Preparation of silver nanoparticles confined in SBA-15 mesoporous silica by ultra-short pulsed laser ablation in liquid

COLA 2013 ITALY
Conference on Laser Ablation
Ischia – ITALY
October 6th – 11th, 2013

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Introduction

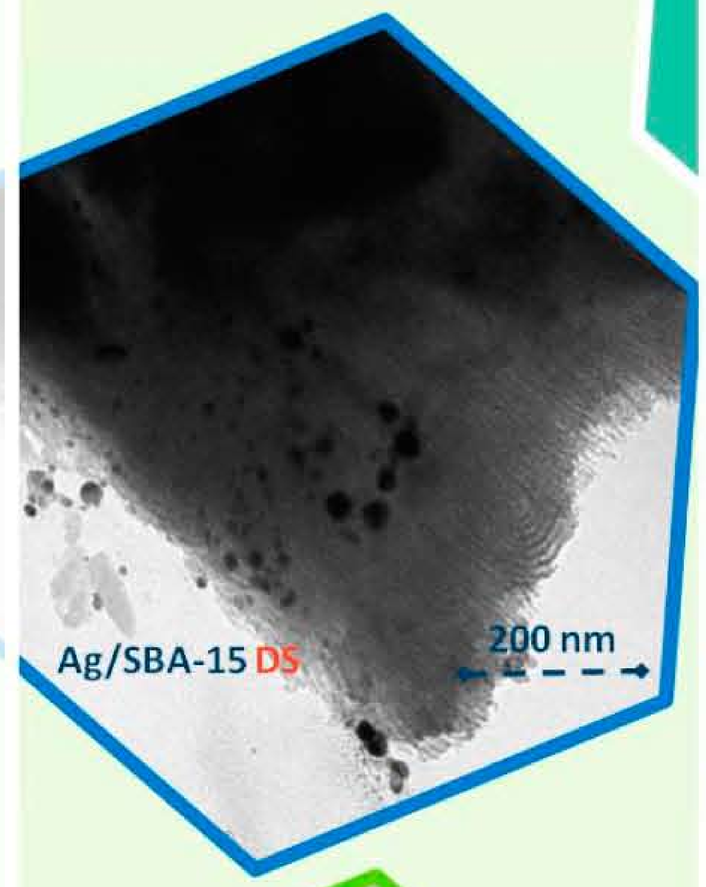
Catalytic total oxidation is an efficient method for the removal of volatile organic compounds (VOCs). Supported noble metals (Pt, Pd) are widely applied for this process. Research is however focusing on the development of less expensive and more environmentally friendly catalysts. It has been shown that nano-sized silver particles can be active for such a purpose [1]. With their high specific surface area and uniform pore structure ordered nanoporous silica materials are excellent supports for noble and transition metal catalysts [2]. Through the combination of these systems an enhanced effect can be achieved. With this regard different methods for producing metal nanoparticles within the silica matrix can be employed, such as direct hydrothermal synthesis, template ion-exchange and pulsed laser ablation in liquid [3]. Peculiarities of the nanoporous structure as well as dispersity of the metal can strongly influence the catalytic activity.

