Supporting Information

Exploring the Support Modification Effects over the $CrO_x/VO_x/SiO_2$ Bimetallic Catalyst for Bimodal UHMWPE/HDPE In-reactor Blends: A View from Experimental and Theoretical Approaches

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Details for catalyst preparation

For a typical process to prepare CrO_x/VO_x/silica, about 5 g silica was weighted and impregnated with aqueous solution of $(CH_3CO_2)_7Cr_3(OH)_2$ and NH_4VO_3 in a flask. The mixture was stirred at 80°C for 4 h and subsequently dried at 120°C for 6 h to get easily flowable particles, which was transferred to a quartz fluid bed (diameter = 2 cm) and fluidized by dry air. Then, the fluid bed was put into a furnace for calcination, in which the temperature was raise to 500°C at a rate of 2°C/min and kept for 4 h. Afterward, the calcination system was cooled down to room temperature, and the obtained catalyst powder with a color of yellow was collected and reserved in a glove box filled with N_2. For sulfate modified catalyst, the same preparation process as for CrO_x/VO_x/silica was employed, except that a certain amount of $(NH_4)_2SO_4$ was added together with $(CH_3CO_2)_7Cr_3(OH)_2$ and NH_4VO_3. The alumina/silica was prepared by impregnating silica with aqueous solution of $Al(NO_3)_3 \cdot 9H_2O$, which was dried and calcinated in the fluid bed subsequently. The calcination was also carried out at 500°C for 4 h under dry air. The obtained alumina/silica was used for the preparation of alumina and alumina/sulfate modified catalysts with the similar process as for CrO_x/VO_x/silica and sulfate modified CrO_x/VO_x/silica, respectively.

Details for SEM characterization

The morphology of the catalysts was characterized by a scanning electron microscope (SEM) of Tescan (Mira Lms). The samples were previously sprayed by gold with a sputter coater apparatus of Oxford Quorum (SC7620).

Details for NH_3-TPD

For each NH_3-TPD test, about 50 mg sample was weighted and dried at 300°C under He flow (50 mL/min) for 1 hour. After cooling to 50°C, 10% NH_3/He (50 mL/min) was introduced for 1 hour to saturation. Then, it was switched to He flow for 1 hour to remove the physically and weakly adsorbed NH_3. Finally, desorption was performed under the He atmosphere from 50 to 600°C at a heating rate of 10°C min^{-1}.

Details for pyridine-FTIR

For each pyridine-FTIR test, about 20 mg catalyst powder was weighed and finely ground with an agate mortar, which was then pressed into an intact self-supporting wafer. The wafer was transferred and sealed into a quartz cell, which was heated to 400°C for 2 h under vacuum. When the cell was cooled down to room temperature, the background signal was recorded at a resolution of 4 cm^{-1} and the sample was exposed to pyridine vapor for 1 h. Then the pyridine was desorbed at 350°C for 30 min under vacuum, and the signal was recorded at the same resolution. The acid amount was determined by the band area.

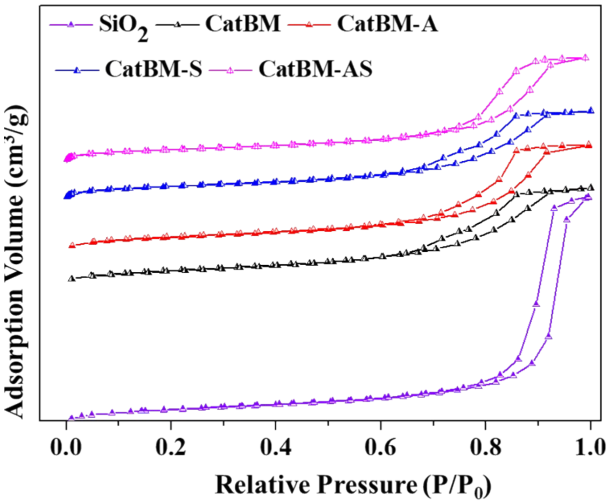


Figure S1. N_2 adsorption-desorption isotherms of silica support and catalysts.

