

## Supporting Information

### Direct Methane Oxidation over Pt-modified Nitrogen-Doped Carbons

Mario Soorholtz,<sup>a</sup> Robin J. White,<sup>\*b,c</sup> Tobias Zimmermann,<sup>a</sup> Maria-Magdalena Titirici,<sup>b</sup> Markus Antonietti,<sup>b</sup> Regina Palkovits<sup>\*a,d</sup> and Ferdi Schüth<sup>\*a</sup>

<sup>a</sup> Max-Planck-Institut für Kohlenforschung, Kaiser-Wilhelm-Platz 1, 45470 Mülheim an der Ruhr, Germany. Fax: +49 208 306 2995; Tel: +49 208 306 2373; E-mail: schueth@mpi-muelheim.mpg.de

<sup>b</sup> Max-Planck-Institute of Colloids and Interfaces, Am Mühlenberg 1, 14476 Potsdam, Germany. Fax: +49 331 567 9502; Tel: +49 331 567 9508; E-mail: robin.white@mpikg.mpg.de

<sup>c</sup> Technische Universität Berlin, Fakultät II, Institut für Chemie, Sekretariat BA 2, Hardenbergstraße 40, 10623 Berlin, Germany. Fax: +49 30 314 29271; Tel: +49 30 314 28767; E-mail: robin.j.white@tu-berlin.de (current address)

<sup>d</sup> RWTH Aachen, Worringerweg 1, 52074 Aachen, Germany. Fax: +49 241-80-22177; Tel: +49 241 80 26497; E-mail: palkovits@itmc.rwth-aachen.de

### Experimental Details

Nitrogen-doped carbons<sup>1-3</sup> (NDC) (*i.e.* crustacean exoskeletons of lobsters (ExLOB) and nitrogen-doped carbon aerogel (NCA)), Covalent Triazine Framework (CTF)<sup>4</sup> and dichlorobipyrimidyl platinum(II) (Pt(bpym)Cl<sub>2</sub>)<sup>5</sup> were synthesized as described elsewhere. For the coordination of platinum, analogous to the method of P. M. Kiernan *et al.*<sup>5</sup>, 400 mg of the carbon material was added to 1 L water that contained 46 mg of dissolved K<sub>2</sub>PtCl<sub>4</sub>. The mixture was stirred for 24 h at room temperature. After filtration, the solid was extensively washed with water to remove non-coordinated Pt species.

Initial screening followed a method similar to that given by Periana *et al.*<sup>6</sup> Using a simple batch set-up, 60 mg of catalyst and 15 mL Oleum (20 wt.% SO<sub>3</sub>) were given into an autoclave (Hastelloy C), which was flushed with Ar, pressurized with 45 bar CH<sub>4</sub> and heated to 215°C for 2.5 h. After cooling, the gas phase was analyzed by FT-IR, the solid catalyst was filtered off and an aliquot of the reaction mixture (10 mL) was slowly added to 20 mL of H<sub>2</sub>O. After hydrolysis at 90°C for 3 h, the methanol content was determined by HPLC. For recycling tests, the catalyst was filtered off, washed with water (500 mL) and acetone (90 mL) and dried in a vacuum oven at 50°C. TONs were calculated from the ratio of produced methanol and Pt content of the catalyst prior to reaction determined

