Formation of Pt-Ag alloy on different silicas - surface properties and catalytic activity in oxidation of methanol

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SUPPORTING DATA

S1

1. Synthesis of MCF materials [1,2]

Pluronic 123 (poly(ethylene glycol)-block-poly(propylene glycol)-block-poly(ethylene glycol)-block) (16 g, 2.8 mmol) was dissolved in 600 g of 0.7 M HCl solution at 308–313 K. Then 1,3,5-trimethylbenzene (Aldrich) (16 g, 133.12 mmol) and NH_4F (Aldrich) (0.1868 g, 5.04 mmol) were added under vigorous stirring. After 1 h of stirring, TEOS (Fluka) (34,108 g, 163.98 mmol) was added. The final mixture was stirred at 308–313 K for 24 h and then transferred into a polypropylene bottle and heated at 373 K under static conditions for 24 h. The solid product was recovered by filtration, washed with distilled water and dried at room temperature. The template was removed by calcination at 773 K for 8 h.

For the preparation of NbMCF material, niobium(V) ethoxide was added to the synthesis gel 5 min after TEOS addition. The nominal Si/Nb ratio was 64. In order to establish niobium content in MCF samples, XRF technique were applied. The catalysts obtained were labelled as MCF and NbMCF.

2. Functionalization of supports with 3-mercaptopropytrimethoxysilane (MPTMS) [2]

Supports were grafted with 3-mercaptopropyltrimethoxysilane (MPTMS) (95%, Sigma-Aldrich) to functionalize their surface before modification with metals. 7 g of the support powder was refluxed in a dry toluene solution (200 mL) containing 18.9 mL MPTMS at 373 K for 18 h. The reagents were not purified before use. The materials were recovered by filtration followed by washing in: dry toluene (200 mL), ethanol (200 mL) and distilled water (100 mL). The powders were dried in an oven at 353 K.

S2

Modification of functionalized supports with platinum and/or silver [2,3]

To obtain monometallic catalysts, the functionalized supports (MCF-SH, NbMCF-SH, SiO_2-SH) was stirred for 4 h in 50 mL of water solution of silver nitrate ($AgNO_3$, ≥99.8% - Sigma-Aldrich) (1.0 and 2.0 wt % of Ag as assumed) or hexachloroplatinate(IV) hydrate (H_2PtCl_6, 38.84%, Johnson Matthey) (0.5 and 1.0 wt% of Pt as assumed) at room temperature (RT).The solid was recovered by filtration and washed with 80 mL of distilled water. The recovered material was stirred at room temperature with 60 mL of 0.1 M ($NaBH_4$> 99.8%, Sigma–Aldrich) solution. After 40 min, the solid was recovered by filtration, washed with 80 mL of distilled water. The materials were dried at 333 K for 12 h (labelled as D) and calcined in air at 773 K for 4 h.

The preparation procedure of the bimetallic Pt-Ag system was as follows: 25 mL of water solution of silver nitrate and 25 mL of water solution of hexachloroplatinate(IV) hydrate (H_2PtCl_6, 38.84%, Johnson Matthey) were prepared separately and then mixed for 5 min in one flask. Then the functionalized support was stirred for 4 h with the prepared solution at room temperature. Next steps are the same as for monometallic samples (described above). The assumed Ag/Pt wt. ratio was 2.0 and 4.0 (with different metals content).

In catalysts symbols, numbers indicate the assumed metals loading, e.g. 0.5Pt2Ag/M means that the assumed metals amount is: 0.5 wt. % for platinum and 2.0 wt. % for silver. All dried materials are indicated by D at the end of the sample symbol.

S3

Characterization [2,3]

X-ray fluorescence (XRF)

The real molar ratio of Si/Nb was determined by X-ray fluorescence (XRF) using MiniPal-Philips. The experiments were done using calibration curve based on the XRF measurements for the mixtures prepared from silica (Degussa) and niobium oxide (Alfa Aesar). The calibration curve was created by 10 points related to different SiO_2/Nb_2O_5 molar ratios in the range from 3 to 300. The metal concentration in the materials was received by the amount of emitted X-ray radiation related to the values in the calibration curves.

X-ray diffraction (XRD)

XRD measurements were carried out on a Bruker AXS D8Advance diffractometer with Cu Kα radiation (λ= 0.154 nm), with a step size of 0.05° in the small-angle range (1°–10°) and with a step size of 0.2° in the wide-angle range (6°–60°). X-ray diffraction line broadening analysis was used for characterisation of supported Ag and Pt particles. The Scherrer formula was applied to estimate the average particle size (with a size error of ±0.5 nm).

UV–Vis spectroscopy

UV–Vis spectra were recorded using a Varian-Cary 300 Scan UV–Visible spectrophotometer. Powder samples were placed in a cell equipped with a quartz window. The spectra were recorded in the range from 800 to 190 nm. Spectralon was used as the reference material.

Transmission electron microscopy (TEM)

For transmission electron microscopy (TEM) measurements, the powders were deposited on a grid covered with a holey carbon film and transferred to JEOL 2000 electron microscope operating at 80 kV. Samples were made in the form of suspension in 1-butanol.

