Supporting Information: Table of Contents

General Procedures. All experiments were carried out under controlled atmosphere. The syntheses and the treatments of the surface species carried out using high vacuum lines (< 10^{-5} mbar) and glove-box techniques. Pentane was collected from a Solvant Purification System following by a freez-pump. Elemental analyses were performed at the Mikroanalytisches Labor Pascher. $LiNMe_2$ and $ZrCl_4$ were purchased from Sigma Aldrich. $Zr(NMe_2)_4$ was prepared by allowing $ZrCl_4$ to react with $LiNMe_2$ according to the literature procedures. [1]

Fourier Transformed Infrared Spectroscopy. FTIR spectra were recorded on a Nicolet 6700 FT-IR spectrometer equipped with a cell under controlled atmosphere. Typically, 16 scans were accumulated for each spectrum (resolution 4 cm^{-1}).

Solid State Nuclear Magnetic Resonance Spectroscopy:

One dimensional 1H MAS and 13C CP-MAS solid state NMR spectra were recorded on a Bruker AVANCE III spectrometer operating at 400 and 100 MHz resonance frequencies for ^1H, and ^{13}C respectively, with a conventional double resonance 4mm CPMAS probe. The samples were introduced under argon into zirconia rotors, which were then tightly closed. The spinning frequency was set to 17, and 10 KHz for ^1H and ^{13}C spectra, respectively. NMR chemical shifts are reported with respect to TMS as an external reference. For CP/MAS ^{13}CNMR, the following sequence was used: 90^o pulse on the proton (pulse length 2.4 s), then a cross-polarization step with a contact time typically 2 ms, and finally acquisition of the 13C signal under high power proton decoupling. The delay between the scan was set to 5 s, to allow the complete relaxation of the 1H nuclei and the number of scans was between 3,000-5,000 for carbon and 32 for proton. An apodization function (exponential) corresponding to a line broadening of 80 Hz was applied prior to Fourier transformation.

The 2D ^{1}H-^{13}C heteronuclear correlation (HETCOR) solid state NMR spectroscopy experiments were conducted on Bruker AVANCE III spectrometer using a 3.2 mm MAS probe. The experiments were performed according to the following scheme: 90^{0} proton pulse, t1 evolution period, cross- polarization (CP) to carbon spins, and detection of carbon magnetization under TPPM decoupling. [2,3] For the crosspolarization step, a ramped radio frequency (RF) field centered at 75 KHz was applied to protons, while the carbon RF field was matched to obtain optimal signal. A total of 32 t1 increments with 2000 scans each were collected. The sample spinning frequency was 8.5 kHz. A 2D Fourier transformation gives through space between pairs of neighboring carbon (in F2) and proton (in F1) nuclei. Using a short contact time (0.5 ms) for the CP step, the polarization transfer in the dipolar correlation experiment is expected to be quite selective, that is to lead to correlation only between pairs of attached ^{1}H-^{13}C spins (C-H directly bonded).

^{1}H-^{1}H multiple-Quantum Spectroscopy: Two-dimensional double-quantum (DQ) and triple-quantum (TQ) experiments were recorded on Bruker AVANCE III DSX-600 spectrometer with a conventional double resonance 3.2 mm CPMAS probe, according to the following general scheme: excitation of DQ coherences, t1 evolution, Z-filter, and detection. The spectra were recorded in a rotor synchronized fashion in t1; that is the t1 increment was set equal to one rotor period (4.545 μs). One cycle of the standard back-to-back (BABA) recoupling sequence was used for the excitation and reconversion period. Quadrature detection in w1 was achieved using the States-TPPI method. A spinning frequency of 22 KHz was used. The 90^o proton pulse length was 2.5 μs, while a recycle delay of 5 s was used. A total 128 t1 increments with 32 scan each were recorded. Double (DQ)- and Triple (TQ)-quantum proton spectroscopies under fast MAS have recently shown to be powerful techniques to probe the structural information and dynamics inherent proton-proton dipolar couplings. The DQ frequency in the w1 dimension corresponds to the sum of two single quantum (SQ) frequencies of the two coupled protons and correlates in the w_2 dimension with the two corresponding proton resonances. The TQ frequency in the w1 dimension corresponds to the sum of the three SQ frequencies of the three coupled protons and correlates in the w2 dimension with the three individual proton resonances. Conversely, groups of less than three equivalent spins will not give rise to diagonal signals in the spectrum. Two-dimensional DQ and TQ correlations experiments can thus applied to determine in a reliable way the number of attached equivalent proton.

