Embryonic zeolite carriers decorated with metal oxides and metal sulfides nanoparticles

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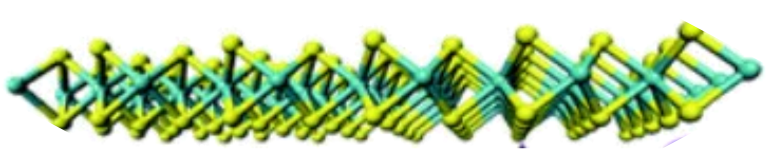
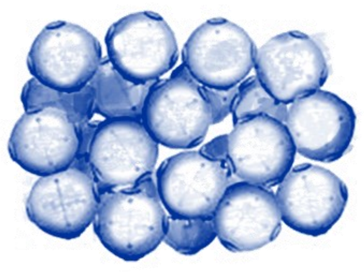
Objective of study:

The object of the study is the synthesis and physicochemical characterization of metal sulfide catalysts on highly porous aluminosilicate carries and study of their catalytic performance in non-oxidative methane conversion.

State-of-the-art



MoS_2 are non-porous materials working the temperature range below 500 °C.



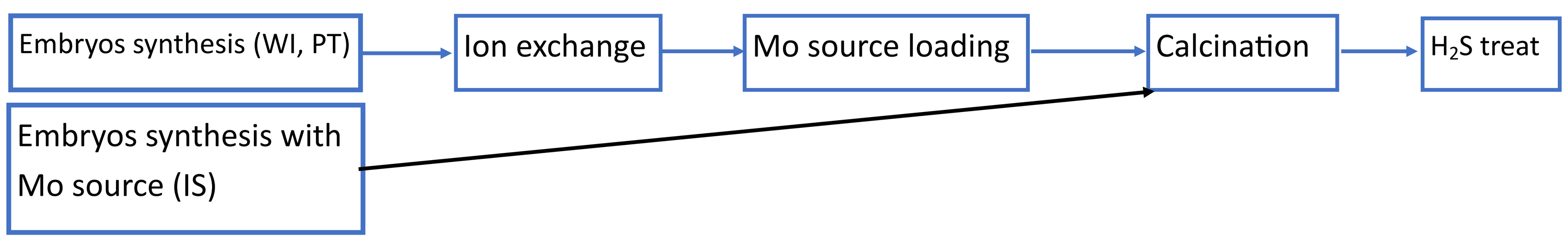
The embryonic zeolite (EZ) are small size (3-5 nm) particles prepared with the identical composition to zeolite. It has an open-porous structure with micropore volume and specific surface area much higher than the fully crystalline counterpart.

Synthesis procedure

EZ composition: $4.5(TPA)_2O:0.25Al_2O_3:25SiO_2:430H_2O:100EtOH$.

Mo loadings routes: wet-impregnation (WI); *in situ* synthesis (IS); post-treatment (PT).

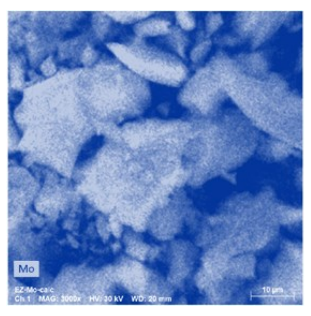
Sulfurizing procedure: sulfurizing agent-H_2S/H_2, 10 vol% H_2S; 2h at 350 °C.



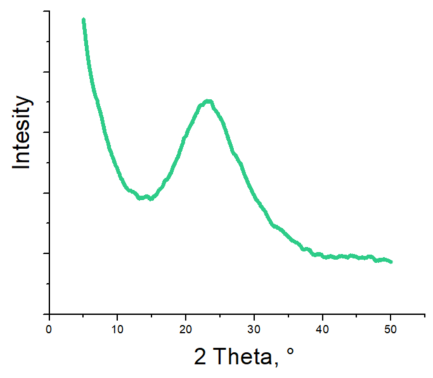
Elements distribution

Embryonic zeolite carriers offer the following advantages: high metal sites accessibility and uniform Me-dispersion.