N_2 adsorption/ desorption

The N_2 adsorption-desorption isotherms were obtained at 77 K using a Micromeritics ASAP 2020 Physisorption Analyzer. Before the measurements, samples were degassed at 573 K for 8 h. The surface area was calculated by the BET method, and the average pore size was estimated from the adsorption branch.

X-ray photoelectron spectroscopy (XPS)

X-ray photoelectron spectroscopy (XPS) was performed on an Ultra-high vacuum photoelectron spectrometer based on Phoibos150 NAP analyzer (Specs, Germany). The analysis chamber was operated under vacuum with a pressure close to 5×10^{-9} mbar and the sample was irradiated with a monochromatic Al Kα (1486.6 eV) radiation (15 kV; 10 mA). Binding energies were referenced to the Si 2p peak from silica 103.4 eV.

Scanning transmission electron microscopy (STEM)

The STEM images were obtained with the use of a Tecnai Osiris 200 kV TEM/STEM system equipped with HAADF detektor and Super-EDX windowless detector. STEM micrographs (512 × 512 points) were coupled with EDX data for the presentation of the chosen elements distribution.

S4

Methanol oxidation [2,3]

A portion of 0.04 g of granulated catalyst of the size fraction of $0.5 < \phi < 1$ mm was placed into a tubular reactor (diameter $\Phi = 5$ mm, length $l = 70$ mm). The height of the catalyst bed was 6-7 mm. The temperature control was carried out by a thermocouple located in the catalyst bed. The samples were activated in argon flow (40 $cm^3 \, min^{-1}$) at 673 K for 2 h (with a ramp of 15 K/min). Then, the temperature was decreased to that of the reaction. The reactant mixture of $Ar/O_2/CH_3OH$ (88/8/4 mol %) was supplied at the rate of 40 cm^3 min^{-1}. The external (inspected by tests with the use of different volumes of catalysts and constant granular size of catalysts and contact time) and internal (inspected by tests with the use of different granular sizes of catalyst and constant volume of catalyst and contact time) diffusion do not limit the reaction rate at these conditions. Methanol (Chempur, Poland) was introduced to the flow reactor by bubbling argon gas through a glass saturator filled with methanol. The reactor effluent was analysed using two online gas chromatographs. One chromatograph, GC 8000 Top, was equipped with a capillary column of DB- 1, operated at 313 K, and a FID detector applied for analyses of organic compounds, while the other GC chromatograph containing Porapak Q and 5A molecular sieves columns (used for analyses of O_2, CO_2, CO, H_2O, and CH_3OH) had a TCD detector. The columns in the second chromatograph with TCD were heated according to the following program: 5 min at 358 K, temperature increase to 408 K (heating rate 5 K/min), 4 min at 408 K, cooling to 358 K (for the automatic injection on the column with 5A), 10 min at 358 K, temperature increase to 408 K (heating rate 10 K/min), and 11 min at 408 K. Argon was applied as a carrier gas. The outlet stream line from the reactor to the gas chromatograph was heated at about 373 K to avoid condensation of the reaction products. The selectivity, S_i, was calculated as the molar concentration of the indicated product, i, divided by the sum of the concentrations of all products detected, $S_i = c_i / \sum c \times 100$ %. The following products detected by FID and TCD detectors were taken into account: methanol, formaldehyde, methyl formate, dimethoxymethane, dimethyl ether, and carbon dioxide. The product distribution was illustrated by selectivities.

References

1 P. Schmidt-Winkel, W. W. Lukens, D. Zhao, P. Yang, B. F. Chmelka and G. D.

Stucky, *J. Am. Chem. Soc.*, 1999, **121**, 254–255.

2 J. Wisniewska, M. Ziolek, N. Artioli and M. Daturi, *J. Catal.*, 2016, **336**, 58–75.

3 J. Czaplinska, P. Decyk and M. Ziolek, *Appl. Catal. A Gen.*, 2015, **504**, 361–372.

Table S1. Comparison between the amount of platinum and silver in the bulk (estimated from ICP OES) and on the surface of the materials (calculated from XP spectra).

Catalyst	Bulk Pt [wt. %]	Bulk Ag [wt. %]	Surface Pt [wt. %]	Surface Ag [wt. %]
1Ag/M	-	0.7	-	0.4
2Ag/M	-	1.8	-	0.6
0.5Pt/M	0.5	-	0.2	
1Pt/M	1.0	-	1.4	-
0.5Pt1Ag/M	0.5	0.7	0.3	0.3
0.5Pt2Ag/M	0.5	1.1	0.3	0.5
1Pt2Ag/M	1.0	0.9	0.4	1.2
0.5Pt1Ag/NbM	0.5	0.8	0.2	0.5
0.5Pt2Ag/NbM	0.5	1.4	0.2	0.6
1Pt2Ag/NbM	1.0	1.3	0.3	0.8
0.5Pt1Ag/Si	0.5	1.0	0.3	0.5
0.5Pt2Ag/Si	0.5	1.4	0.3	0.8
1Pt2Ag/Si	1.0	1.4	0.4	0.7

