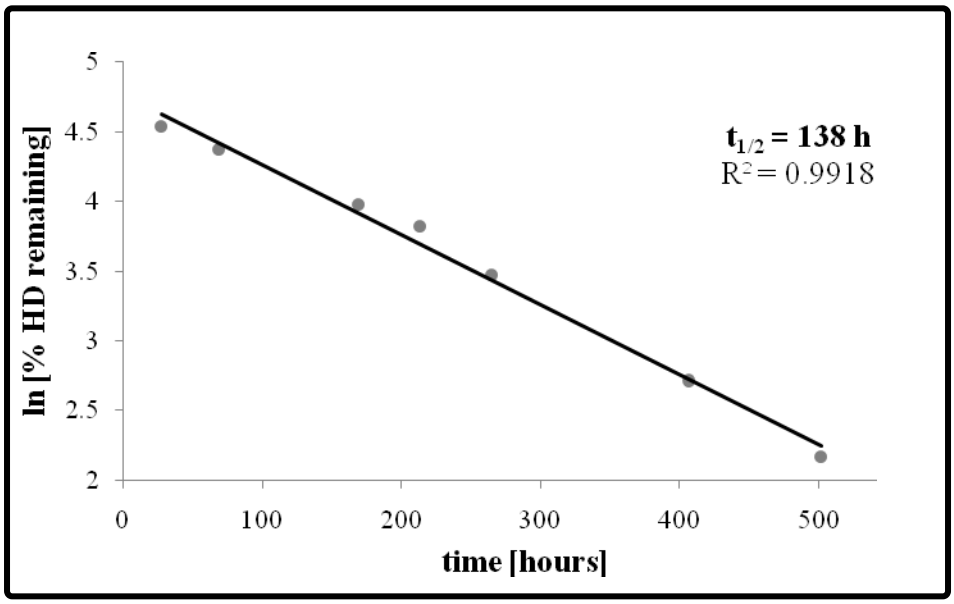
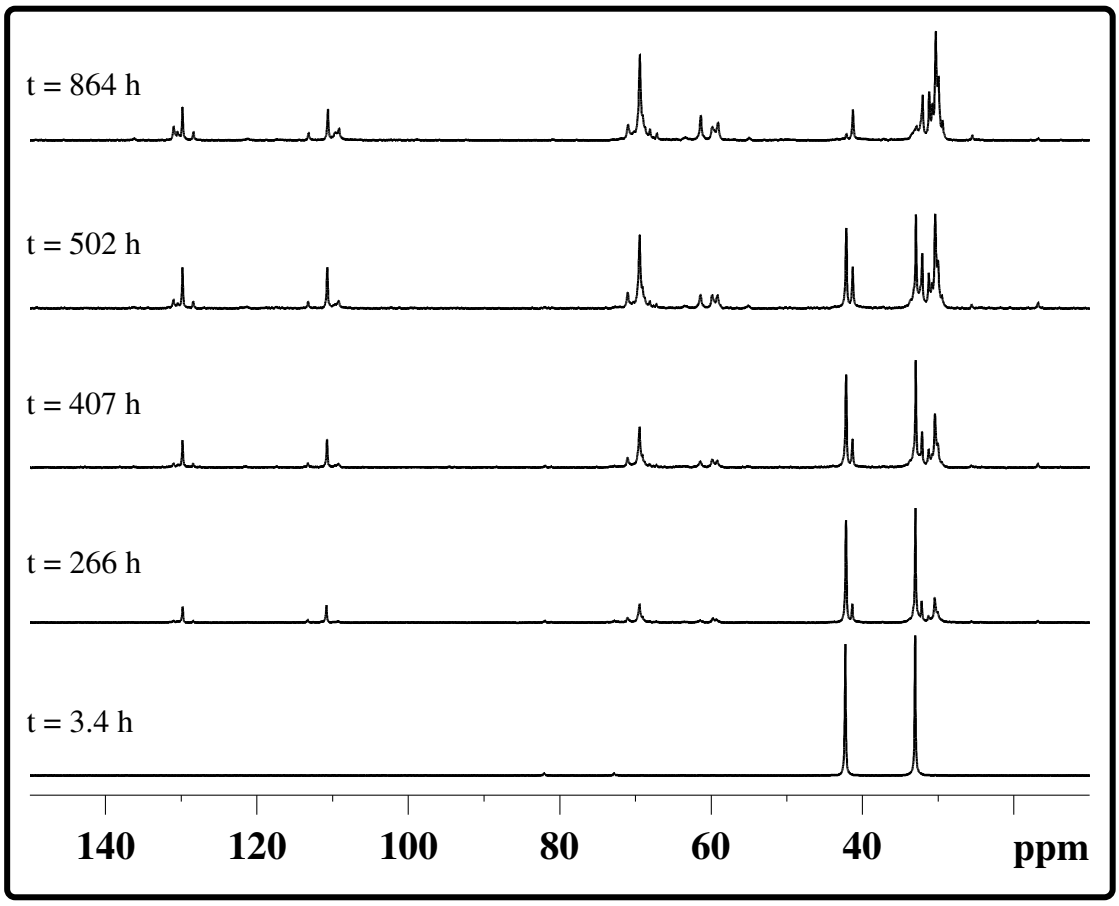


Figure S5. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5% wt) on KF/Al_2O_3 (20, H_2O, 160) using H_2O (10%) as an additive and its degradation profile onto this sorbent.



