

Supplementary Information

Mesoporous Organo-Silica Supported Chromium Oxide Catalyst for Oxidative Dehydrogenation of Ethane to Ethylene with CO₂

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N₂-adsorption–desorption isotherms and BJH pore distributions of fresh and used Cr(8)/MOS catalyst are displayed in Fig. S1-A&B. There is no significant difference in the N₂-isotherms shape and pore size distributions, however specific surface area calculated by BET (SBET) method drop from SBET = 673 m²/g for fresh catalysts to SBET = 482 m²/g (Table S1), for the used one after 10h time on stream. On the other hand, the presence of organic component on the wall pore prevents the collapse of the mesoporous structure where is the total pore volumes (V_{total}) slightly dropped from 0.47 cm³.g⁻¹ for the fresh to 0.45 for the used catalyst. Moreover, the pore size for fresh and used catalyst is 3.51 and 3.46, respectively.

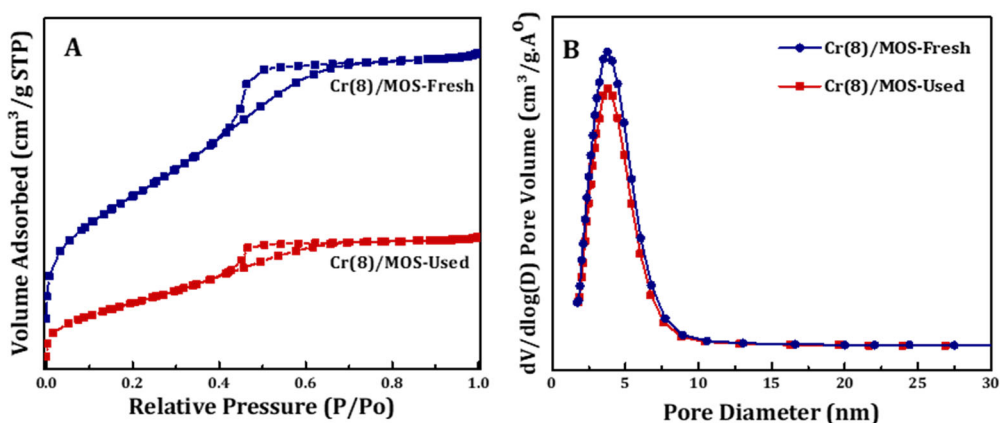


Fig S1.(A) N₂ sorption isotherms and (B) pore size distribution of Cr(8)/MOS catalysts before and after the reaction

Fig. S2.A summarizes the UV–vis DR measurement and the spectrum for fresh and spent Cr(8)/MOS catalysts. The two intensive bands characteristic for Cr⁶⁺ charge transfer of chromates (at 260 nm and 370 nm) is almost disappeared while at the same time the intensity of the Cr³⁺ (at 470 and 600 nm) are increased.

From the above measurement it is clear that the potentially active in oxidative dehydrogenation Cr⁶⁺ species, present in the fresh catalyst and it is reduced to Cr³⁺ species at the dehydrogenation process. Increasing Cr³⁺ indicate to form irreversible and nonredox crystalline Cr₂O₃.

Fourier-transform infrared spectroscopy measurement of fresh and used Cr(8)/MOS catalysts were conducted in the 680–4000 cm⁻¹ range and spectra are illustrated in Fig. S2A&B. It can be seen that there is no noticeable difference for the two samples, as similar FTIR bands are detected.