Figure S1 shows that silica support and all the catalysts belong to typical mesoporous materials with type IV isotherms and type H1 hysteresis loop.[1] The area of the loop for the catalysts is smaller than that for silica, which is consistent with the decreased pore volume of the catalysts. Comparing the curves of the catalysts before and after support modification, their hysteresis loops exhibit similar shape and area, indicating their similar pore structure and pore volume. The analogous starting point of the hysteresis loop for the four catalysts implies their average pore size is also almost the same.

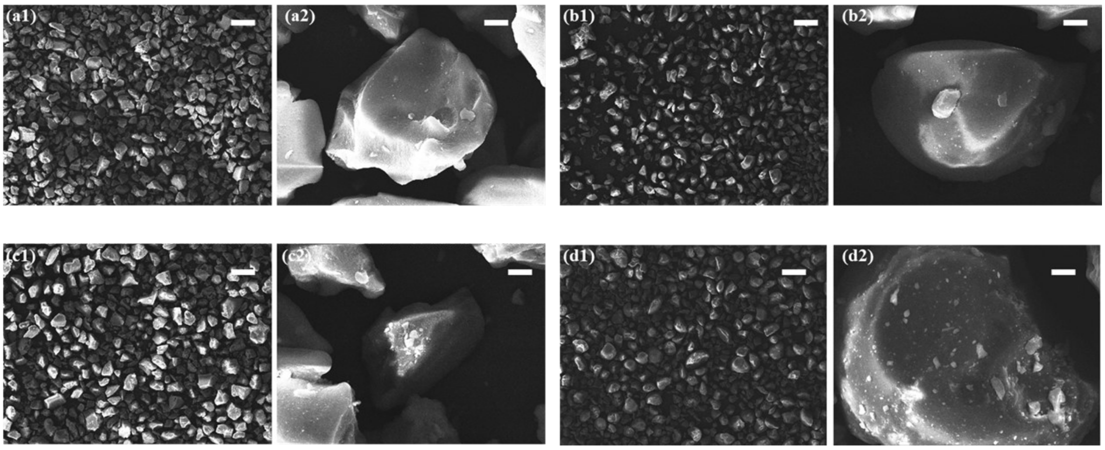


Figure S2. The SEM images of CatBM ((a1) and (a2)), CatBM-A ((b1) and (b2)), CatBM-S ((c1) and (c2)) and CatBM-AS ((d1) and (d2)). The scale bars for (a1)-(d1) and (a2)-(d2) are 100 and 5 μm, respectively.

The SEM images in **Figure S2** show the size and surface morphology for all the catalyst granules are analogous. In addition, though the median particle size (d_{50}) of the catalysts is halved in comparison to the silica support due to mechanical fracture during the catalyst preparation, the size looks uniform for all the catalysts. Together with the similar pore size and pore volume, the diffusion resistance of ethylene monomer in all the catalysts is comparable. It ensures a fair comparison of the activity for ethylene polymerization.

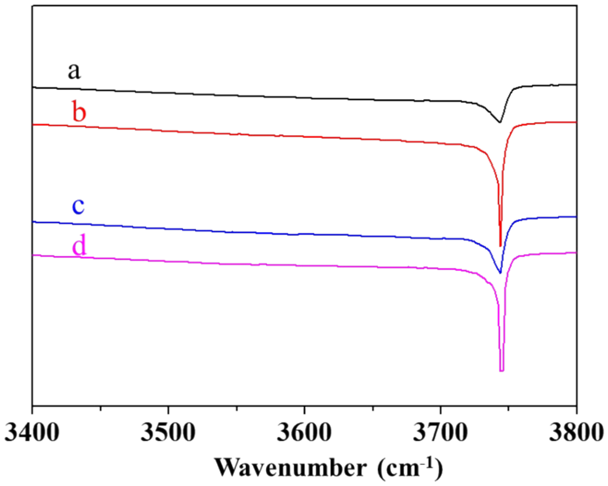


Figure S3. The FTIR spectra of a. CatBM, b. CatBM-A, c. CatBM-S and d. CatBM-AS.