Nitrogen Adsorption–Desorption. Isotherms at 77 K were measured using a Micromeritics ASAP 2024 physisorption analyzer. Specific surface areas were calculated following typical BET procedures. Pore size distribution was obtained using BJH pore analysis applied to the desorption branch of the nitrogen adsorption/desorption isotherm.

X-Ray Powder Diffraction. The small-angle X-ray powder diffraction (XRD) data were acquired on a Bruker D8 advance diffractometer using Cu Kα monochromatic radiation (λ = 1.054184 Å) to confirm the hexagonal ordered structure of the samples.

Preparation of ≡SiOZr(NMe_2)($NMeCH_2$). 0.100 g of Zr(NMe_2)$_4$ in slight excess (1.1 equivalent) with respect to the amount of surface accessible silanols (1.28 mmol silanols groups per gram) was reacted with 0.260 g of SBA-15 at room temperature in pentane for 1 h. After filtration and four washing cycles, all volatile coumpounds were evaporated and the solid was dried for 1 h under dynamic vacuum (< 10^{-5} mbar). The reaction was following by FT-IR showing that the isolated silanol disappeared (Figure 1) with an appearance of intense bands at 2967-2776 cm^{-1} and weak bans in the 1500-1400 cm^{-1} (according to C-H) and a weak band at 3292 cm-1 (according to N-H of physisorbed dimethyalmine). Elemental analysis gave 10.1% of Zr, 10.11 % of C and 5.58% of N consistent with ≡SiOZr(NMe_2)($NMeCH_2$) and 1.6 mmol of $HNMe_2$.

Support	Metal	C	N	Silanol	ratio C/N
%w	10.1	10.11	5.58		
Mol per gram of SBA	0.001107	0.0084	0.0040	0.001	
Ratio per mol of metal		7.61	3.60	0.86	2.11
Contribution from 1	1	4	2	1	
Xs from the grafted species	0	3.61	1.60	0	
Xs from the grafted species MOL		0.0040	0.00177138		2.26

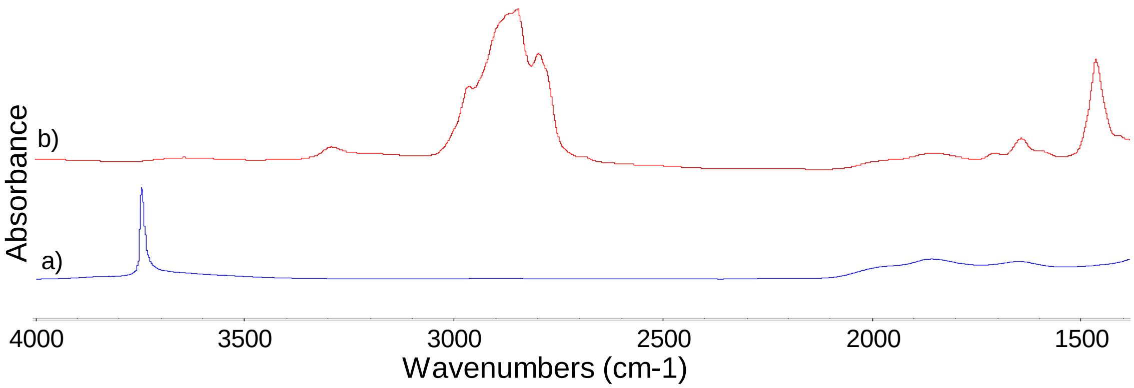

Figure S1: *In-situ* IR difference spectra of (a)self supporting SBA15-700 pellet and (b) after reaction with $Zr(NMe_2)_4$

Preparation and Characterization of SBA-15 and SBA-15$_{(700)}$. The SBA-15 was synthetized according to literature.[4,5] The BET analysis show a specific area of 822 m^2/g and a pore size of 5.21 nm. This prepared SBA-15 was treated at 700 °C for 12 h under high vacuum (< 10^{-5} mbar) to obtain SBA-15(700). After thermal treatment, the overall structure features of SBA-15 and its properties as large specific area and narrow pore distribution are retained. However, a small decrease in these 2 parameters was remarked after grafting the Zr complex. SBA-15 and the subsequent products were characterized by nitrogen adsorption at 77 K (N2 adsorption) for determination of the specific surface and size distribution of the pores (Table 1).