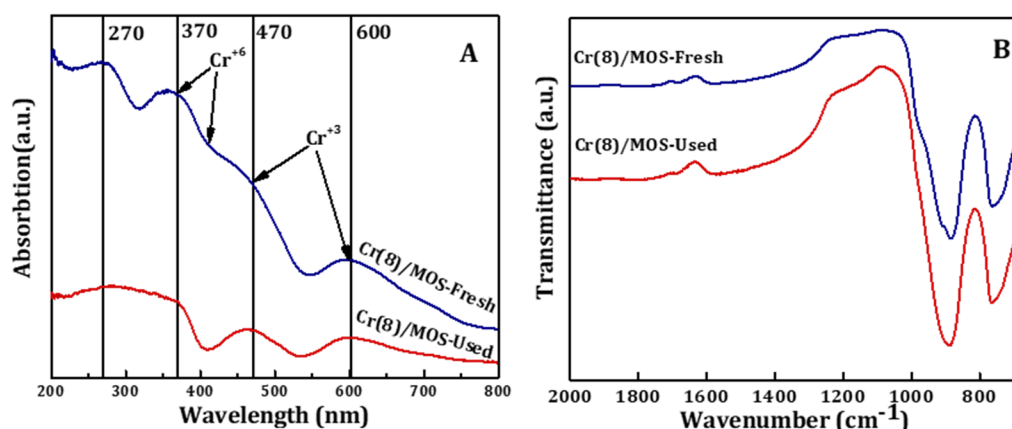


Fig S2 (A) UV-Vis-DR and (B) FTIR patterns of Cr(8)/MOS catalysts before and after the reaction.

TEM images of the fresh and used Cr(8)/MOS samples are presented on Fig S3-A&B. For the fresh sample the Cr species are good dispersed onto support matrix and the cubic Cr oxide nanoparticles with to 50-100 nm sizes were formed.

On the other hand, the Cr oxide nanoparticles size were increased and it were agglomerated to cause the formation cubic nanoparticles with bigger size range and poor distribution character onto mesoporous organo-silica matrix

This conclusion is in agreement with our and other researchers' observations according to which the deactivation of Cr(8)/MOS material is due to the reduction of active sites and it considered as the major cause of catalyst deactivation for the dehydrogenation of alkane with CO_2

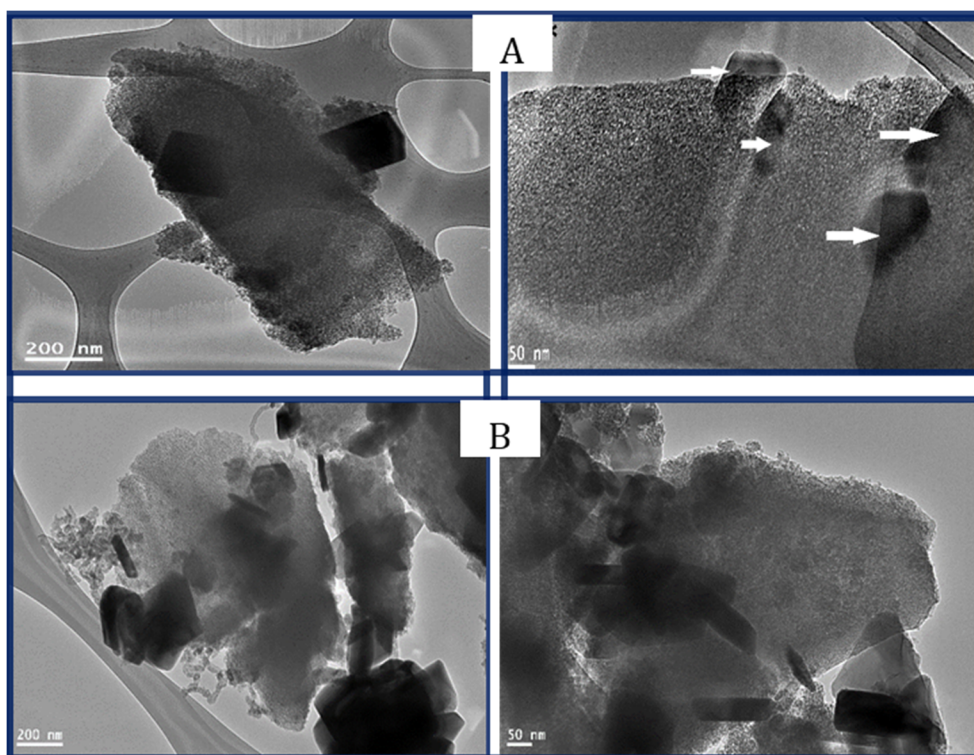


Fig S3 TEM images of Cr(8)/MOS catalysts(A) before and (B) after the after the reaction.

Table S1: Textural properties of fresh and used Cr(8)/MOS catalysts.

Sample	Cr Content Wt. %	BET (m ² /g)	Pore volume (cm ³ /g)	Pore Size (nm)	Cr content by EDX Wt%	Cr surface density (CrO _x /nm ²) ^a
Cr(8)/MOS-Fresh	8	673	0.47	3.51	7.77	1.38
Cr(8)/MOS-used	8	482	0.45	3.46	7.32	1.92