As all the catalysts were calcinated at high temperature (500^{o}C) under the atmosphere of dry air, which should remove the H_2O preserved in catalysts mostly. In addition, the introduction of moisture to the catalysts was also avoided by Schlenk technique or N_2 filled glove box. Therefore, the origin of the strong Bronsted sites on catalyst comes from the surface silanol, which has a band around 3750 cm^{-1}. The intensity of this band for the four catalysts is also in accordance with the one for Bronsted sites around 1540 cm^{-1} in the FTIR-pyridine spectra, namely CatBM-AS ＞CatBM-A ＞CatBM-S ＞ CatBM (see **Figure 3**).

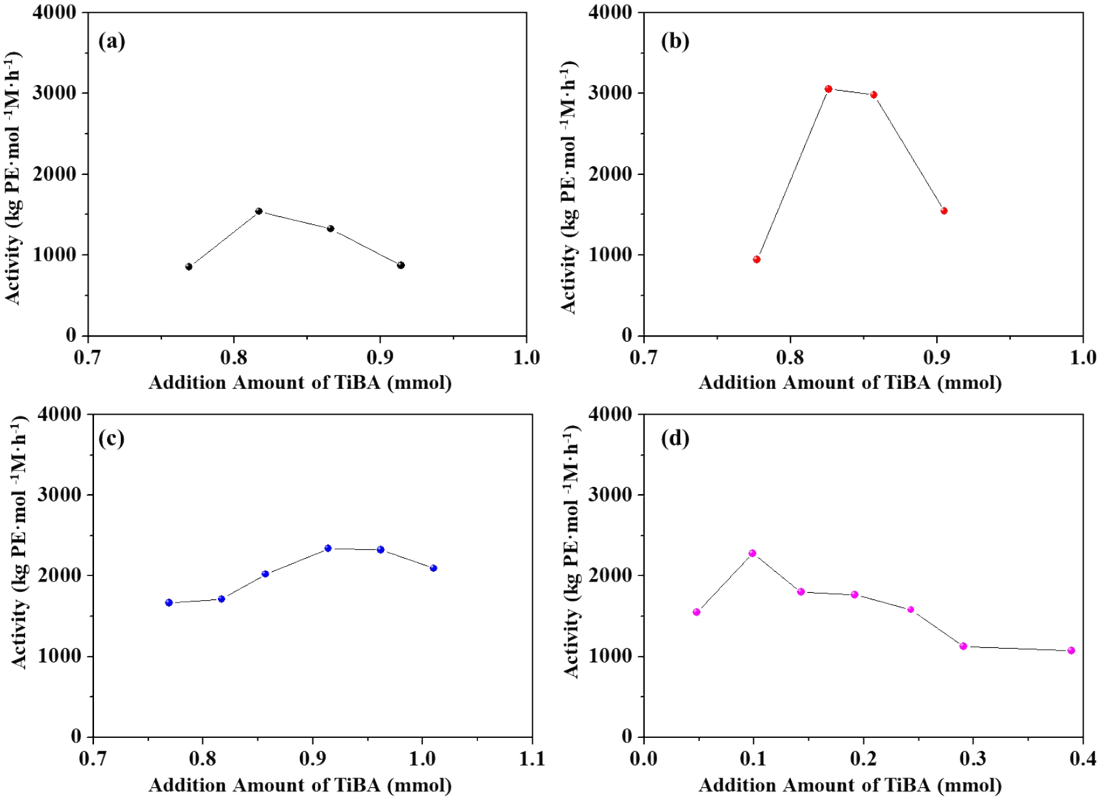
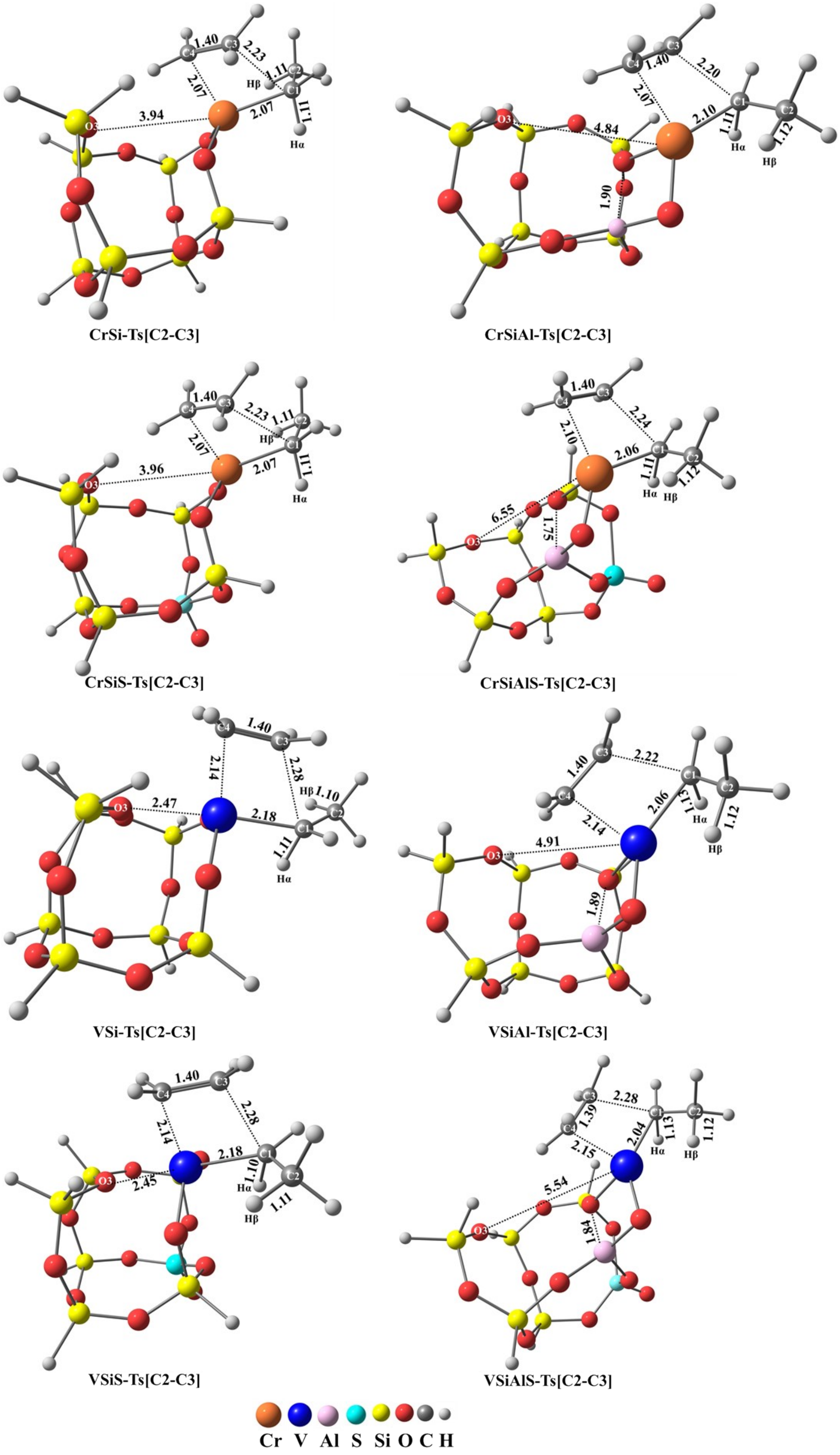


Figure S4. The effect of the amount of TiBA cocatalyst on the activity of (a). CatBM, (b). CatBM-A, (c). CatBM-S and (d). CatBM-AS. (150 mL n-hexane, 100 mg catalyst, 1MPa ethylene, 75^{o}C, 1h).