Table S2. The results of methanol oxidation on the selected samples

Catalyst	Temp. [K]	MeOH conv., [%]	Selectivity [%]				
			CO_2	HCHO	$HCOOCH_3$	CH_2CH_2	CH_2OCH_2
NbMCF-Ar	323	0	0	0	0	0	0
	373	0	0	0	0	0	0
	423	0	0	0	0	0	0
	473	8	12	72	6	6	4
	523	8	23	33	36	0	8
0.5Pt/M-Ar	373	100	98	0	2	0	0
	423	100	100	0	0	0	0
	473	100	100	0	0	0	0
2Ag/M-Ar	323	0	0	0	0	0	0
	373	0	0	0	0	0	0
	423	1	20	0	80	0	0
	473	79	43	1	56	0	0
	523	89	55	1	44	0	0
2Ag/M-H_2	323	0	0	0	0	0	0
	373	11	0	0	97	3	0
	423	8	6	0	94	0	0
	523	97	97	0	3	0	0
0.5Pt2Ag/M-Ar	323	0	0	0	0	0	0
	373	100	37	4	59	0	0
	423	100	27	0	73	0	0
	473	74	68	15	17	0	0
0.5Pt2Ag/M-H_2	323	4	0	0	92	8	0
	373	35	5	3	92	0	0
	423	100	95	0	0	5	0
	473	100	100	0	0	0	0
0.5Pt2Ag/NbM-Ar	323	18	0	0	93	7	0
	373	17	0	0	97	3	0
	423	99	78	8	13	1	0
	473	85	71	17	12	0	0
	523	91	69	18	12	0	0
0.5Pt2Ag/NbM -H_2	323	0	0	0	0	0	0
	373	3	6	8	86	0	0
	423	100	94	0	6	0	0
	473	100	100	0	0	0	0
0.5Pt2Ag/Si-Ar	333	100	77	0	23	1	0
	373	100	63	0	36	1	0

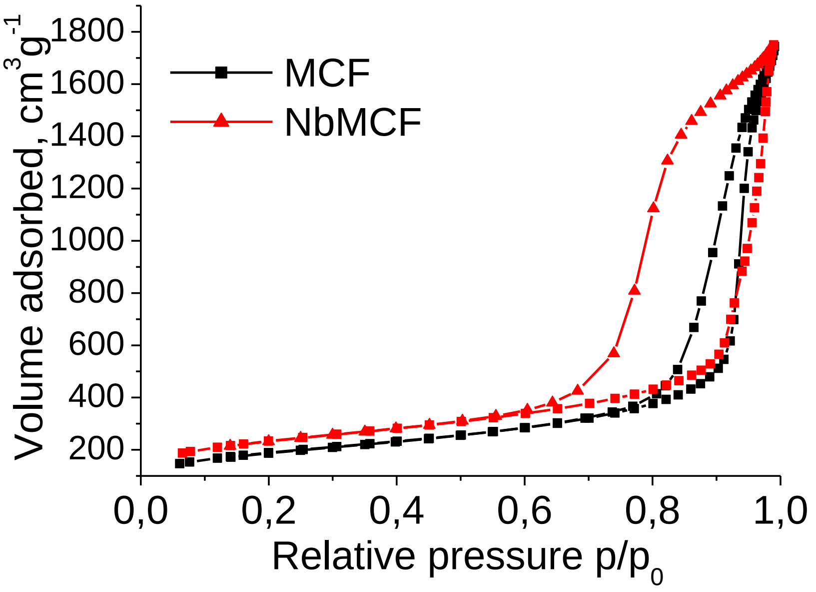


Fig. S1. Nitrogen adsorption/desorption isotherms of the supports (MCF and NbMCF).