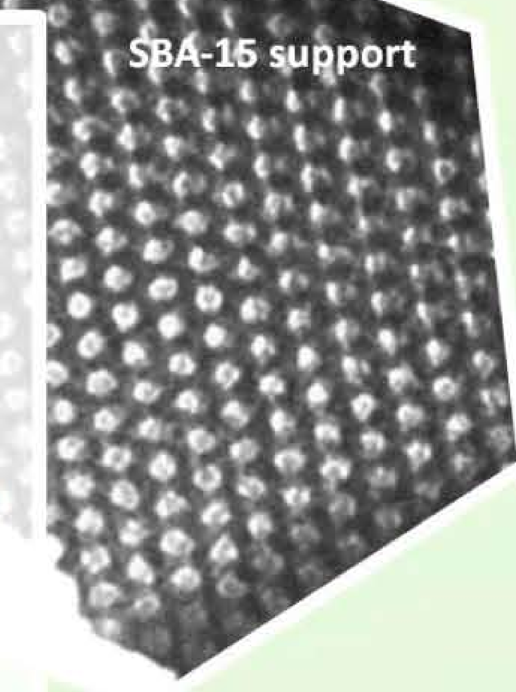
Experimental

Supports: SBA-15, MCM-41 (SiO_2) hexagonal , P6mm
5 wt. % Ag, 8 wt.% Ag

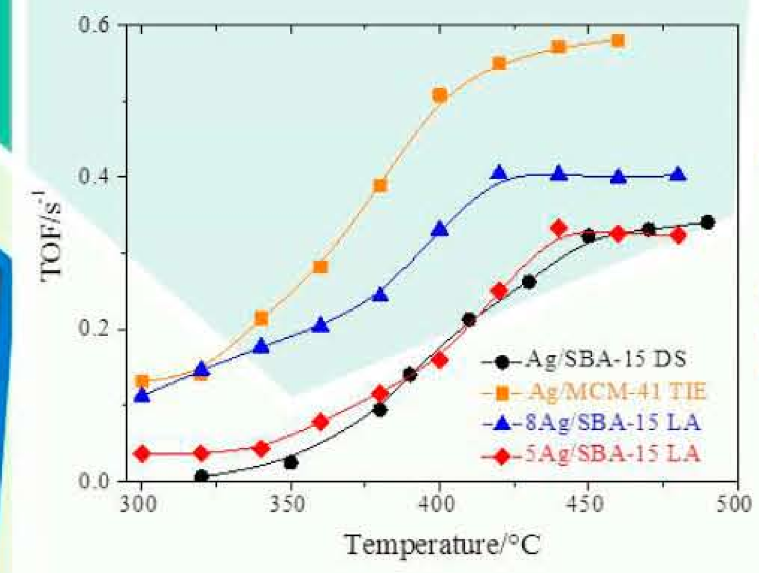
Ag/SBA-15 (DS): Direct, hydrothermal synthesis, 8 wt.% Ag
40°C-20h, 100°C - 48h, template removal: 450°C-5h/Air
1 TEOS: 0.017 P123: 0.05 $AgNO_3$: 4.93 HNO_3: 177.9 H_2O.
Ag/MCM-41 (TIE) :Template ion-exchange method, 5 wt.% Ag
0.1 M $AgNO_3$, 50°C - 20 h, template removal: 500°C-5h/Air

Pulsed Laser Ablation in Liquid
- Ti:Sapphire@ 800 nm, 100 fs, 1 KHz, 3 mJ/pulse
- 25 mm water column height; 40 mm lens focal length
- ablation time 10 minutes, 5 wt.%Ag
- ablation time 20 minutes, 8 wt.%Ag
- stirrer speed 400 rpm





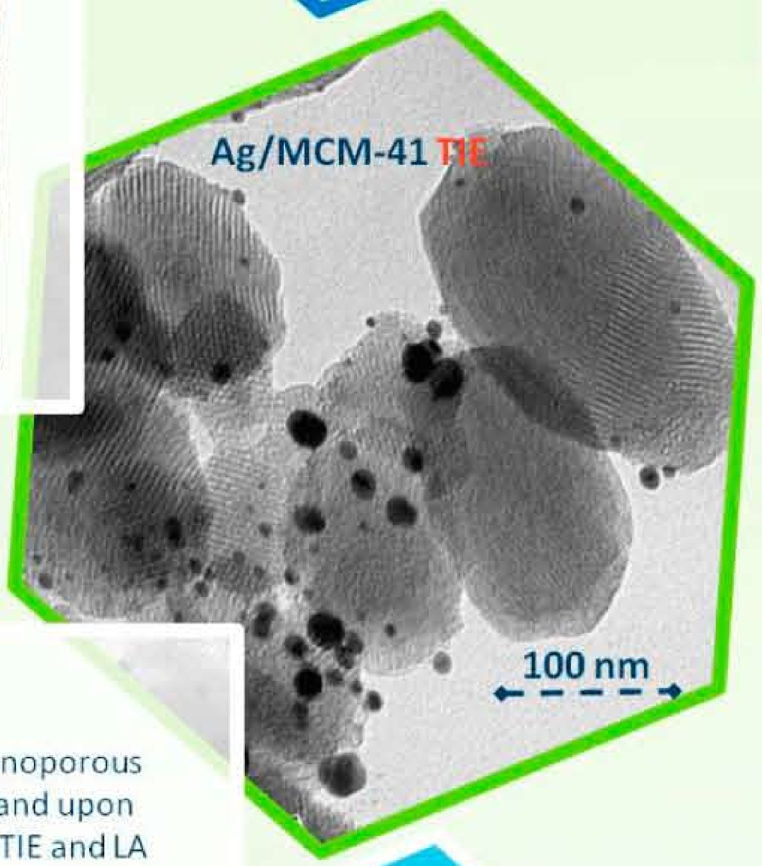
Catalytic results - Total oxidation of toluene