As shown in **Figure S4**, for CatBM, CatBM-A and CatBM-S, 0.8-1.0 mmol TiBA (i.e. the molar ratio of Al/Cr = 80-100) is needed to achieve the highest activity, while for CatBM-AS, the optimum amount of TiBA is only about 0.1 mmol (i.e. the molar ratio of Al/Cr = 10). With the optimum amount of TiBA for each catalyst, the effect of reaction temperature was investigated further (see **Figure 6(A)**). It is well known very small amount of alkyl-aluminum cocatalyst can fully activate the Phillips catalyst CrOx/silica in commercial production to get high activity. Herein, adventitious moisture in the reaction system, which is poisonous to the catalysts and difficult to be totally removed in the lab, should be scavenged by additional alkyl-aluminum. Hence, larger amount of alkyl-aluminum is needed. For CatBM-AS, the optimum amount of TiBA to get high activity is reduced obviously, as the sulfated alumina with superacidity is formed on catalyst surface, which is reported to be a substitute for alkyl-aluminum as scavengers. [2]


CrSi-Ts[C2-C3] CrSiAl-Ts[C2-C3]

CrSiS-Ts[C2-C3] CrSiAlS-Ts[C2-C3]

VSi-Ts[C2-C3] VSiAl-Ts[C2-C3]

VSiS-Ts[C2-C3] VSiAlS-Ts[C2-C3]

Figure S5. The structures of Ts for ethylene insertion. Several key interatomic distances are given in Å.

As shown in **Figure S5**, the key structure of the Ts for ethylene insertion is a four-membered ring consisting of M, C1, C3 and C4. To form such a structure, the ethylene monomer has to get close to Cr or V center. As a result, for MSi-C1 and MSiS-C1 with large %V_{bur}, the O3 atom complexed strongly with the metal center needs to be repulsed away to leave the space for Ts formation, which could partially account for the much higher energy level of their Ts.

The difference in the four-membered ring of the Ts is large for V-based catalysts, which is clearly reflected by the much less elongated V-C1 bond for VSiAl-Ts[C2-C3] (2.06 Å) and VSiAlS-Ts[C2-C3] (2.04 Å) when compared with VSi-Ts[C2-C3] (2.18 Å) and VSiS-Ts[C2-C3] (2.18 Å). It indicates the more facile electronic interactions between ethylene and the V center of the alumina and alumina/sulfate modified catalysts, which is also consistent with the much lower LUMO (α) energy of VSiAl-[C1] and VSiAlS-[C1] in comparison to VSi-[C1] and VSiS-[C1]. While for Cr-based catalysts, the difference in the four-membered ring of the Ts is small, as the LUMO (α) energy of CrSiAl-C1 and CrSiAlS-C1 only gets decreased moderately when compared with that for CrSi-C1 and CrSiS-C1(see **Figure 10**).

Moreover, the longer C1-Hα and C2-Hβ bonds for MSiAl-Ts[C2-C3] and MSiAlS-Ts[C2-C3] implies that their decreased %V_{bur} and LUMO (α) energy facilitate the formation of M-Hα and M-Hβ agostic interactions, which play a vital role to stabilize the Ts.[3]