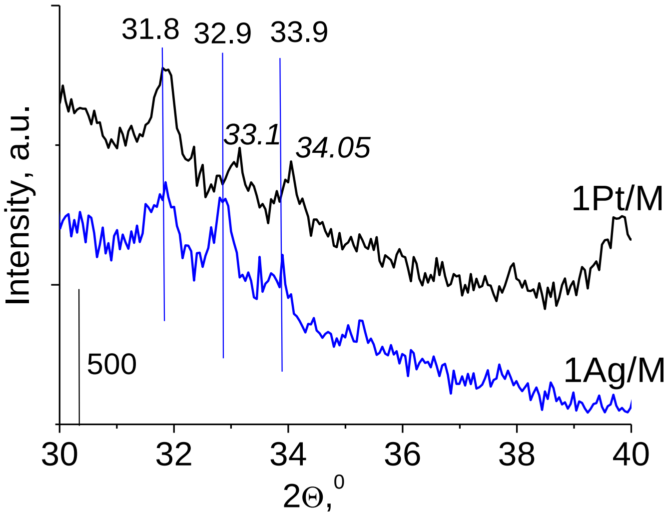
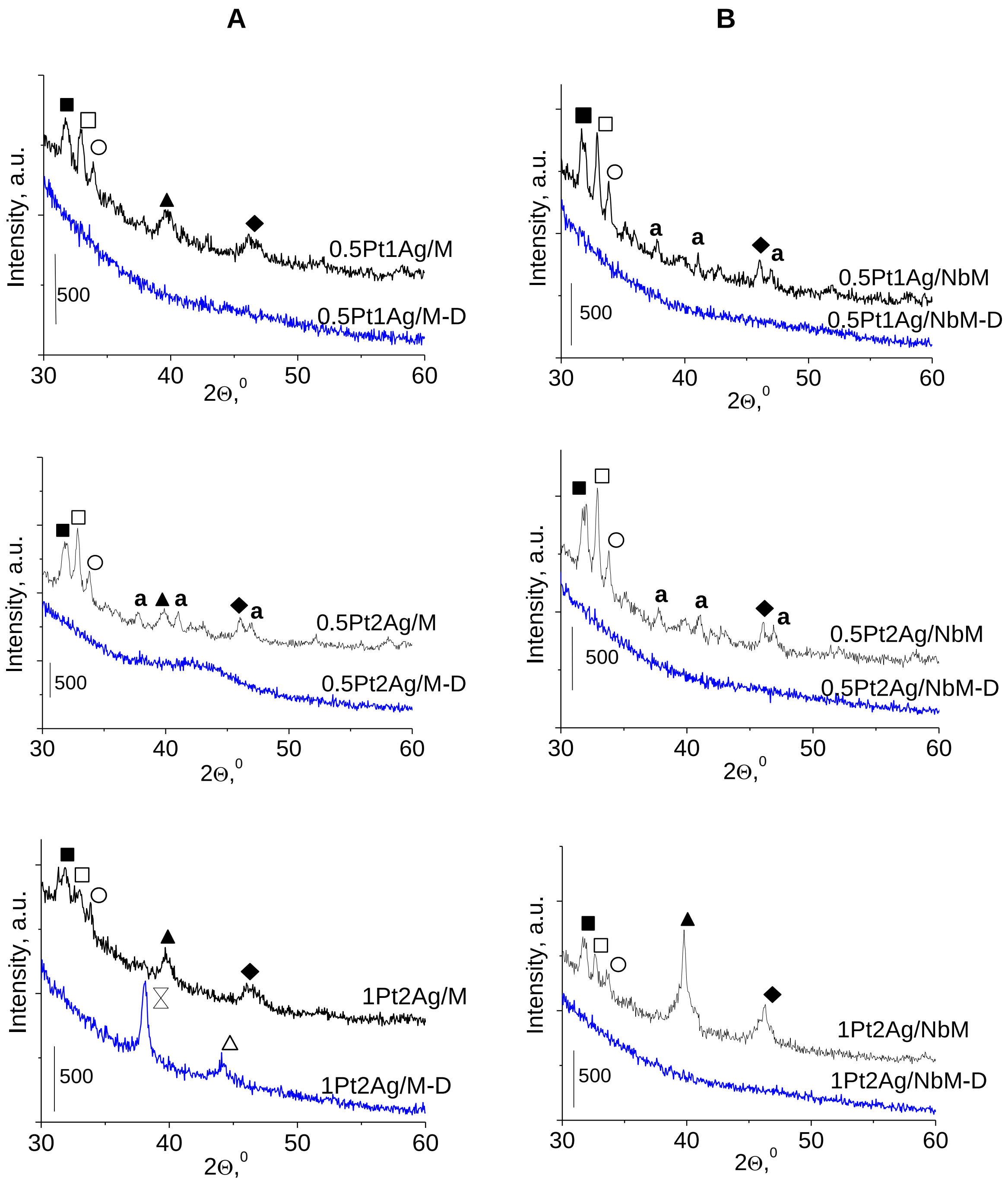


Fig. S2. Comparison of XRD patterns for platinum and silver oxides loaded on MCF after calcination at 773 K.


A
B
Intensity, a.u.
2Θ,⁰
30
40
50
60
500
■
□
○
▲
◆
a
0.5Pt1Ag/M
0.5Pt1Ag/M-D
0.5Pt1Ag/NbM
0.5Pt1Ag/NbM-D
0.5Pt2Ag/M
0.5Pt2Ag/M-D
0.5Pt2Ag/NbM
0.5Pt2Ag/NbM-D
1Pt2Ag/M
1Pt2Ag/M-D
⧖
△
1Pt2Ag/NbM
1Pt2Ag/NbM-D