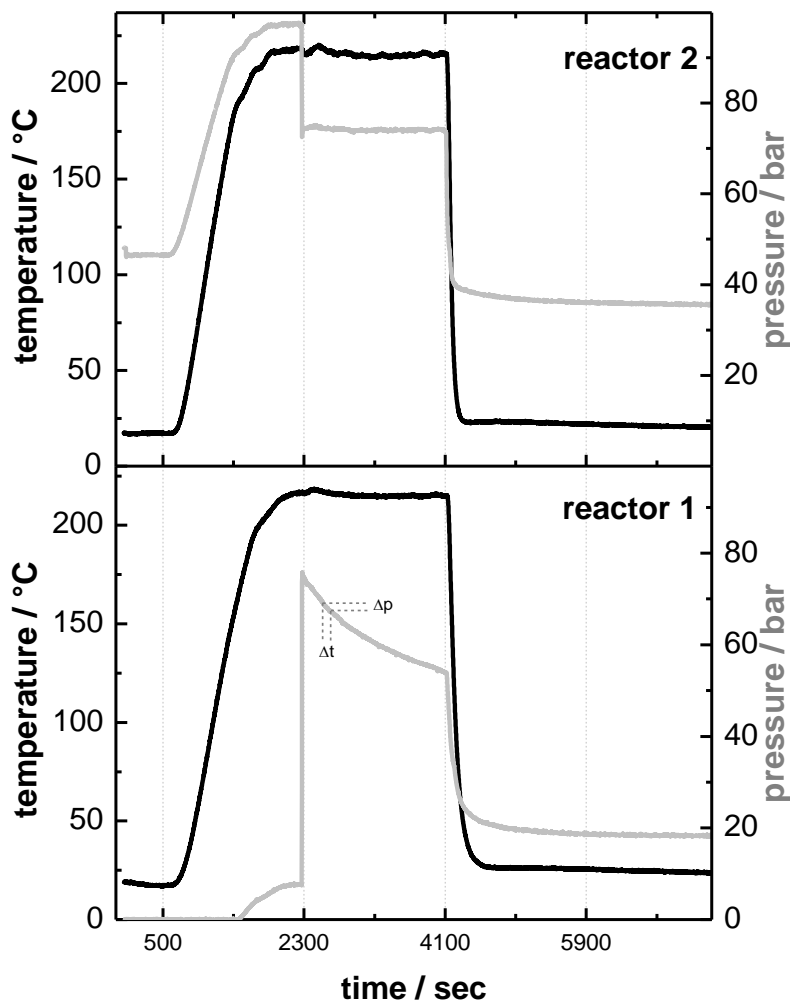
by elemental analysis (atomic absorption spectroscopy). TONs in recycling experiments were corrected for mass loss (10-15 wt.%) induced by filtration and elemental analysis. Calculated TONs should not be taken as face value since catalytic performances are influenced by catalytic reaction during heating period before reaching reaction temperature, different amounts of catalytic material in subsequent runs and different ranges of achieved pressure drops, *i.e.* different consumption of SO<sub>3</sub> until termination of reaction. Therefore, catalytic results are indicated as “apparent TON”. However, given results indicate the applicability of investigated materials in methane oxidation using sulfuric acid as reaction medium.

Catalytic tests for the determination of reaction rates (turnover frequencies) were performed in a modified set-up. The set-up consisted of a Hastelloy autoclave that was partially filled with 15 mL oleum (20wt.% SO<sub>3</sub>), catalyst (10 μmol Pt equivalents) and subsequently flushed with argon. After heating the autoclave to reaction temperature, that induced an autogenous pressure increase, preheated methane from a second autoclave was added to start the reaction (Scheme 1S). The pressure drop as a result of conversion of methane to methylbisulfate could be monitored via pressure indicators. The volumes of both reactors were precisely determined. Due to the relatively high pressure applied in the experiments, the Benedict–Webb–Rubin (BWR) equation was used in the calculations of amounts of gases instead of the ideal gas law.<sup>7</sup> Dissolution of methane into sulfuric acid was assumed to be negligible. Methane oxidation was carried out for 30 minutes before the reactor was quenched in a water bath. Subsequently, the gas phase was quantified by FT-IR, while the liquid phase was filtrated, hydrolyzed and analyzed by HPLC as mentioned above.

Turnover frequencies were calculated either from the pressure drop from 69 to 67.5 bar or from the amount of methanol produced within 30 minutes. The first method is preferable, since rates are compared at identical degree of conversion for different catalysts. The method implies that the pressure drop corresponds only to oxidation of methane to methylbisulfate, *i.e.* selectivity equals one, which is reasonable, since the used catalysts achieved high selectivities to methylbisulfate in the early phases of the reaction. Significant overoxidation to CO<sub>2</sub>, which would influence the pressure, only occurs at

long reaction times, and the consumption of  $\text{SO}_3$  which would also influence pressure, is negligible at this level of conversion.

Comparison of both methods (see TOFs in Table 1) shows that values for respective catalysts are in the same range, indicating that the determination of TOFs from the pressure drop from 69 to 67.5 bar is reasonable. Differences between respective values can be explained by different degrees of considered conversions. Especially, for large pressure drops (high conversions), the reaction rate is significantly influenced by *e.g.* its pressure dependency and consumption of  $\text{SO}_3$ . Thus, the larger the conversion, the larger the difference in TOFs determined via both methods.



**Scheme 1S** Procedure for the determination of reaction rates. Lower graph shows the range for pressure drop that was used for the calculation of turnover frequencies from

69 to 67.5 bar; reactor 1: autoclave containing oleum and catalyst prior to reaction start, reactor 2: autoclave containing methane.