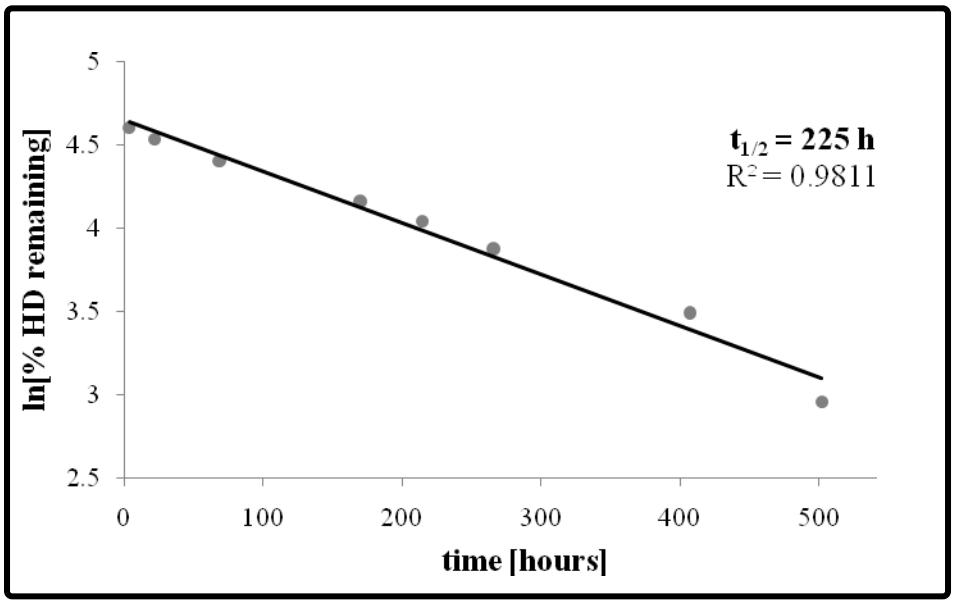
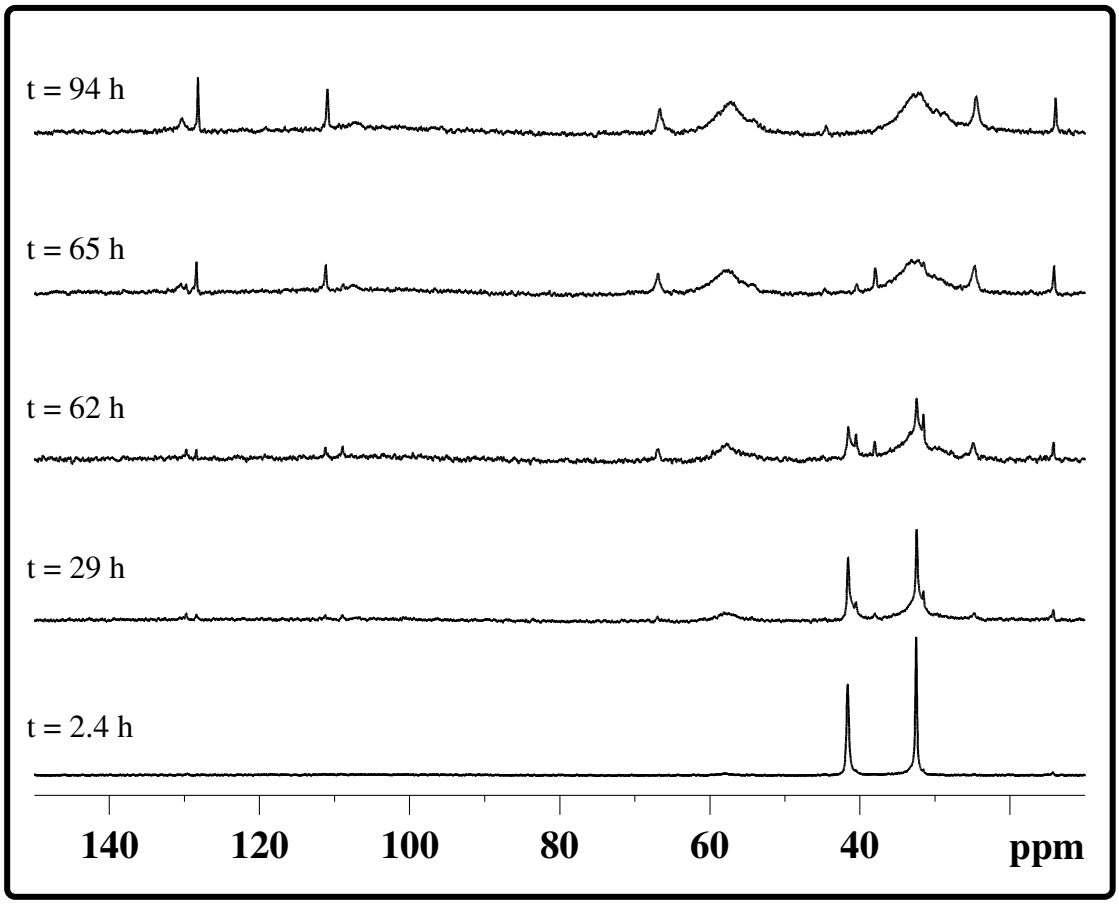


Figure S6. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5% wt) on KF/Al_2O_3 (20, EtOH, 160) using H_2O (10%) as an additive and its degradation profile onto this sorbent.