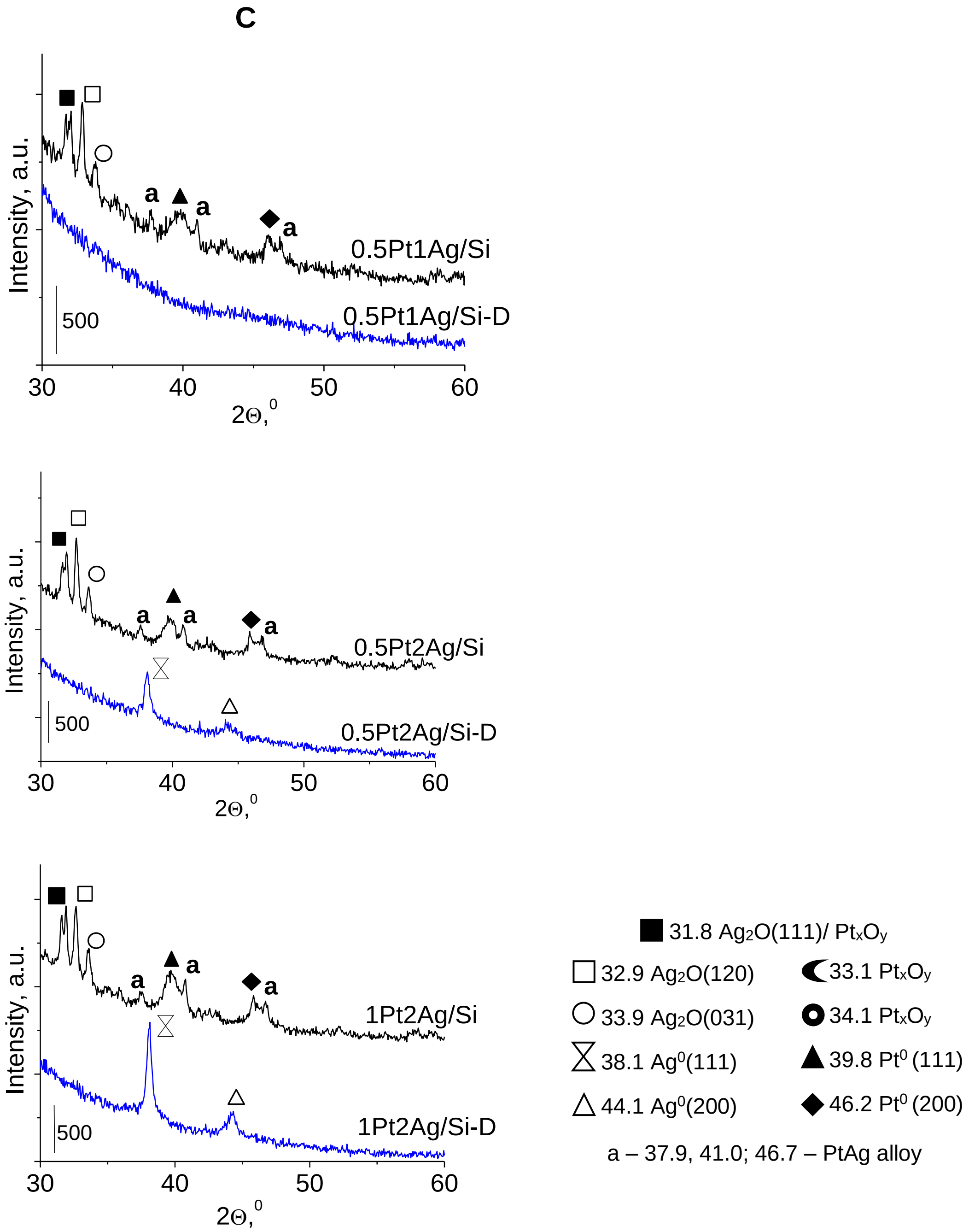


Fig. S3. XRD patterns of bimetallic samples: dried at 333 K (denoted D) and calcined at 773 K based on: **A**-MCF, **B**- NbMCF, **C**- amorphous silica.

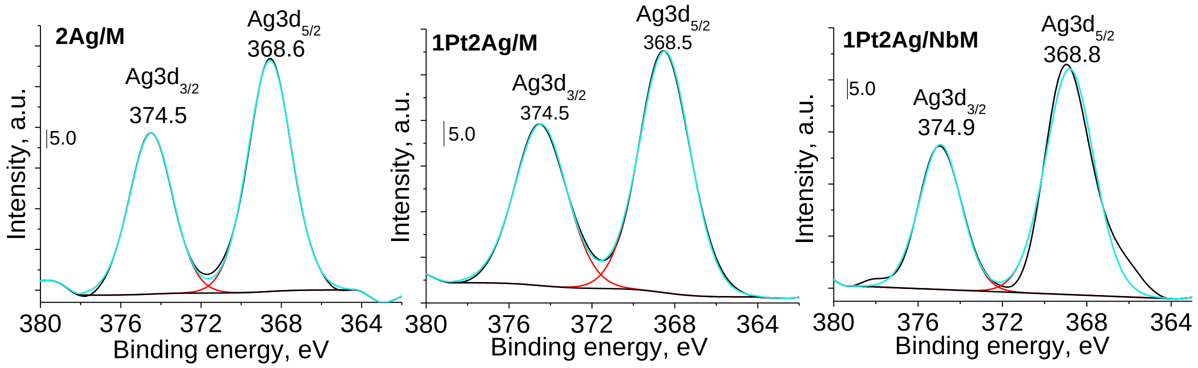


Fig. S4. Ag 3d XP spectra of monometallic and bimetallic samples with the highest metal loadings (the samples after calcination in air at 773 K).