Material	specific area (m^2/g)	Pore sixe (nm)
SBA-15	822	5.21
SBA-15(700)	885	5.25
Catalyst	691	5.16

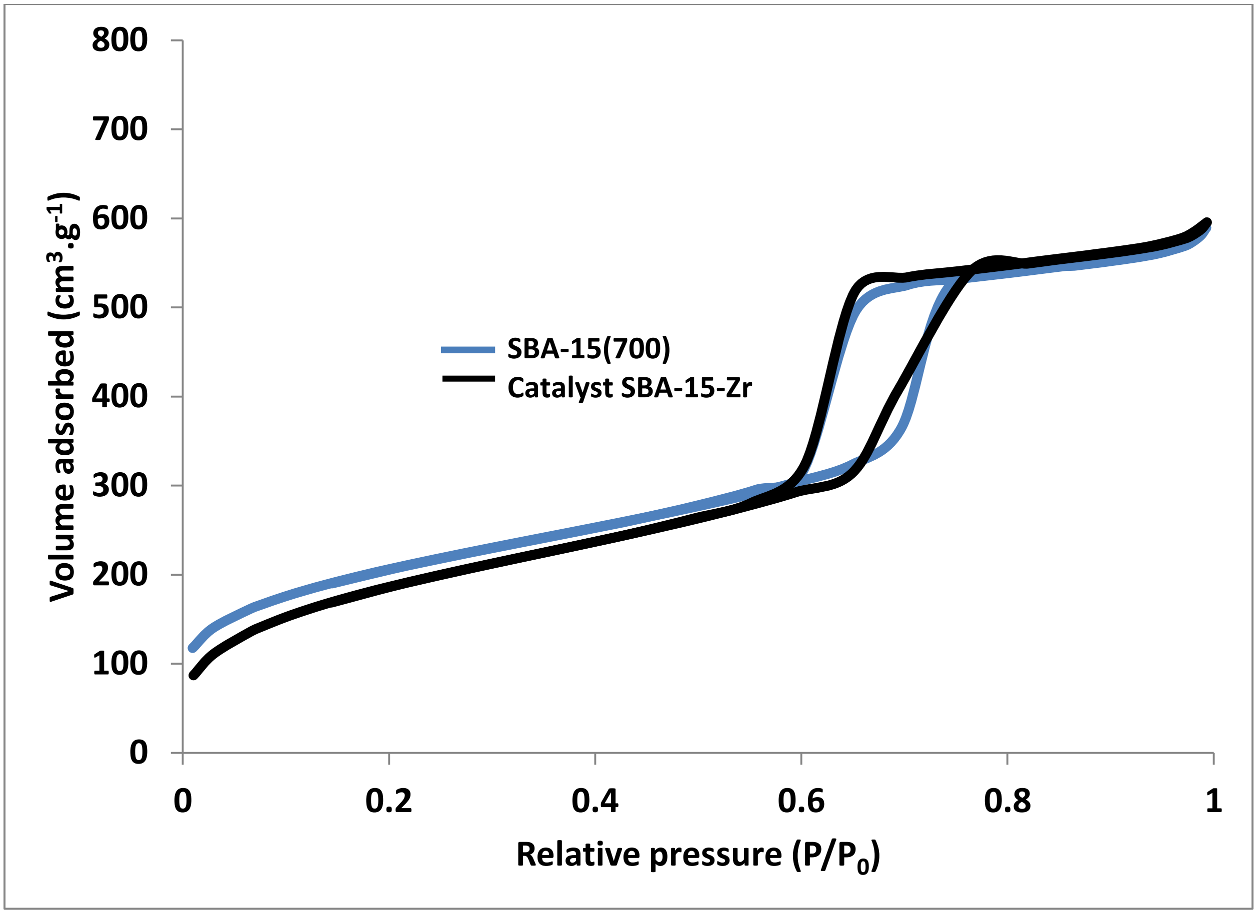

Figure S2: N_2 adsorption of SBA15$_{(700)}$ and SBA$_{(700)}$-OZr(NMe$_2$)(NMeCH$_2$)

PXRD pattern clearly reveals three well-resolved peaks in the 2θ domain at 0.95, 1.60, and 1.83°. They can be respectively indexed as (100), (110), and (200) diffraction peaks associated with p6mm hexagonal symmetry.[6] This symmetry remains unchanged, even after dehydroxylation at 700 °C and grafting of Zr complexes, showing the chemical and thermal stability of this material.