### ***Characterization Details***

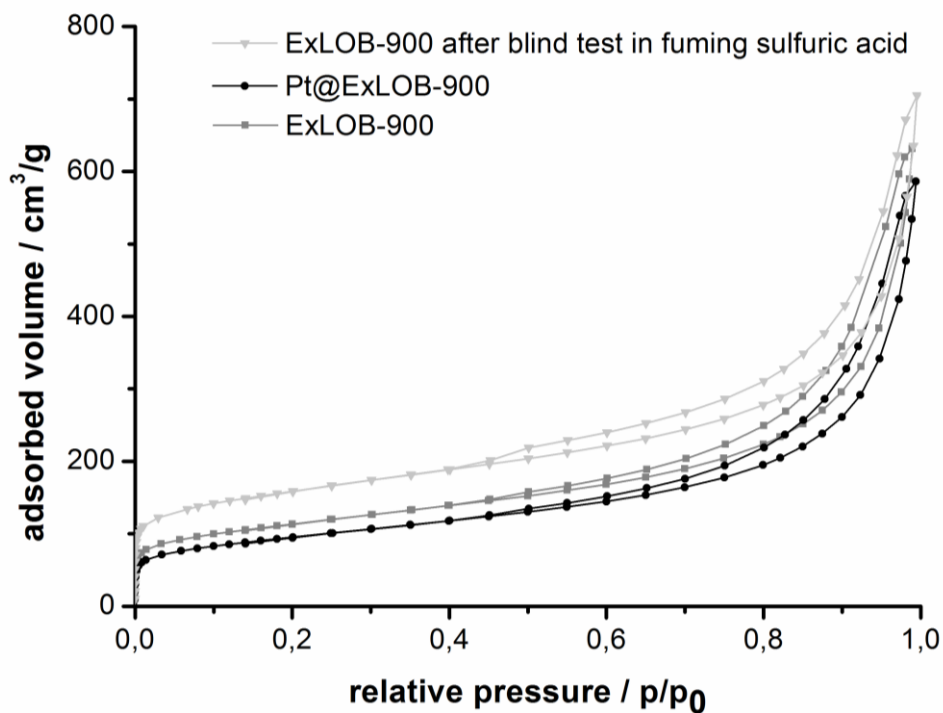
Nitrogen sorption measurements were carried out at 77 K on a Micrometrics ASAP 2010 instrument. Samples were activated under vacuum for at least 15 h at 150 °C. XPS (x-ray photoelectron spectroscopy) measurements were performed with a Kratos HSi spectrometer with a hemispherical analyzer. The monochromatized Al K $\alpha$  X-ray source (E=1486.6 eV) was operated at 15 kV and 15 mA. For the narrow scans, an analyzer pass energy of 40 eV was applied. The hybrid mode was used as lens mode. The base pressure during the experiment in the analysis chamber was  $4 \times 10^{-7}$  Pa. To consider surface charging effects of carbonized samples, the binding energy values were referenced to the graphitic C 1s carbon peak at 284.5 eV. Thermal stability of ExLOB-900 was investigated by TG-DTA using a Netzsch STA 449C thermal analyzer by keeping the temperature isothermal at 200 °C for 24 h in a flow of air of ca. 60 mL min<sup>-1</sup>. SEM (scanning electron microscopy) images were recorded on a Gemini Scanning Electron Microscope.

### ***References***

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6. R. A. Periana, D. J. Taube, S. Gamble, H. Taube, T. Satoh and H. Fujii, *Science*, 1998, **280**, 560-564.
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## Supplementary Results:

### Nitrogen sorption



**Figure 1S** Nitrogen sorption isotherms of *ExLOB-900* before a blind test in oleum (20 wt.% SO<sub>3</sub>), after the blind test and after Pt coordination.

**Table 1S** Porous properties of *ExLOB-900* before and after treatment with fuming sulfuric acid (20 wt.% SO<sub>3</sub>), respectively.

material	S <sub>BET</sub> [m <sup>2</sup> g <sup>-1</sup> ] <sup>[a]</sup>	V <sub>pore</sub> [cm <sup>3</sup> g <sup>-1</sup> ] <sup>[b]</sup>	V <sub>mesopore</sub> [cm <sup>3</sup> g <sup>-1</sup> ] <sup>[c]</sup>
<i>ExLOB-900</i>	401	0.77	0.76
<i>ExLOB-900</i> after oleum treatment	556	0.79	0.68

