

## Supporting information

# New Method for the Preparation of Nonuniform Distributed Co/SiO<sub>2</sub> Catalysts

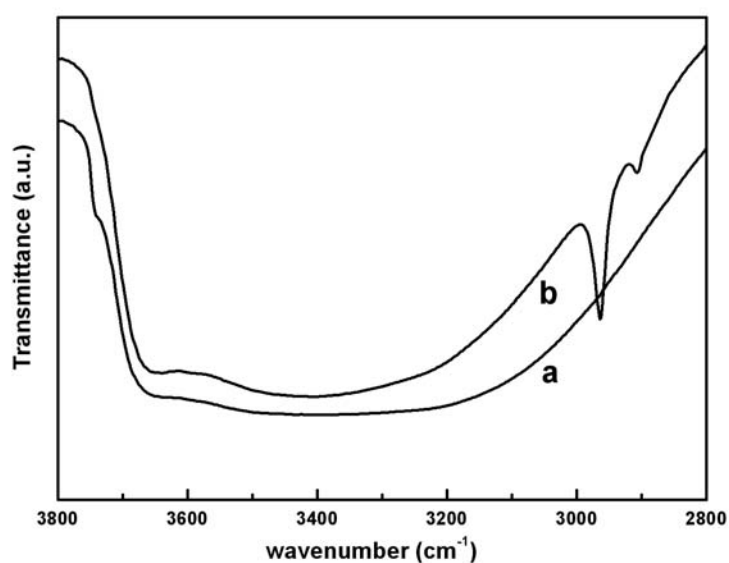
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### 1. The procedure of hydroxylation of silica gel:

The silica gel was heated in air at 500°C for 5h to remove any adsorbed species, and then the material was soaked in deionized water and refluxed for 8h. After refluxing, the material was filtrated and dried at 120°C for 12h in air and at 190°C for 12h in vacuum (1mbar).

### 2. The IR spectra of hydroxylated silica(S1) and silanized silica(MS):

IR spectra were performed at room temperature on pellets pressed without the use of any immersion medium, containing on average 14mg of silica/cm<sup>2</sup>, with Bruker Equinox 55 FTIR equipment.



IR spectra of S1 (a) and MS (b)

Isolated silanols are responsible for the band at  $3745\text{cm}^{-1}$  and hydrogen-bonded silanols correspond to the absorption at  $3650\text{-}3670\text{cm}^{-1}$ . After silanization, the band assigned to the isolated silanols decreased and a series of absorption in the  $2900\text{-}3100\text{cm}^{-1}$  region occurred. The peak, at  $2963\text{cm}^{-1}$ , was attributed to asymmetric stretching of methyl, while its companion near  $2908\text{cm}^{-1}$  is due to  $\text{CH}_3$  symmetric stretching. It was evident that the trimethylsilyl groups ( $-\text{Si}(\text{CH}_3)_3$ ) were grafted on the surface of S1 after silanization.

### **3. The results of physical adsorption of hydroxylated silica(S1) and silanized silica(MS):**

Adsorption/desorption isotherms of  $\text{N}_2$  (77K) were obtained on a Quantachrome Autosorb-1 apparatus. All samples were pre-treated by evacuation below  $10^{-4}\text{mbar}$  at  $200^\circ\text{C}$  for 5h. Continuous corrections were being made for variations in the atmospheric pressure. The area occupied by a  $\text{N}_2$  molecule in the completed monolayer was taken to be  $0.162\text{nm}^2$ .

sample	$A(\text{N}_2)$ ( $\text{m}^2/\text{g}$ )	Mean $d_p$ (nm)	$v_p$ ( $\text{cm}^3/\text{g}$ )
S1	118	26.8	7.92
MS	105	28.0	7.38

#### **4. The equation to calculate the ratios of surface area occupied by trimethylsilyl groups (-Si(CH<sub>3</sub>)<sub>3</sub>) and specific surface area of samples (MS, Reduced U and Reduced ES-3):**

From the carbon content of the samples, determined by elemental analysis on an Elementar Vario EL III apparatus and corrected by the carbon content of an unmodified silica submitted to the same pre-treatment and drying processes, the ratio of sample surface occupied by trimethylsilyl groups was obtained by using the equation:

$$N = \frac{C \cdot (6.023 \times 10^{23}) \cdot 0.55}{12 \cdot A \cdot 10^{18}}$$

Where N is the ratio of sample surface occupied by trimethylsilyl groups, C is the corrected carbon content of the sample (wt.%), A is the specific surface area of S1 (m<sup>2</sup>/g) and the apparent cross area of trimethylsilyl group was taken to be 0.55nm<sup>2</sup>.

#### **5. Details of Fischer-Tropsch reactions with ES-1, ES-2, ES-3 and U:**

The Fischer-Tropsch reactions were conducted in a fixed-bed reactor at 497K and 2.0MPa. Catalysts were reduced in situ at ambient pressure and 673K using 1000h<sup>-1</sup> H<sub>2</sub>. After 8h reduction, the reactor was cooled to 473K and the syngas of molar ratio of H<sub>2</sub>/CO=2 was introduced. The temperature was increased at 1K/min to 497K. The effluent passes through a heated trap (393K) to collect heavy hydrocarbons (C<sub>11</sub>-C<sub>47</sub>), then through a cold trap (283K) to condense the liquid products (C<sub>4</sub>-C<sub>20</sub> hydrocarbons and water). The gaseous

products ( $C_1$ - $C_6$  hydrocarbons and  $CO_2$ ) and unreacted syngas were analyzed by on-line Agilent 6890 GC with a Porapak Q packed column and thermal conductivity detector (TCD). The liquid hydrocarbons were analyzed off-line by Agilent 6890 GC with an OV 101 capillary column and flame ionization detector (FID). The heavy hydrocarbons were analyzed off-line by Varian 3800 GC with a CP-SIMD197 stainless steel capillary column and FID.