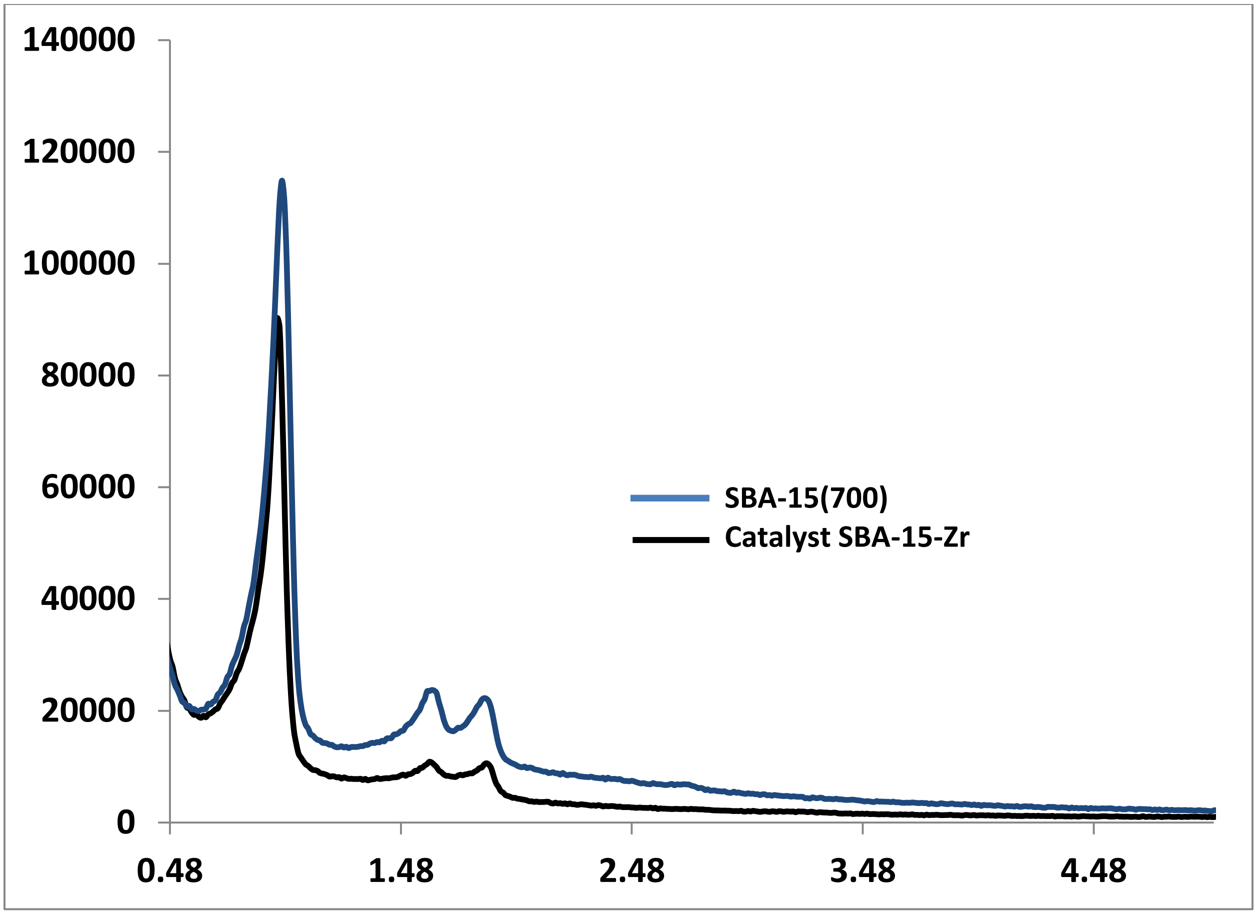

Figure S3: XRD Pattern of $SBA15_{(700)}$ and $SBA_{(700)}$-$OZr(NMe_2)(NMeCH_2)$