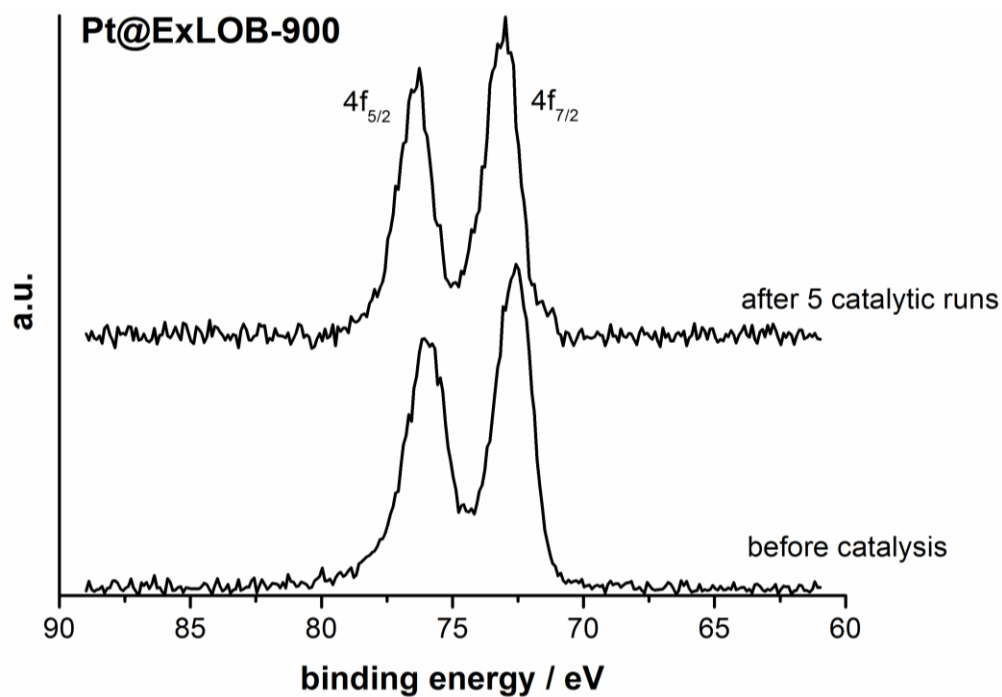
[a] BET equivalent surface area at 0.05 < p/p<sub>0</sub> < 0.2 [b] Total pore volume at p/p<sub>0</sub> = 0.97 [c] Mesoporous volume from BJH method and N<sub>2</sub> adsorption data for pores between 2-50 nm.

**Table 2S** Porous properties of unmodified and Pt-modified NDC prior to catalysis.

material	$S_{\text{BET}}$ [ $\text{m}^2\text{g}^{-1}$ ] <sup>[a]</sup>	$V_{\text{pore}}$ [ $\text{cm}^3\text{g}^{-1}$ ] <sup>[b]</sup>	$V_{\text{mesopore}}$ [ $\text{cm}^3\text{g}^{-1}$ ] <sup>[c]</sup>
Pt@ExLOB-900	339	0.66	0.62
ExLOB-900	401	0.77	0.76

[a] BET equivalent surface area at  $0.05 < p/p_0 < 0.2$  [b] Total pore volume at  $p/p_0 = 0.97$   
[c] Mesoporous volume from BJH method and  $\text{N}_2$  adsorption data for pores between 2-50 nm.

XPS (X-ray photoelectron spectroscopy)