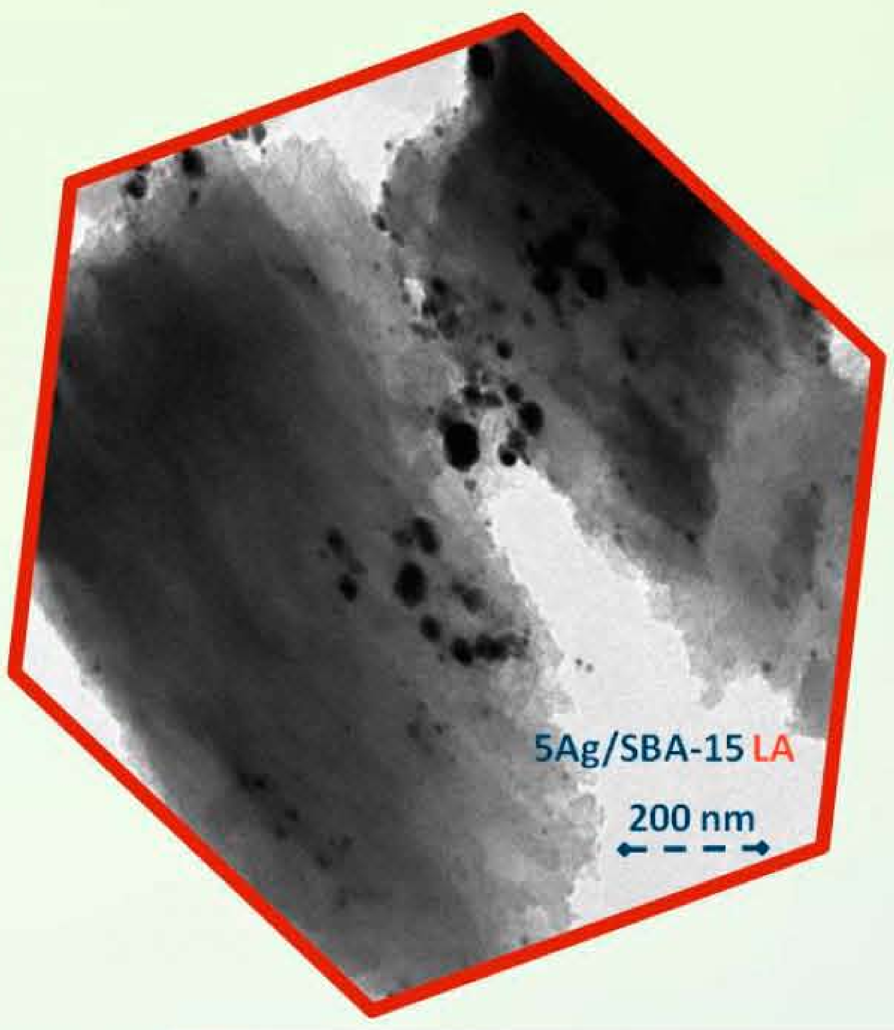


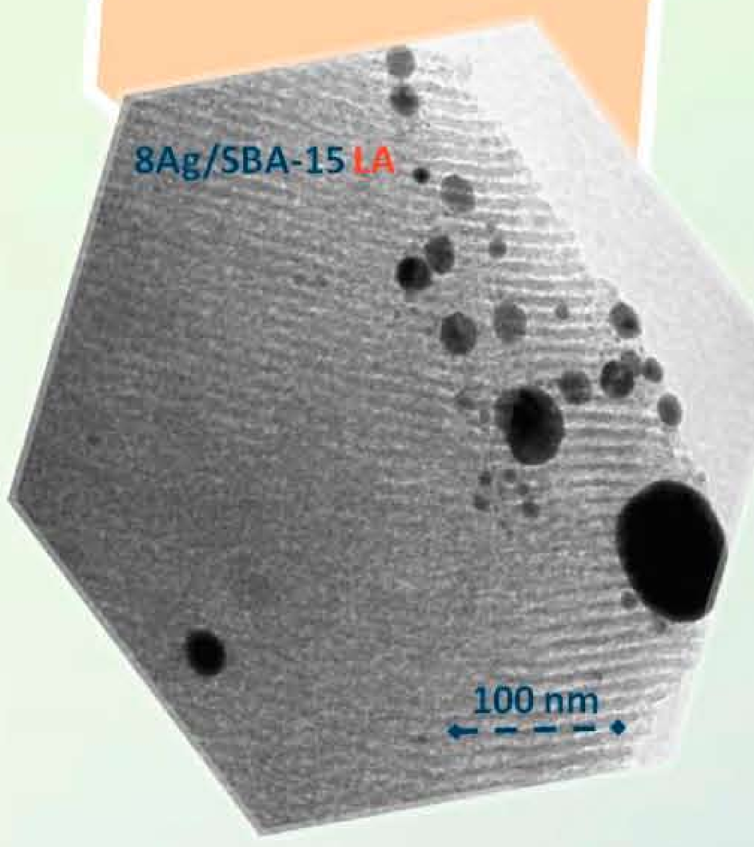
$C_7H_8+O_2= CO_2+H_2O$

- Atm. press., fixed bed flow reactor, 30 ml/min O_2 carrier gas
- $p_{Toluene}$ = 0.9 Pa/30ml/min,
- WHSV=1.2 g/g_{cat}h
- Products: only CO_2 and H_2O

- High catalytic activity on Ag/MCM-41 TIE
  → finely dispersed Ag^0 nanoparticles, smaller pores for the stabilization of metallic particles
- Lower catalytic activity on SBA-15 carriers independently of Ag loading method