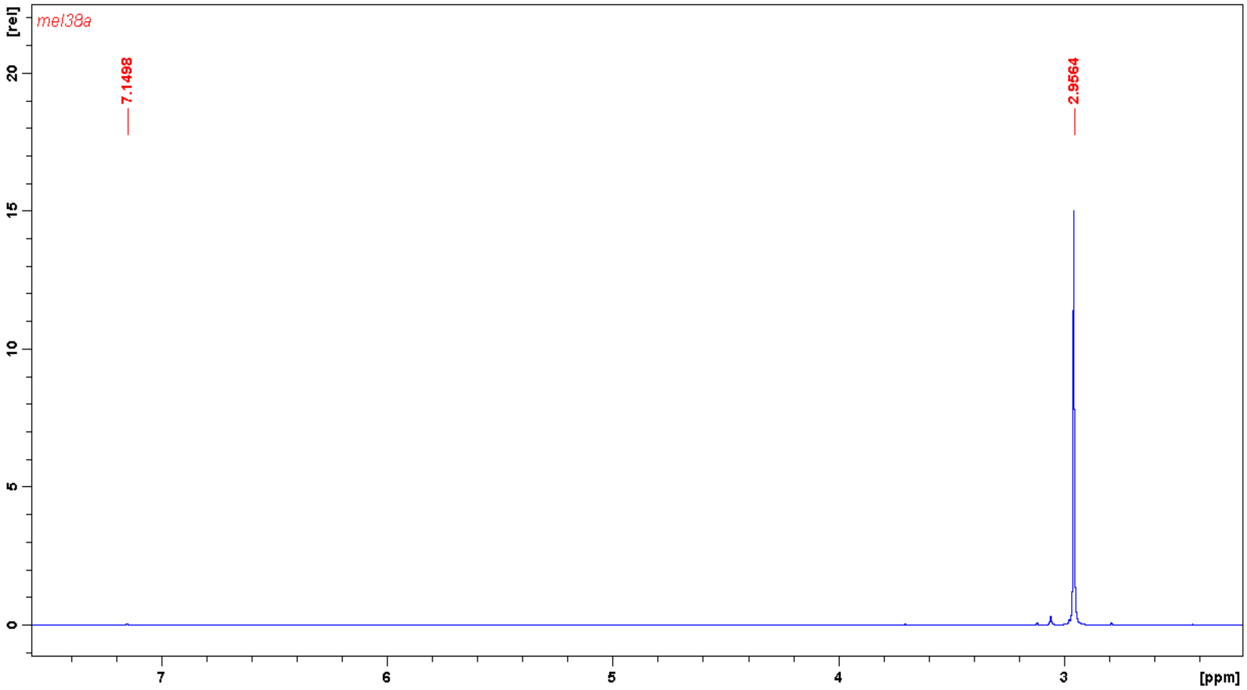

Figure S4: ^{1}HNMR of $Zr(NMe_2)_4$ in C_6D_6

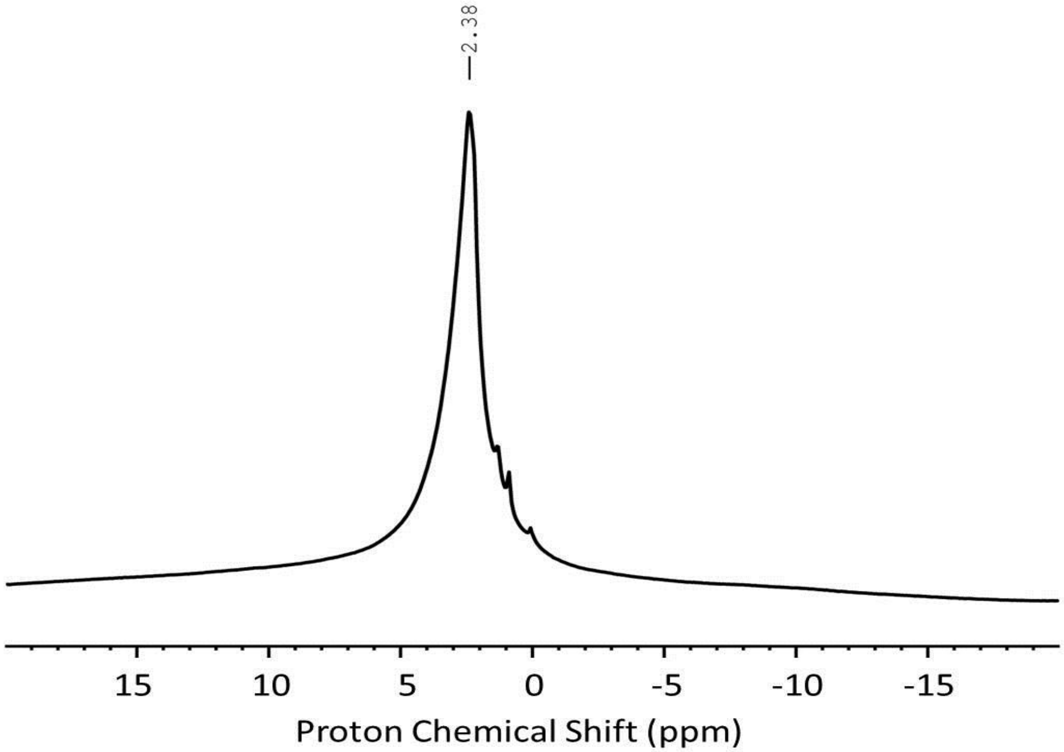

Figure S5: ^{1}H MAS NMR of $SBA_{(700)}$-$OZr(NMe_2)(NMeCH_2)$