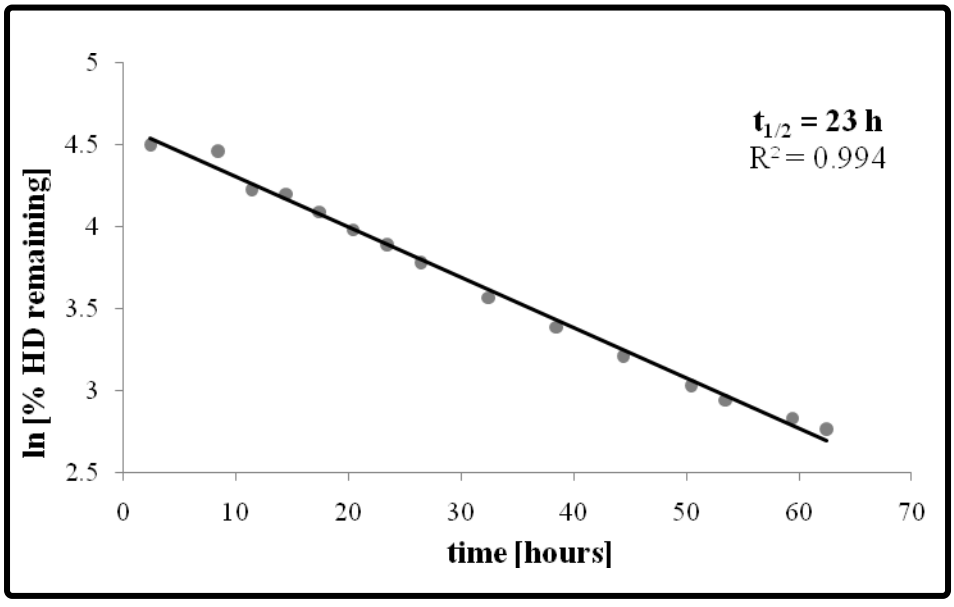
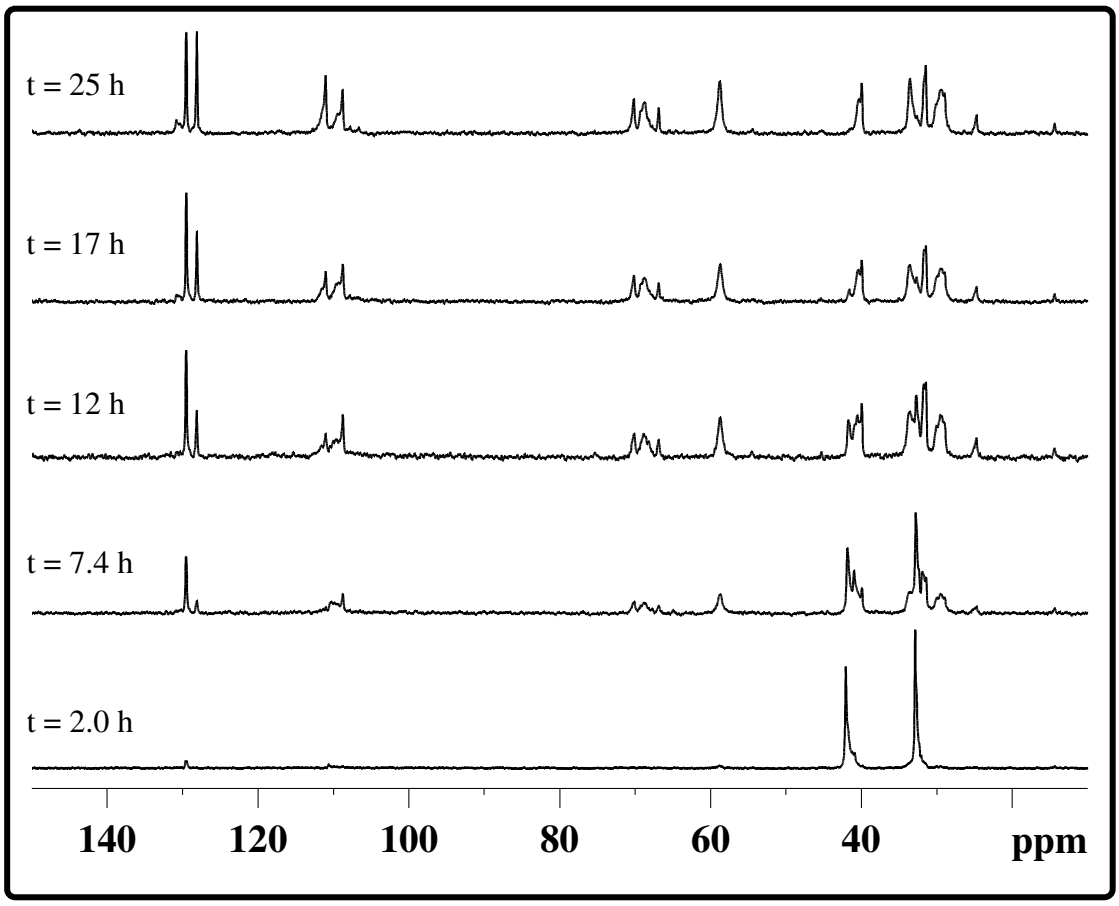