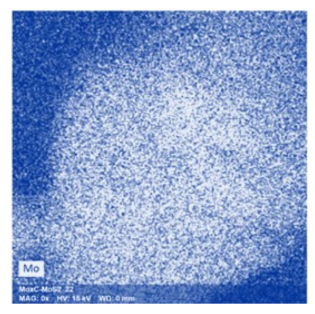
Drawbacks: Mo species aggregate due to high-temperature treatment. The usage of EZ allows guarantees a high uniform particle distribution after a treatment at 700-800 °C. It was confirmed by X-Ray powder diffraction (XRD) and Energy dispersive spectroscopy elemental mapping (EDX).



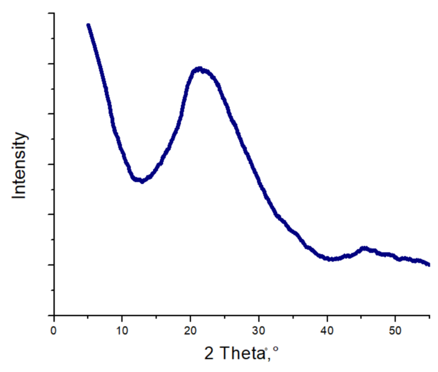
5%Mo-*WI*



XRD patterns of 5%Mo-WI before MC

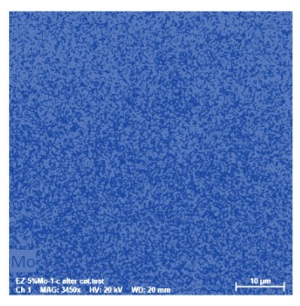


5%MoS_2-*WI*



XRD patterns of 5%MoS_2-WI before MC

after MC, 700 °C

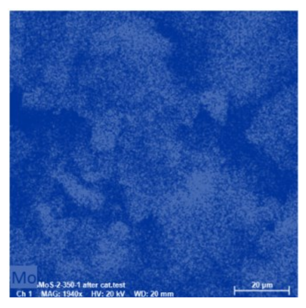


5%Mo-*WI*

(5%Mo_xC/MoO_3-WI)