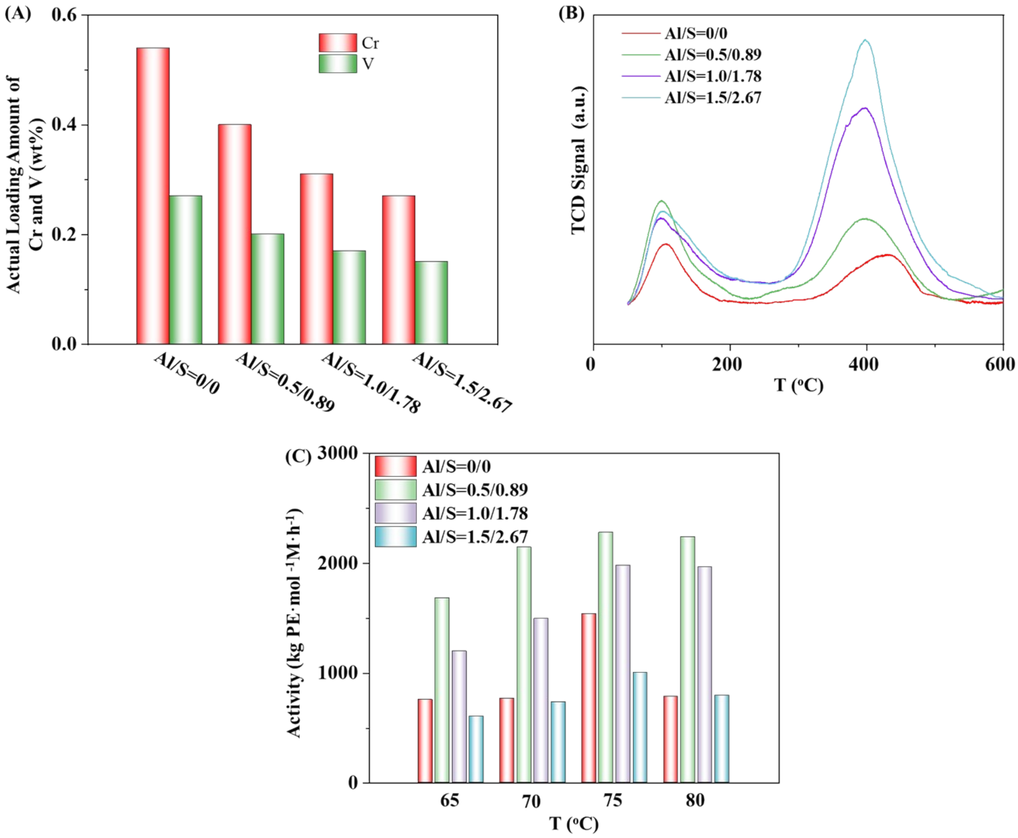


Figure S6. (A) The actual loading amount of Cr and V at CrO_x/VO_x/silica modified by increasing amount of alumina/sulfate. (B) The NH_3-TPD curves of the catalysts. (C) ethylene polymerization activity of the catalyst. For all the catalysts, the theoretical loading amount of Cr and V was kept at 0.5 wt% and 0.24 wt%, respectively. Polymerization conditions: 150 mL n-hexane, 100 mg catalyst, the optimum amount of TiBA (ca. 0.1 mmol) for each catalyst was added as cocatalyst, 1MPa ethylene, 1h.

To investigate the effect of the amount of strong acidity on the actual loading amount of Cr and V, we prepared four catalysts with the loading amount of Al/S = 0/0, 0.5/0.89, 1.0/1.78 and 1.5/2.67 wt%. It is clear that the actual loading amount of Cr and V decreased with increasing amount of Al/S modifier (see **Figure S6(A)**). As sulfated alumina is a kind of solid superacid, the amount of strong acidity would increase with the loading amount of Al/S (see **Figure S6(B)**). It indicates that too strong acidity would retard the anchoring and stabilization of Cr and V. As a matter of fact, when the added amount of Al/S got as high as 1.5/2.67 wt%, a color of greenish yellow was observed for the catalyst, which indicates high relative content of Cr^{3+}. C_2H_4 polymerization was conducted with these catalysts as well. As shown in **Figure S6(C)**, activity decreases gradually with increasing amount of Al/S modifier, and for the catalyst with Al/S = 1.5/2.67 wt%, the activity is even lower than the unmodified one.