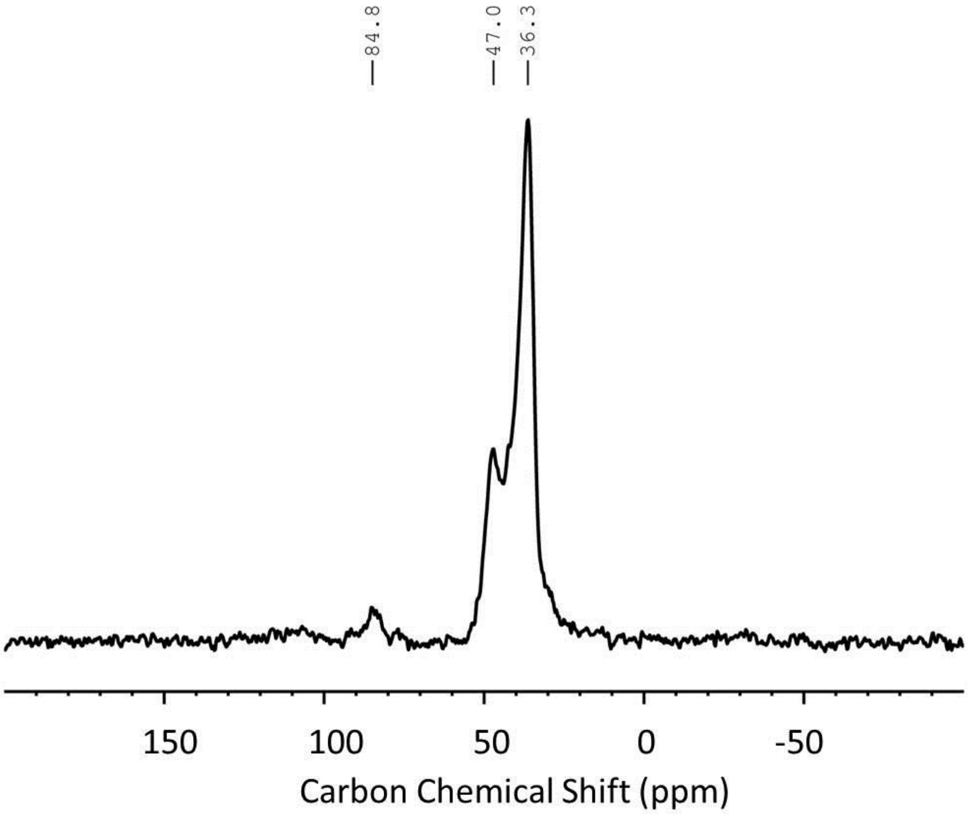

Figure S6: ^{13}C MAS NMR of $SBA_{(700)}$-$OZr(NMe_2)(NMeCH_2)$

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