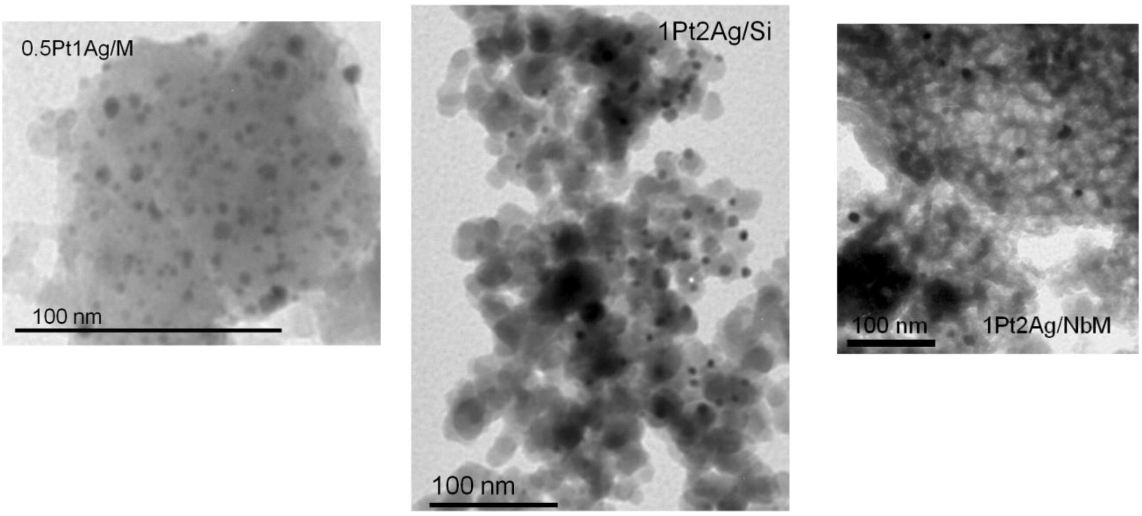
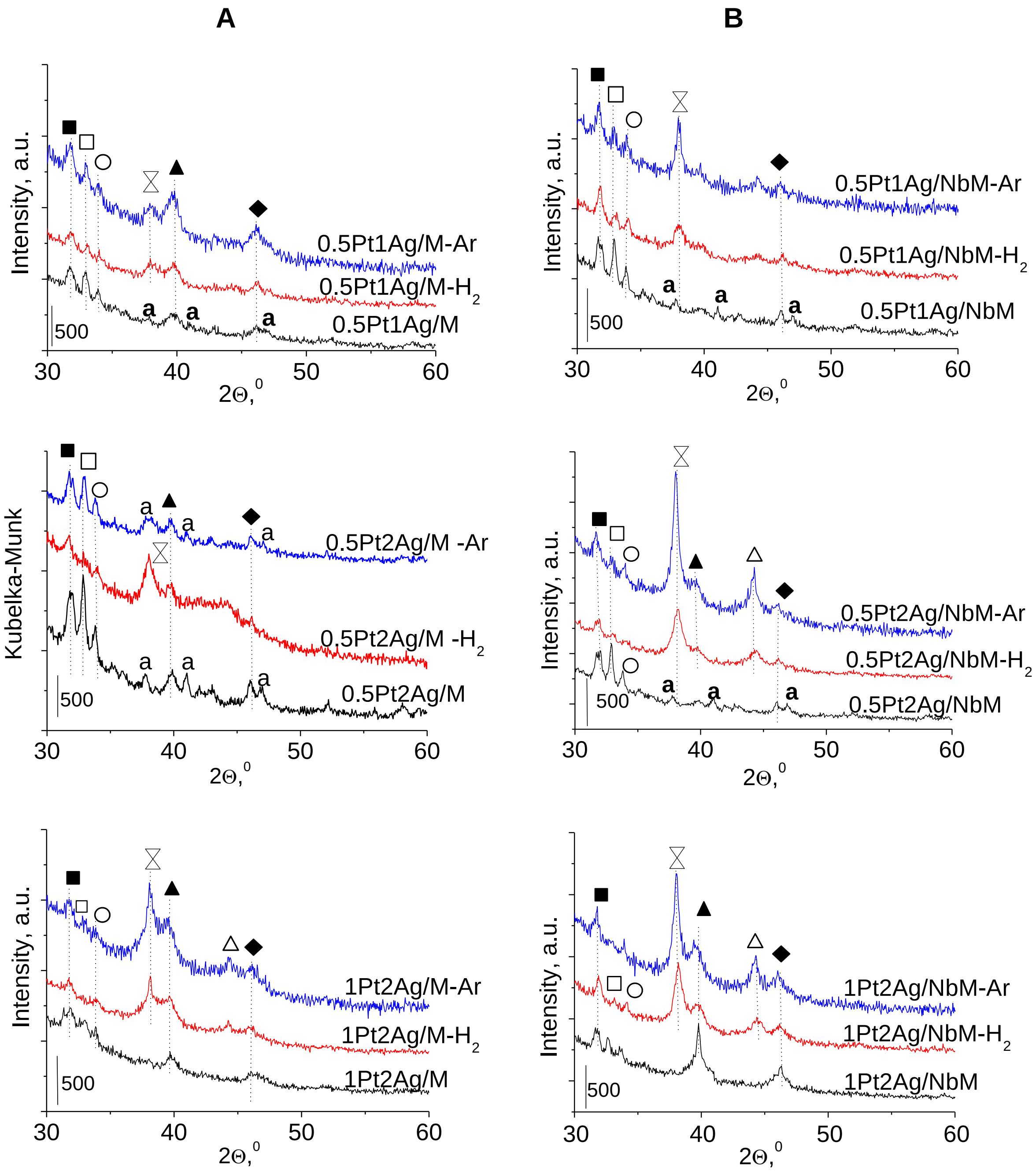


Fig. S5. TEM images of the selected materials.