  → bigger Ag^0 nanoparticles, larger pores for the agglomeration of silver particles during the reaction

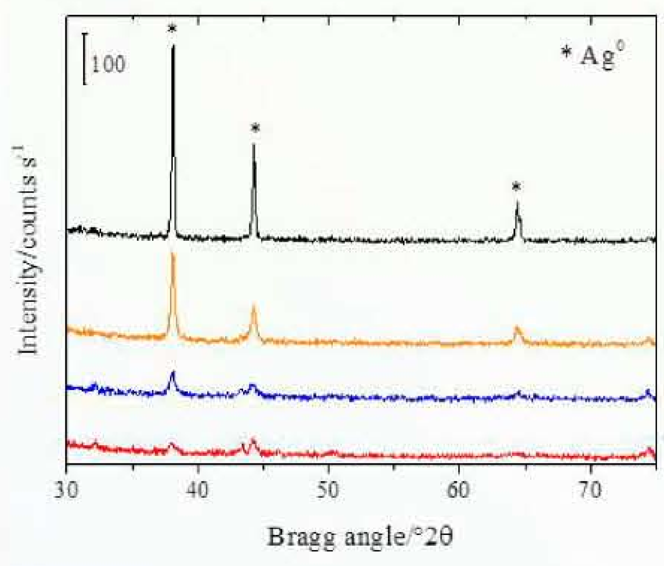






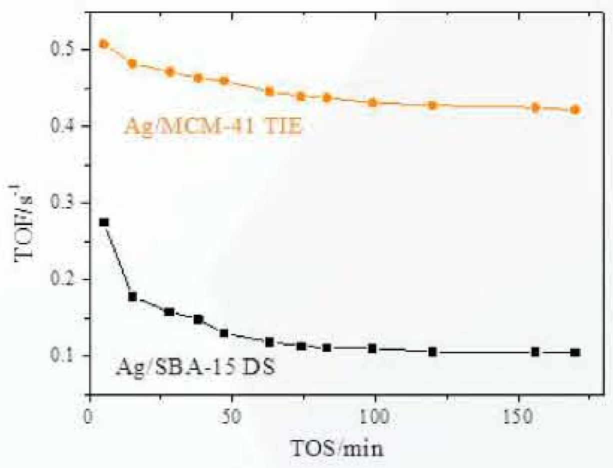
Results

Texture - XRD



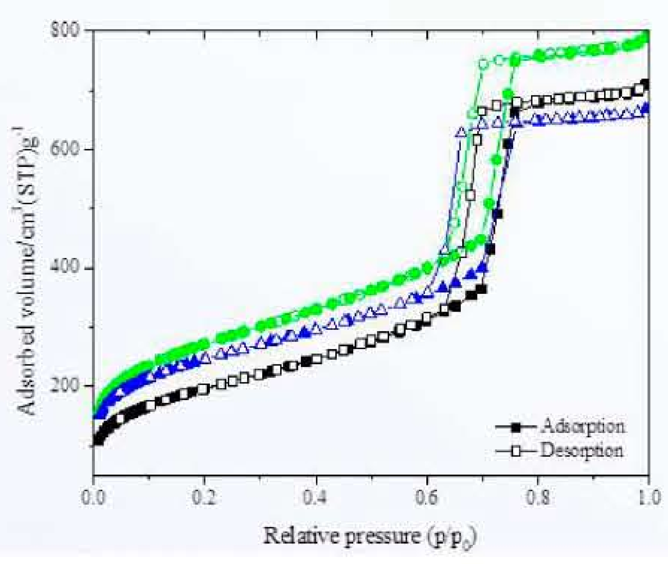
- Well ordered nanoporous structure by DS and upon modification by TIE and LA
- Only Ag^0 phase
- Crystallite size of Ag^0 (by Sherrer equation)
  Ag/SBA-15 DS: 1 μm
  Ag/MCM-41 TIE: 45 nm
  8Ag/SBA-15 LA: 45 nm
  5Ag/SBA-15 LA: 45nm
- Increasing Ag^0 intensity after catalysis