Figure S7. Selected ^{13}C MAS NMR spectra of adsorbed HD* (1% wt) on dry KF/Al_2O_3 (20, EtOH, 160) and its degradation profile onto this sorbent.



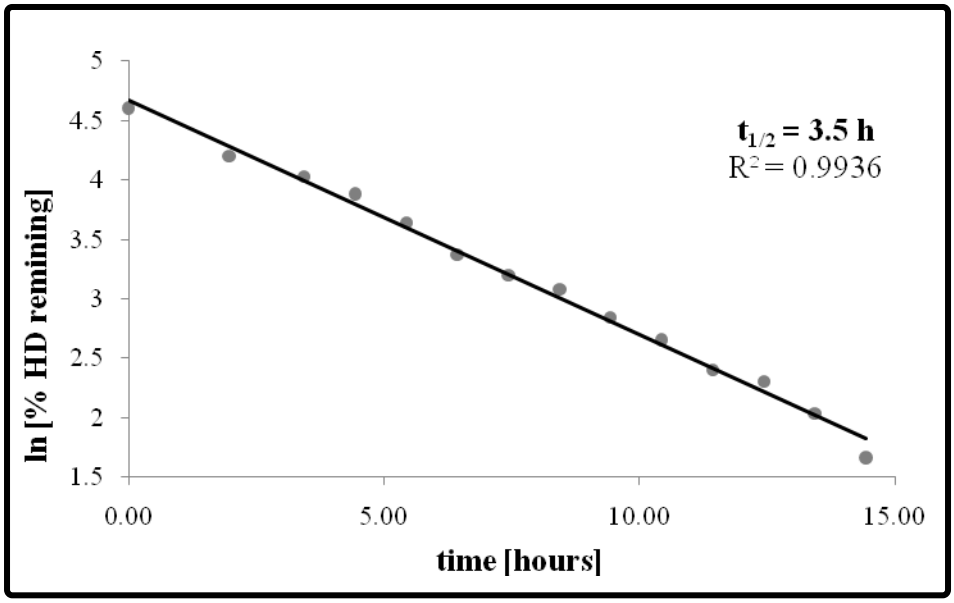
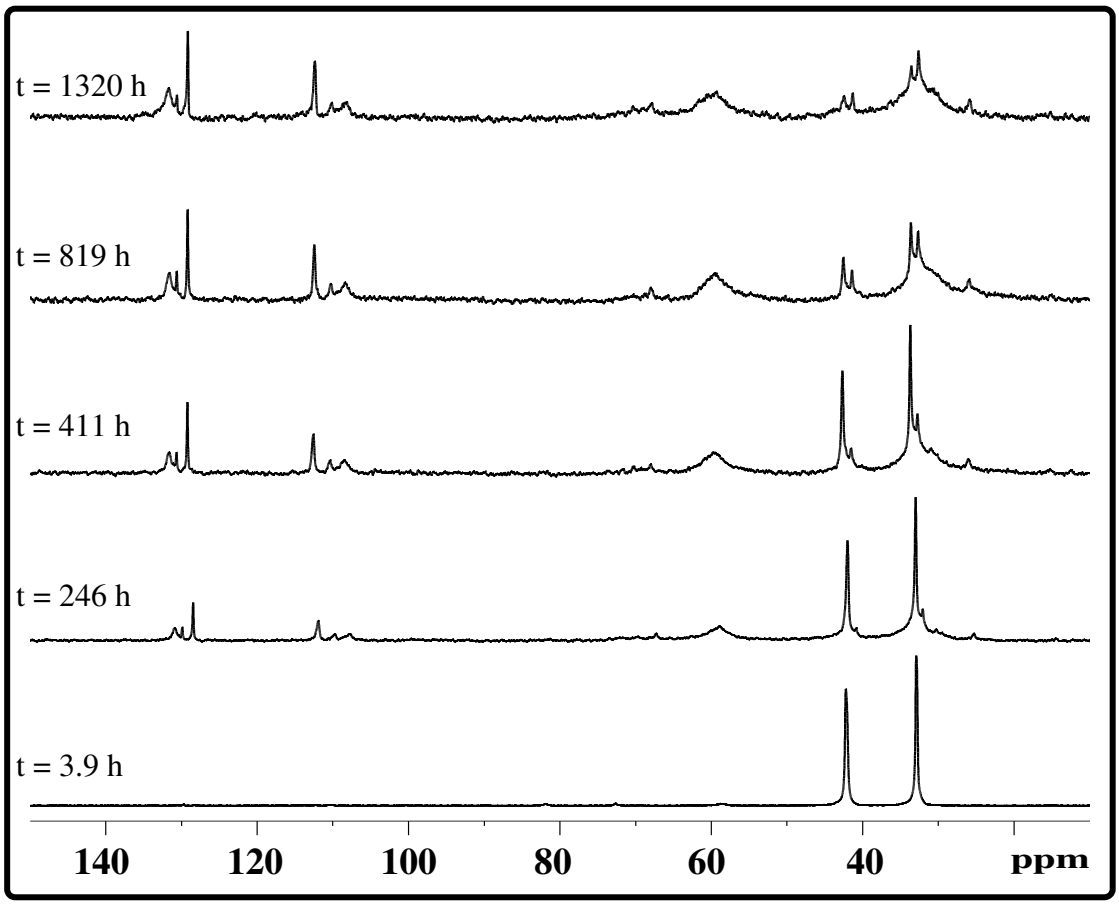