A
B
Intensity, a.u.
Kubelka-Munk
2Θ,⁰
30
40
50
60
500
■
□
○
▲
△
◆
a
0.5Pt1Ag/M-Ar
0.5Pt1Ag/M-H2
0.5Pt1Ag/M
0.5Pt1Ag/NbM-Ar
0.5Pt1Ag/NbM-H2
0.5Pt1Ag/NbM
0.5Pt2Ag/M -Ar
0.5Pt2Ag/M -H2
0.5Pt2Ag/M
0.5Pt2Ag/NbM-Ar
0.5Pt2Ag/NbM-H2
0.5Pt2Ag/NbM
1Pt2Ag/M-Ar
1Pt2Ag/M-H2
1Pt2Ag/M
1Pt2Ag/NbM-Ar
1Pt2Ag/NbM-H2
1Pt2Ag/NbM

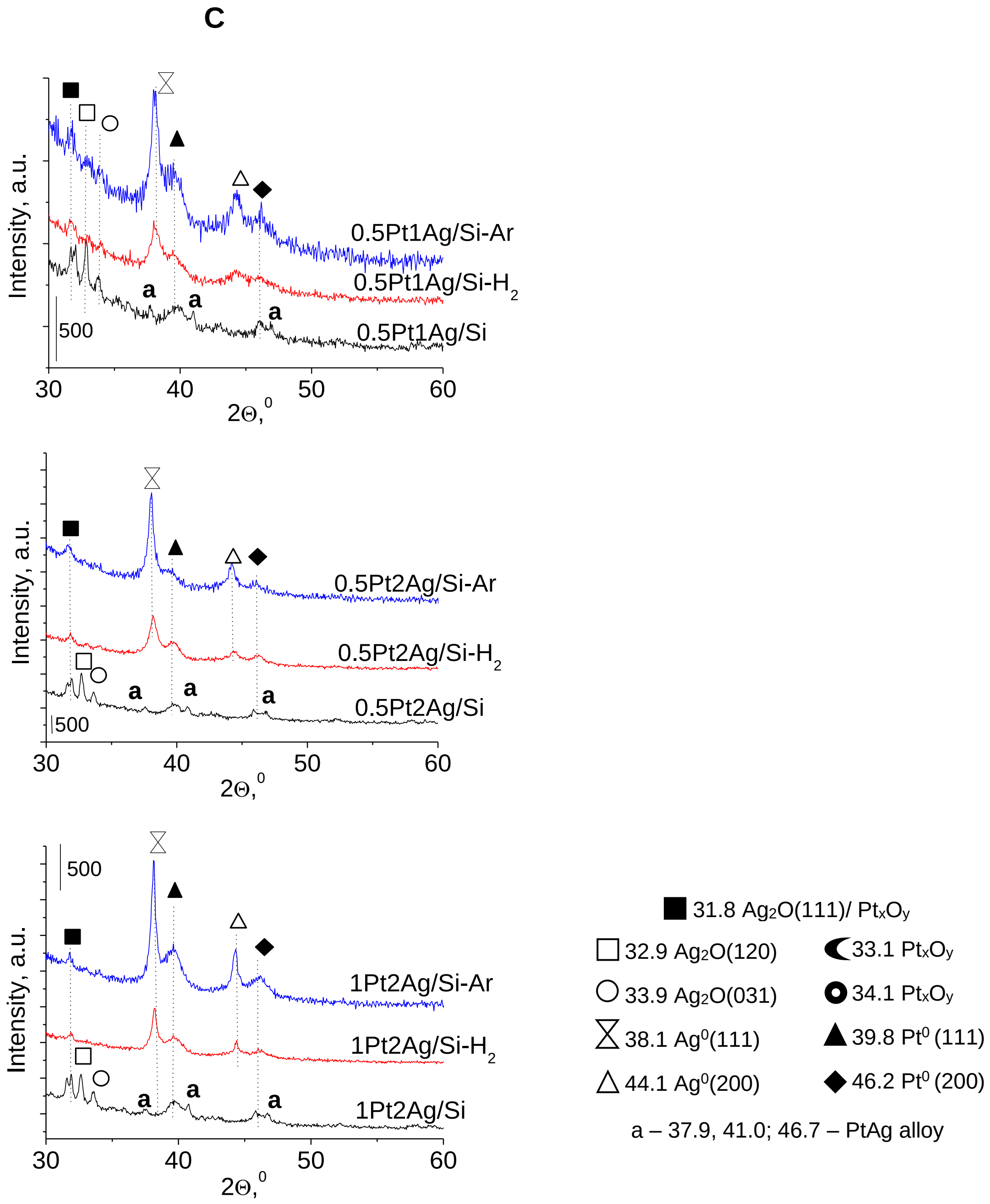


Fig. S6. XRD patterns of bimetallic samples: calcined at 773 K and after activation at 673 K in Ar or H_2 flow (**A**- based on MCF, **B**-based on NbMCF, **C**- based on amorphous silica).