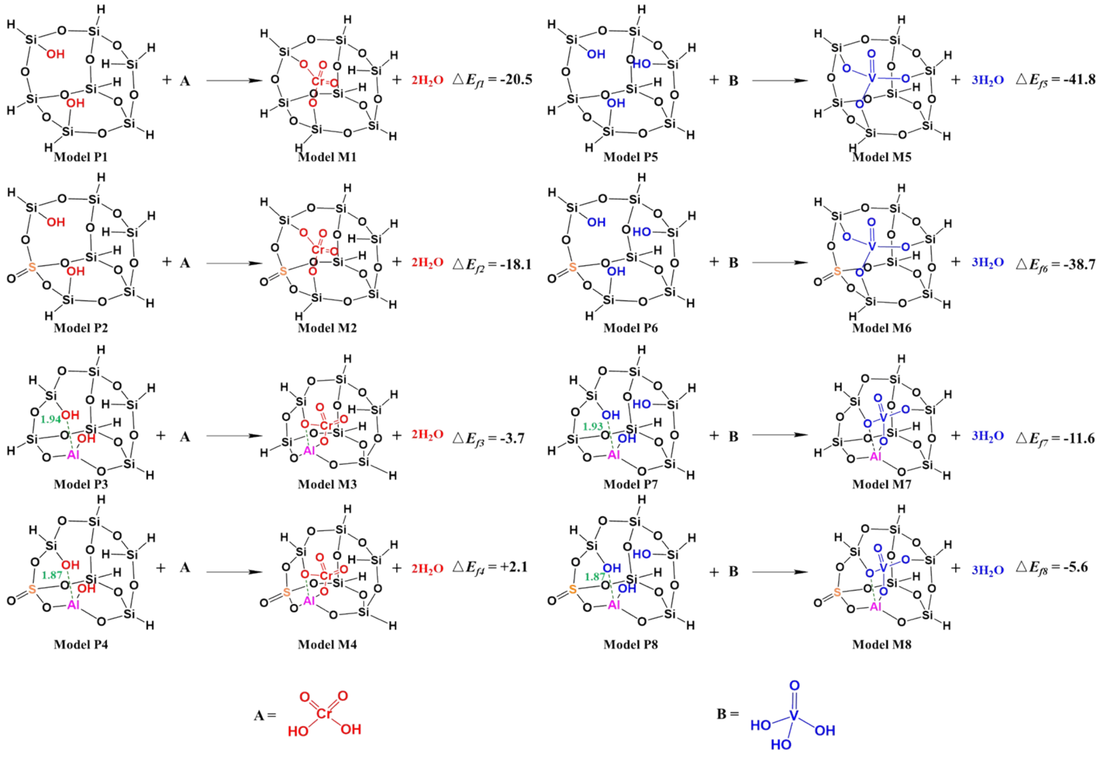


Figure S7. The formation energy of Cr(VI) and V(V) on various models. The formation energy $\triangle E_{fn}$ in kcal/mol was calculated by subtracting the total free energies of the products (H_2O and Model Mn) with those of the reactants (A or B and Model Pn), n = 1-8. The same theoretical level as for chain propagation was used. The free energies were thermally corrected at 1 atm and 773 K at which the catalysts were calcinated. The distance of Al···OH interaction in Å is given.

To evaluate the anchoring process of Cr and V centers with silica support before and after modification, the formation of Cr(VI) and V(V) oxide precursors was studied by the condensation reaction between chromic-/vanadic-acid and the hydroxyls of POSS, and the formation energy (E_f) was calculated (see **Figure S7**). It is evident that the E_f of the sulfate modified and unmodified models are low and comparable, which is ~-20 and -40 kcal/mol for Cr(VI) and V(V), respectively. This is consistent with the nearly full loading of Cr and V for CatBM and CatBM-S. As to the alumina modified POSS, the Lewis acidic Al^{3+} is prone to constrain the nearby hydroxyl tightly, which is the prelude for generating the highly active four-membered ring with great strain. Notably, the E_f of the alumina modified Cr and V models becomes ~15 and ~30 kcal/mol higher than the unmodified ones. Because the hydroxyl acting as an anchoring point is characterized by greater Bronsted acidity and larger steric hindrance owing to the strong Al···OH interaction. Pertaining to the alumina/sulfate modified models, because of the electron withdrawal effect of the sulfate ligand, the coordination of Al^{3+} to the nearby hydroxyl becomes stronger, which is reflected by the decreased atomic distance of Al···OH. It improves the Bronsted acidity and steric hindrance of the hydroxyl further, which makes the E_f even more than 5 kcal/mol higher than the alumina modified models. The difficult formation of Cr(VI) and V(V) precursors on the alumina/sulfate modified models is in accordance with the lower actual loading amount of Cr and V and the relatively lower content of Cr^{6+} and V^{5+} sites for CatBM-AS.

References

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