Figure S8. Selected ^{13}C MAS NMR spectra of adsorbed HD* (1% wt) on KF/Al_2O_3 (20, EtOH, 160) using H_2O (5%) as an additive and its degradation profile onto this sorbent.



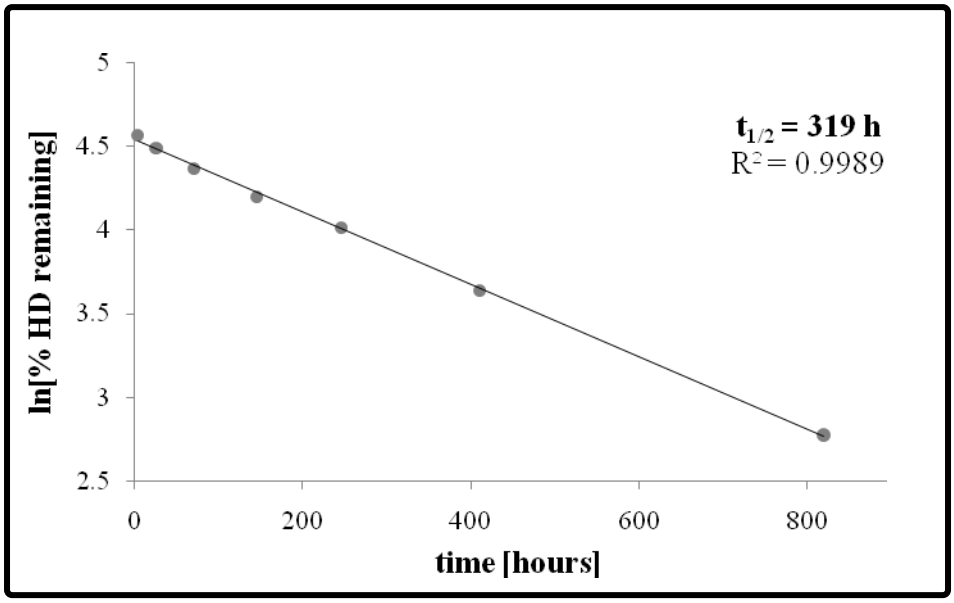
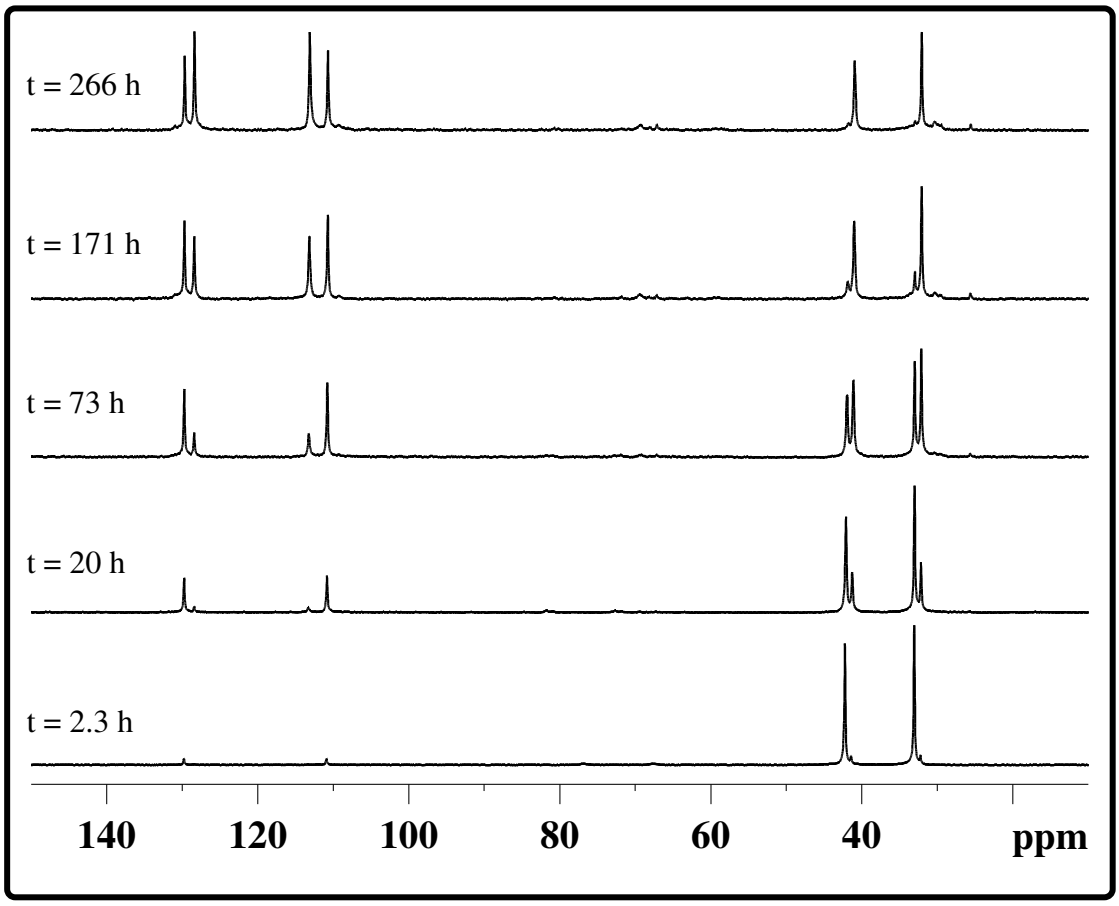