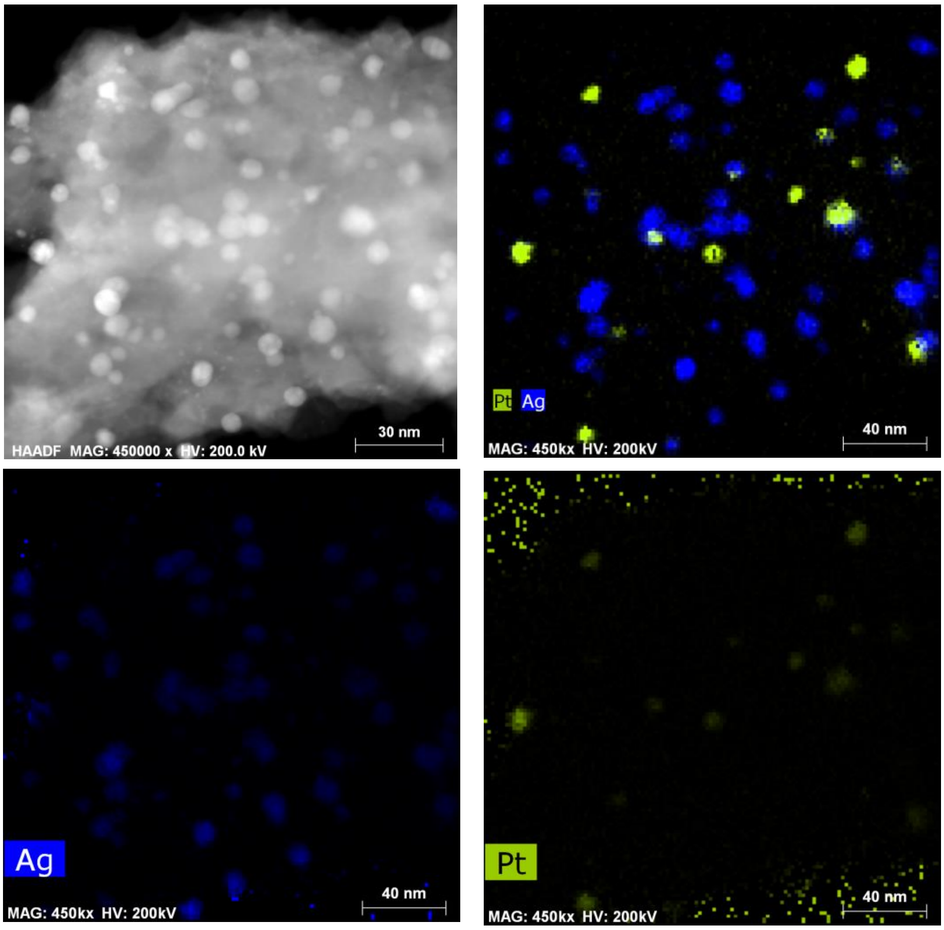


Fig. S7. HAADF-STEM images and EDX analysis of 0.5Pt2Ag/M after activation at 673 K in H_2 flow.

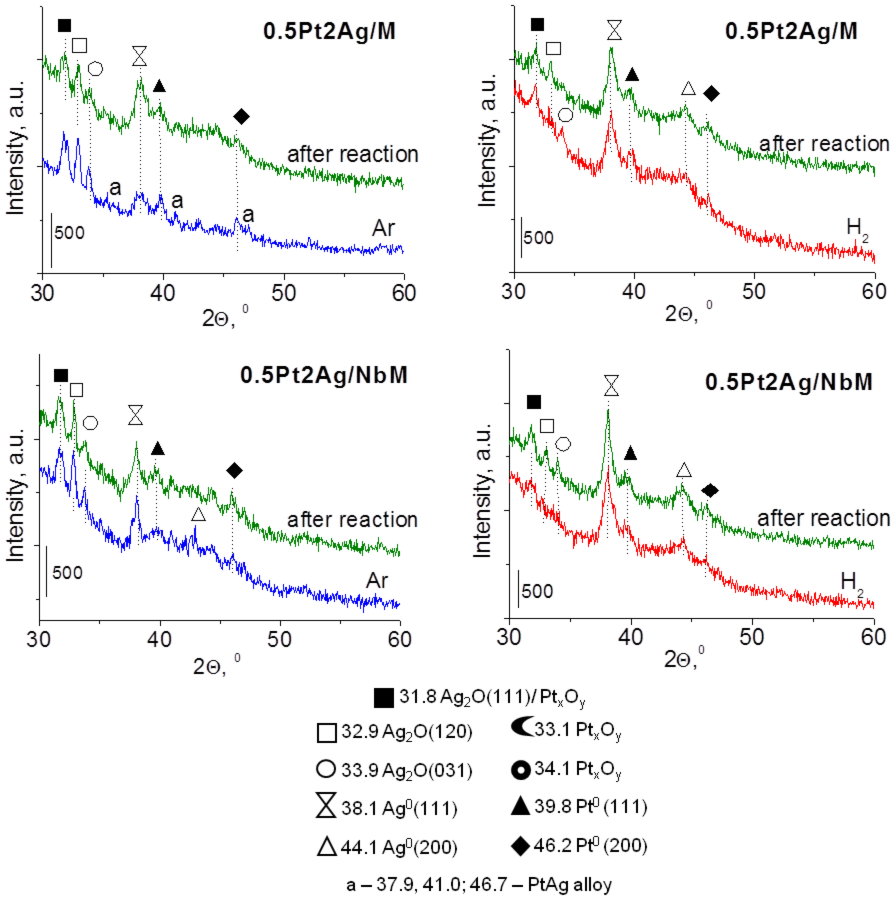


Fig. S8. XRD patterns of the catalysts before and after oxidation of methanol.