MC-Methane conversion

after MC, 700 °C

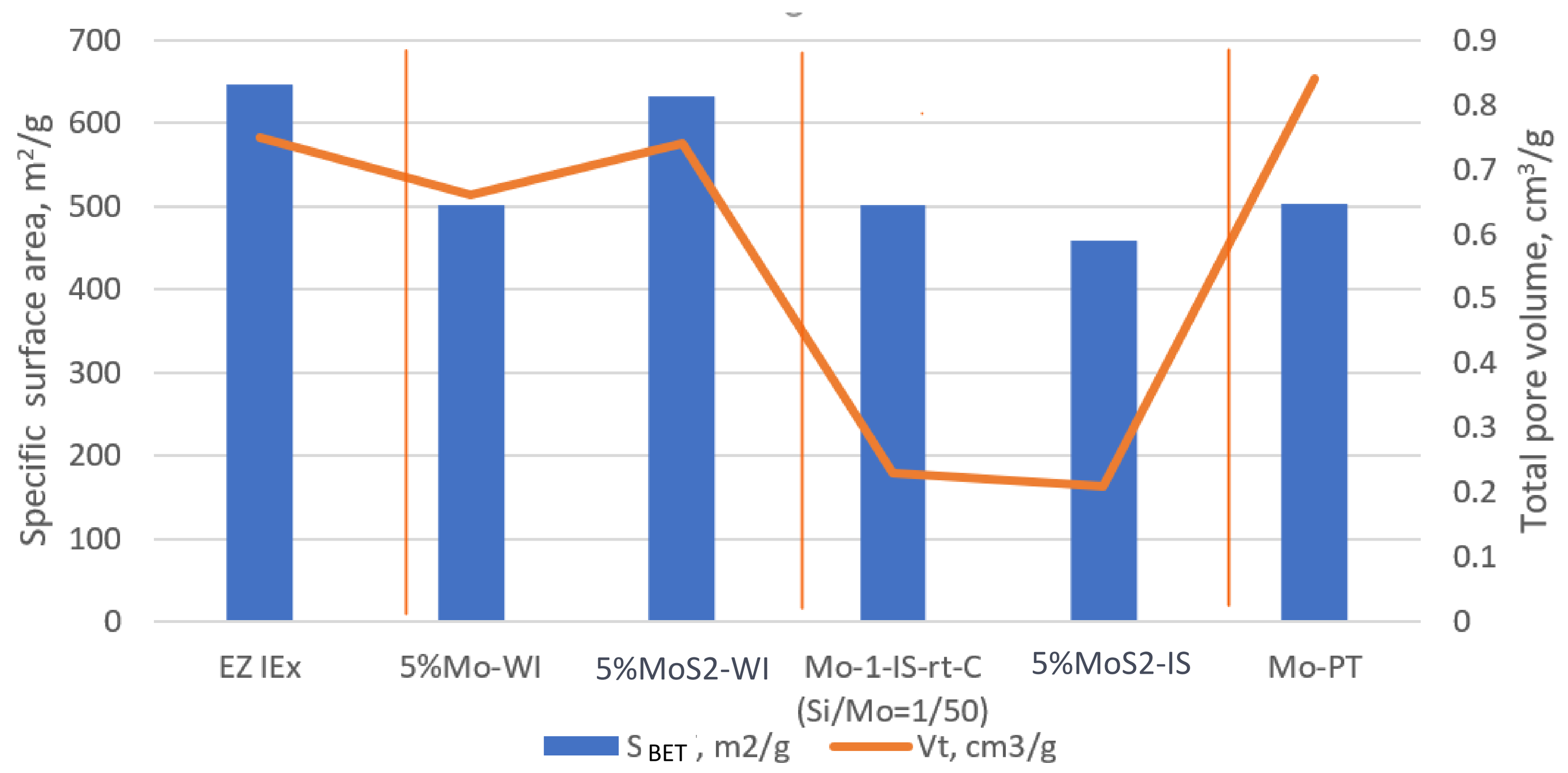


5%MoS_2-*WI*

(5%Mo_xC/MoS_2-WI)

Porous properties

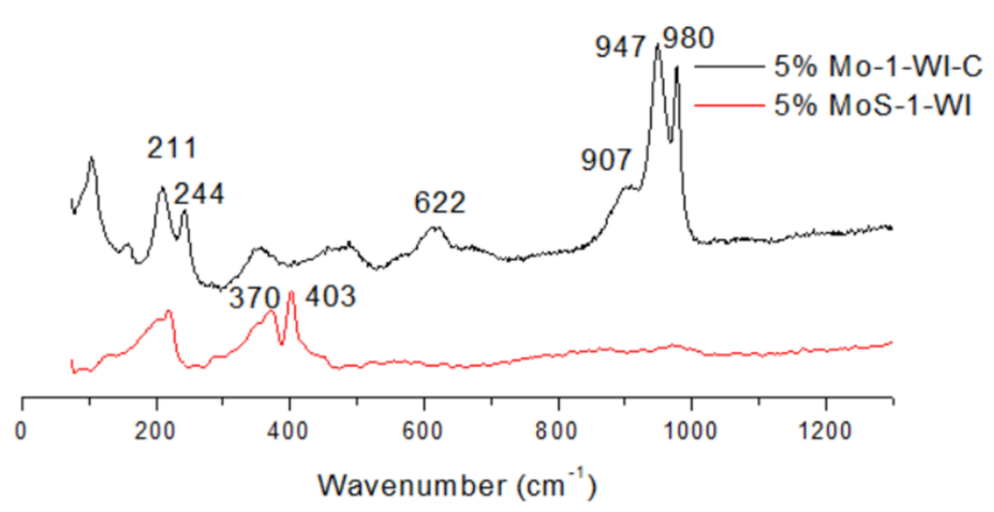
Specific surface area and porosity



Embryonic zeolite carriers advantages: retain the high specific surface area (SSA) and total pore volume after Mo loading and conversion to MoS_2.

Raman spectrometry

Both phases (MoO_3 and MoS_2) formation was confirmed by Raman spectrometry:

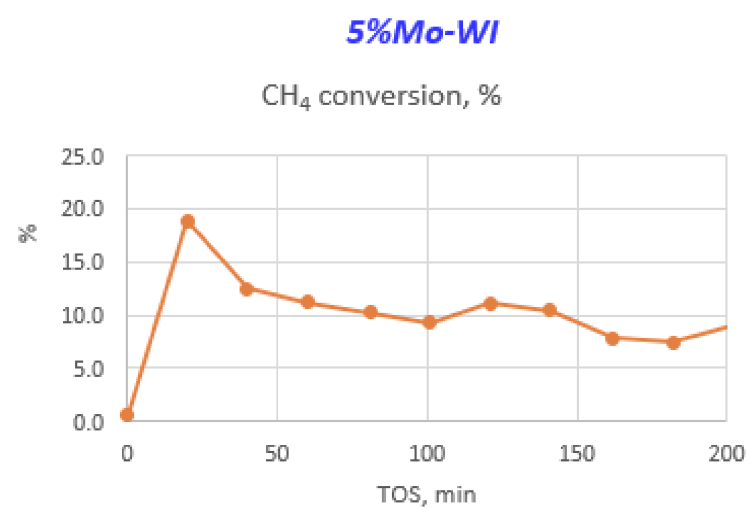


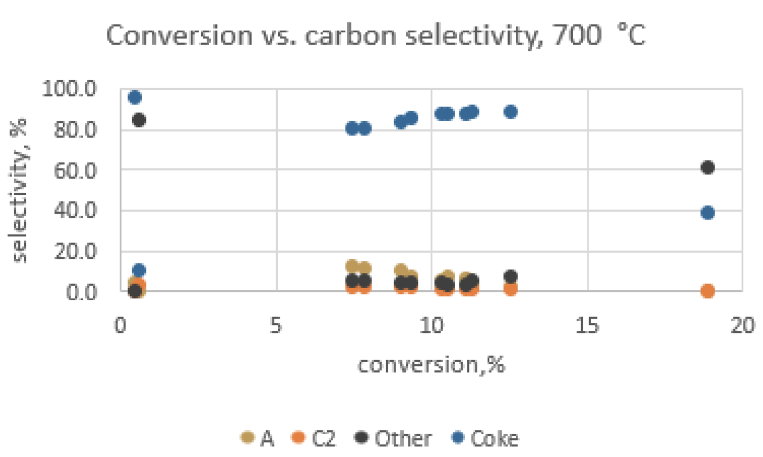
MoO_3: 244,622,980 cm^{-1};
Amorphous MoO_3:
Mo=O-947 cm^{-1};
Si-OH: 980 cm^{-1};
2H-MoS_2: 370, 403 cm^{-1}.

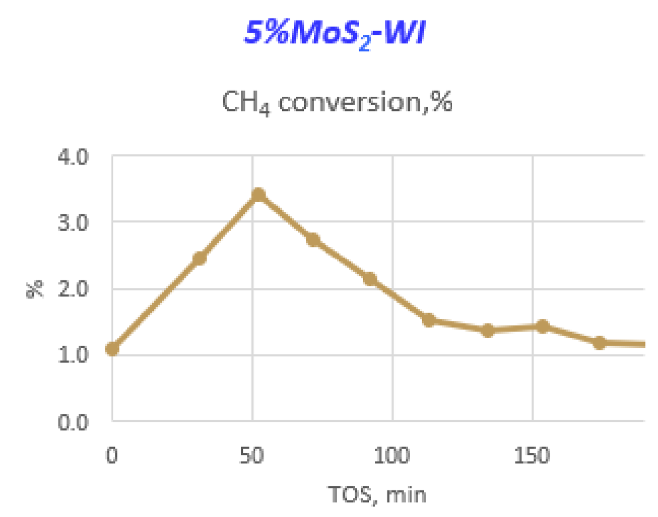
Catalytic properties

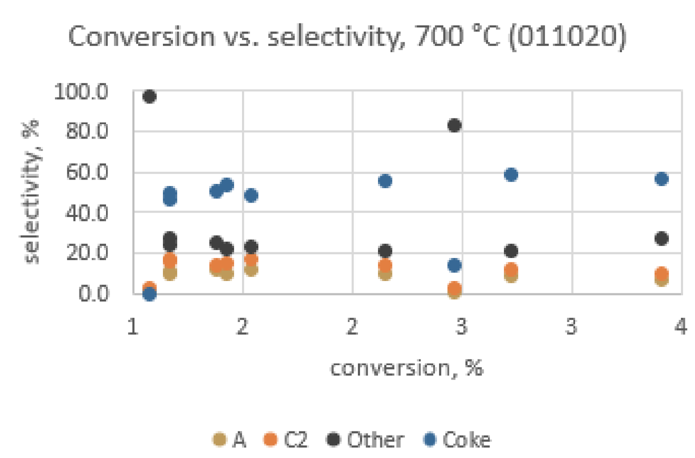
Catalytic application: Non-oxidative methane conversion

T=700°C, CH_4/N_2, WHSV: 1,2 h^{-1}.