Figure S9. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5 wt%) on dry KF/Al_2O_3 (20, EtOH, 160) and its degradation profile onto this sorbent.



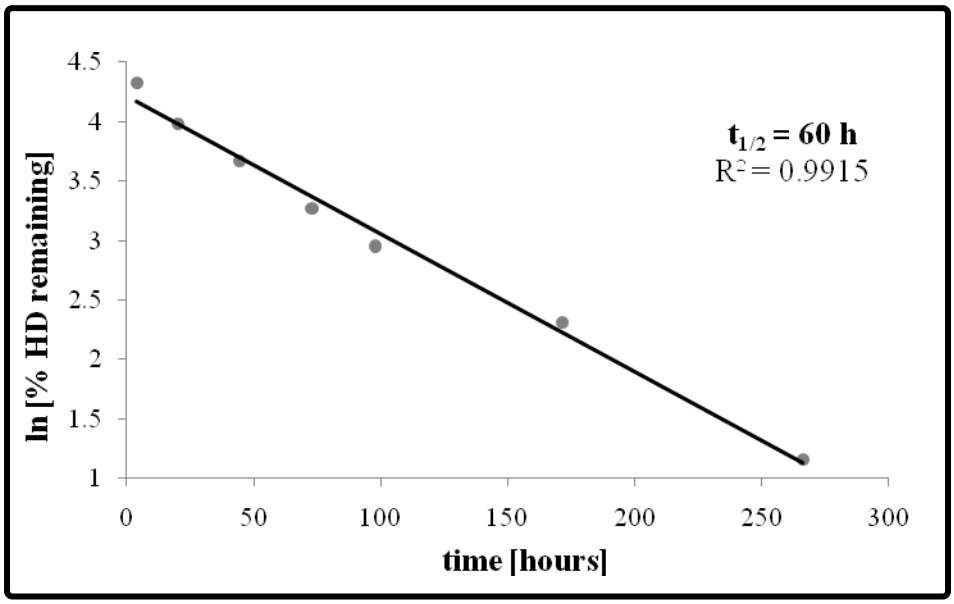
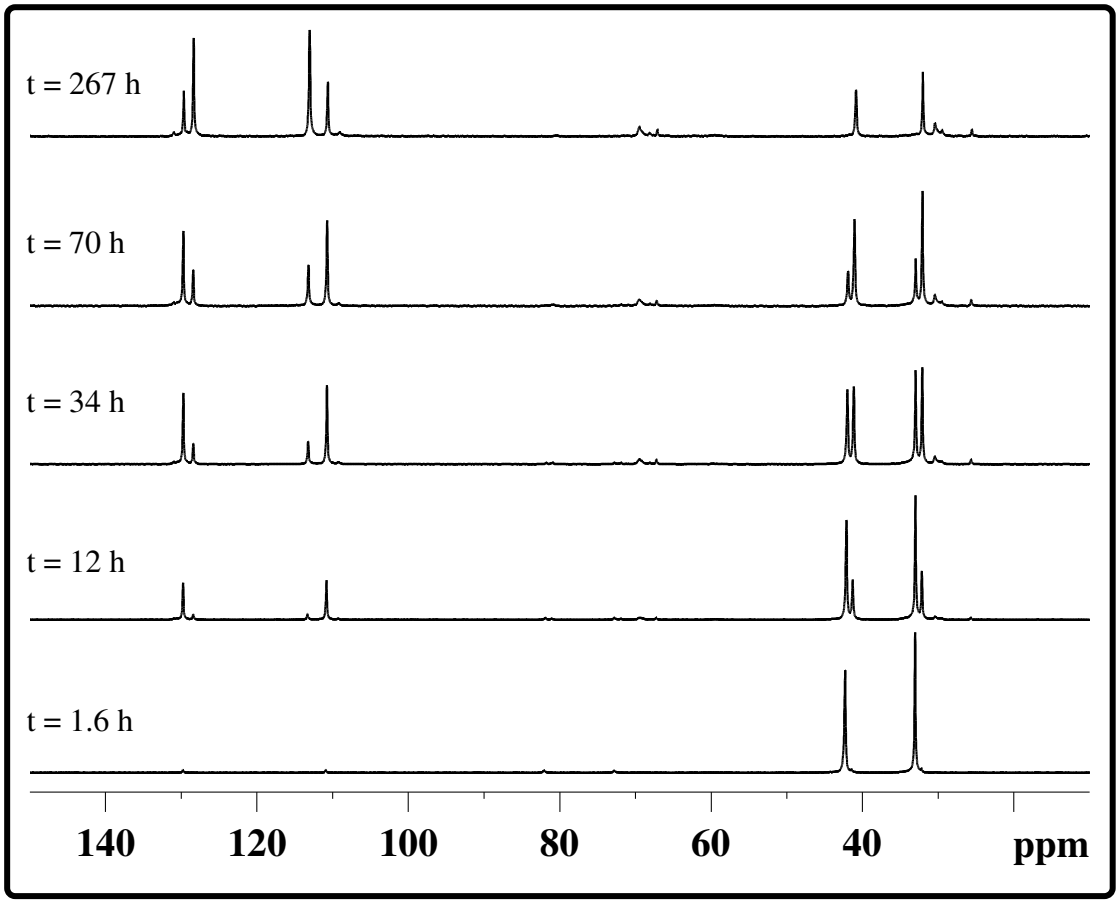