Catalytic results – Time on stream



- Fast deactivation on Ag/SBA-15 DS
- More stable catalytic behavior on Ag/MCM-41 TIE
- More finely dispersed Ag^0 nanoparticles confined in the mesopores of Ag/MCM-41 TIE

Texture - N_2 physisorption

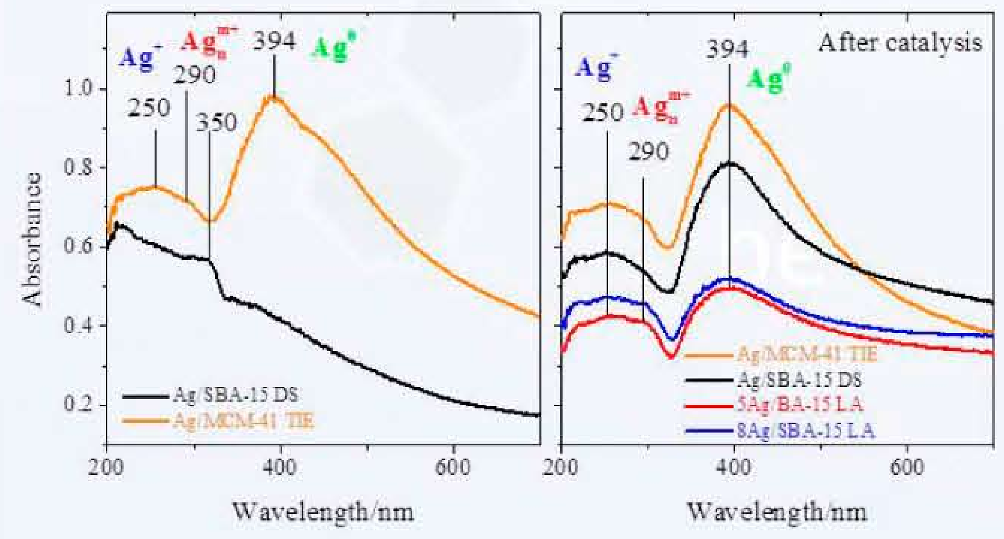


Sample	BET m²/g	PV cm³/g	PD nm
Ag/MCM-41TIE	927	0.76	2.6
SBA-15	1012	1.20	6.0
Ag/SBA-15DS	698	1.08	6.6
Ag/SBA-15LA	880	1.02	6.0

Conclusions

- Silver nanoparticles can be loaded on SBA-15 support by using pulsed laser ablation (LA)
- Physico-chemical and catalytic properties of Ag/SBA-15 materials are similar, independently of the preparation method (direct synthesis or LA)
- Finely and uniformly dispersed Ag^0 nanoparticles confined in small nanopores to avoid agglomeration is necessary for the high conversion and stable catalytic behavior in VOC total oxidation
- Optimization of LA method can improve the silver particle dispersion and penetration into nanopore system

DR UV-Vis spectroscopy



- 250 nm isolated Ag^+
- 290-350 nm Ag nanoclusters
- 394 nm Surface plasmon resonance (SPR) of Ag^0 nanoparticles

- No SPR for Ag/SBA-15 DS
- No changes in Ag/MCM-41 TIE after catalysis
- Appearance of SPR for Ag/SBA-15 SD after catalysis

References

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[3] A. De Bonis, M. Sansone, L. D'Alessio, A. Galasso, A. Santagata, R. Teghil, J. Phys. D: Appl. Phys. (2013) *in press*, D/481996/PAP/212379

Acknowledgements

This poster draws on work undertaken as part of the project *CLaN* (*Combined Laser Nanotechnology*) co-financed by the Operational Programme ERDF Basilicata 2007-2013.