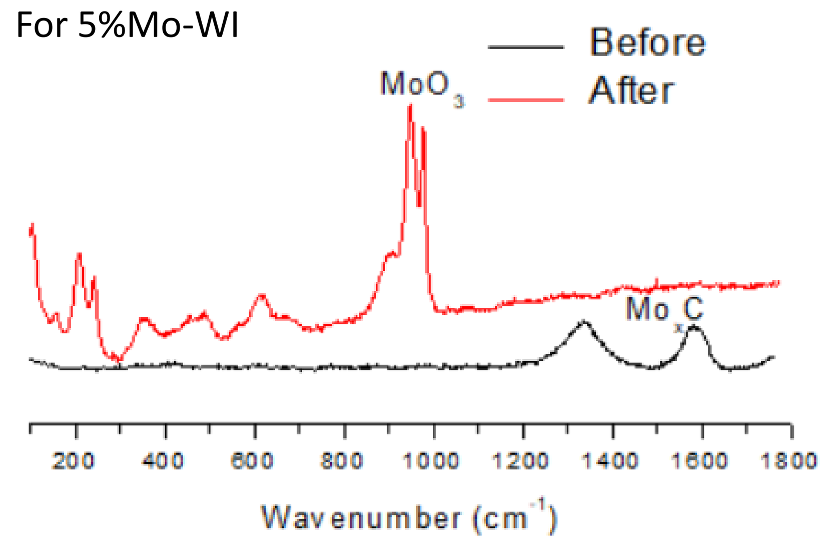






Changes in the Raman spectra of tested samples at 700 °C:

For 5%Mo-WI

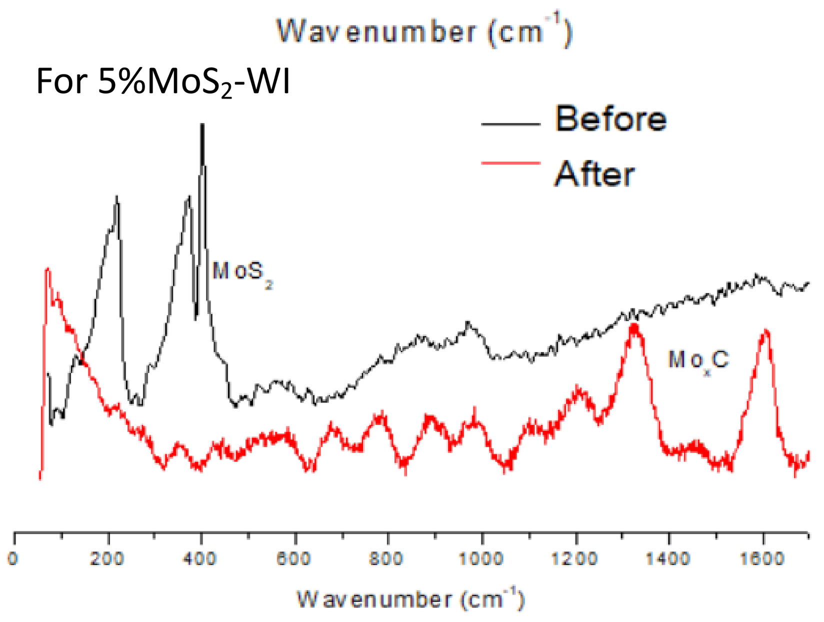


Surface phase change:

MoS_2 to Mo_xC/MoS_2;

MoO_3 to Mo_xC/MoO_3.

For 5%MoS_2-WI



Results:

- Unlimited coke growth;
- Formation the same surface phase;
- Combination low-acidic carrier and Mo_xC phase-only coke and hydrogen as products.

Conclusions:

A: 1) **EZ** as carriers allow to ensure an uniform active phase distribution during several hours high-temperature treatment for each obtained metal oxide/sulfide/carbide; 2) All samples in oxide and sulfide forms were characterized by high S_{BET} (> 460 m²/g) and total pore volume (> 0.55 cm³/g).

B: 1) **The obtained sulfide catalysts** are not active in the methane dehydrogenation reaction; 2) The **sulfide** catalysts change surface composition under CH_4-flow at 700 °C+; 3) **The presence of sulfur** slightly decrease coke formation for high-temperature non-oxidative processes.

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