Figure S10. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5% wt) on KF/Al_2O_3 (40, H_2O, 160) using H_2O (5%) as an additive and its degradation profile onto this sorbent.



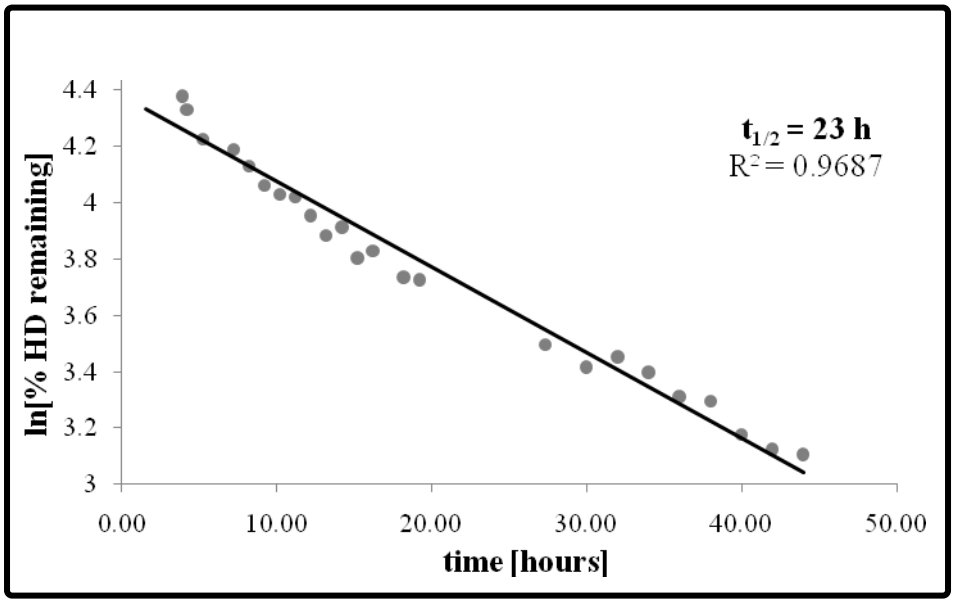
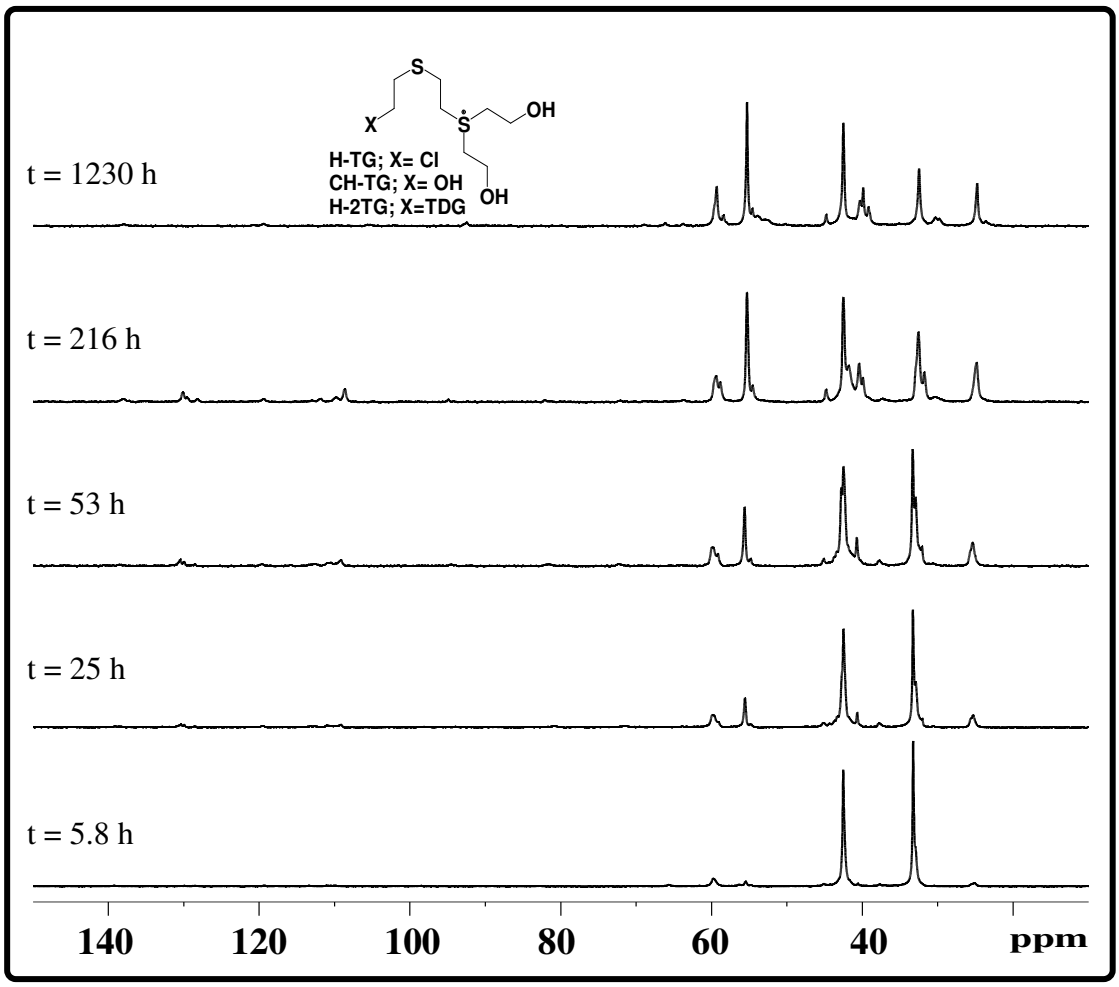


Figure S11. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5% wt) on KF/Al_2O_3 (40, EtOH, 160) using H_2O (5%) as an additive and its degradation profile onto this sorbent.



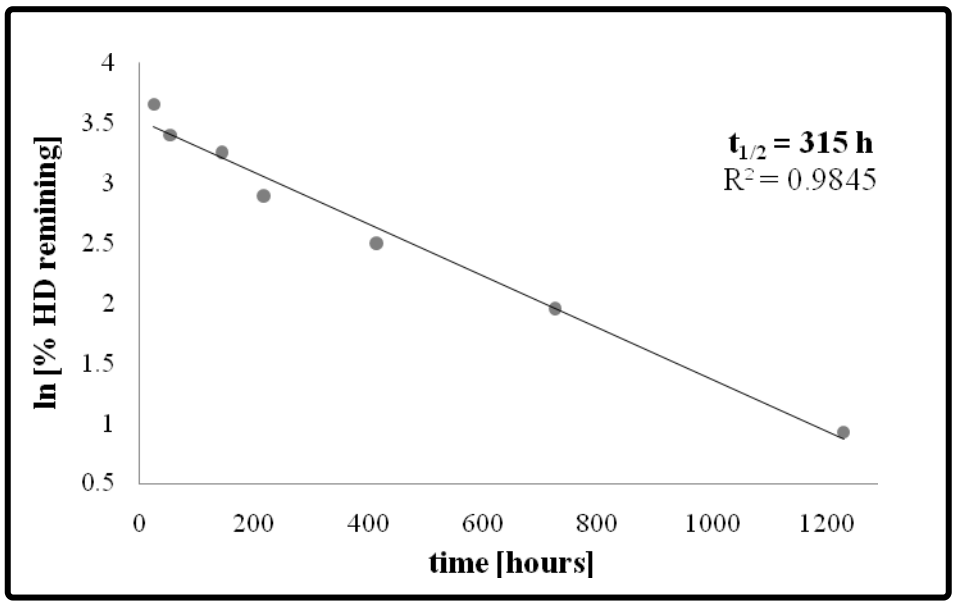


Figure S12. Selected ^{13}C MAS NMR spectra of adsorbed HD* (6.5 wt%) on wetted neutral Al_2O_3 and its degradation profile onto this sorbent.