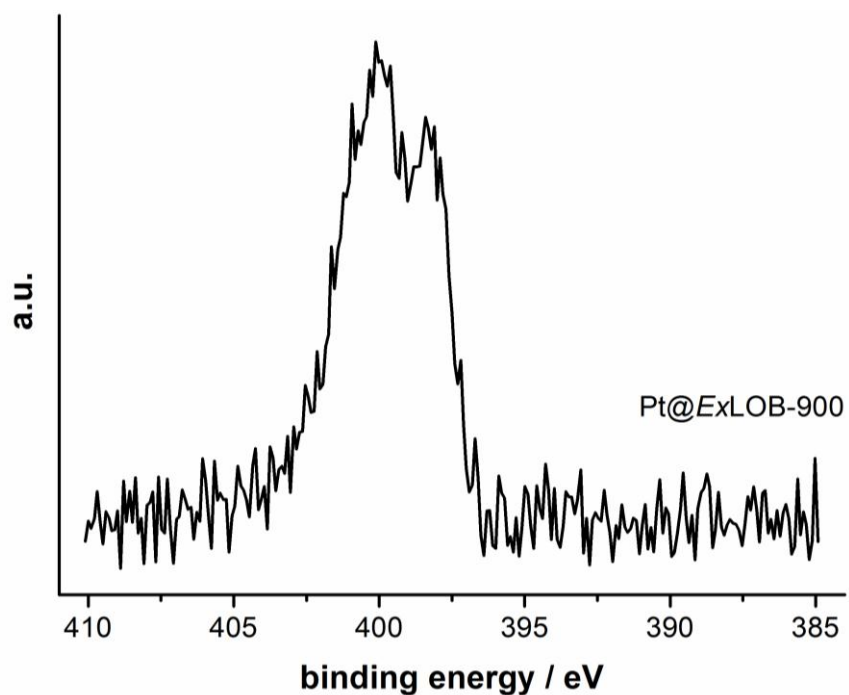


**Figure 2S** XPS Pt 4f spectra for Pt@ExLOB-900 before and after use in catalysis.

**Table 3S** Binding energy values (Pt 4f<sub>7/2</sub>) of Pt-modified NDC before and after catalysis.

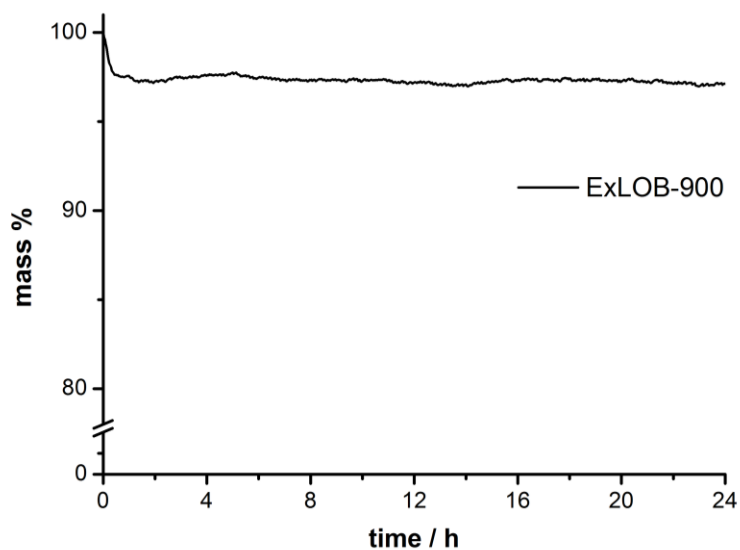
material	binding energy (Pt 4f <sub>7/2</sub> ) / eV <sup>[a]</sup>
Pt@ExLOB-900	72.6
Pt@ExLOB-900 after 5 catalytic runs	72.7

[a] Dependency of the degree of electron bond polarization between nearest neighbor atoms can cause deviations of given binding energies from Pt<sup>2+</sup> reference materials (*e.g.* K<sub>2</sub>PtCl<sub>4</sub>)



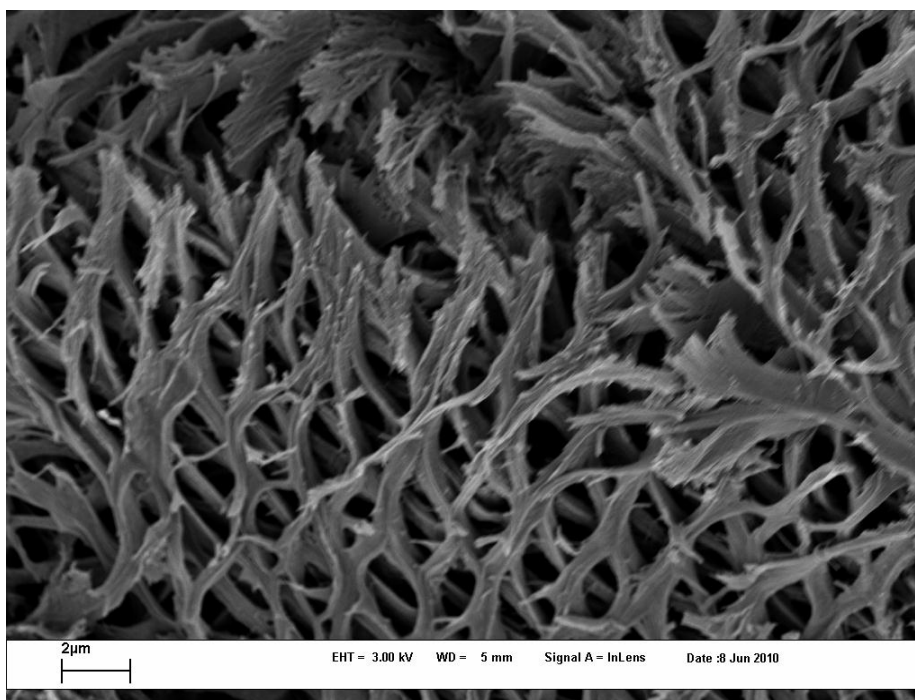
**Figure 3S** XPS N 1s spectra for Pt@ExLOB-900 before catalysis.

### Thermogravimetry



**Figure 4S** Long term thermal stability of *ExLOB-900* in air (60 mL/min) at 200°C.

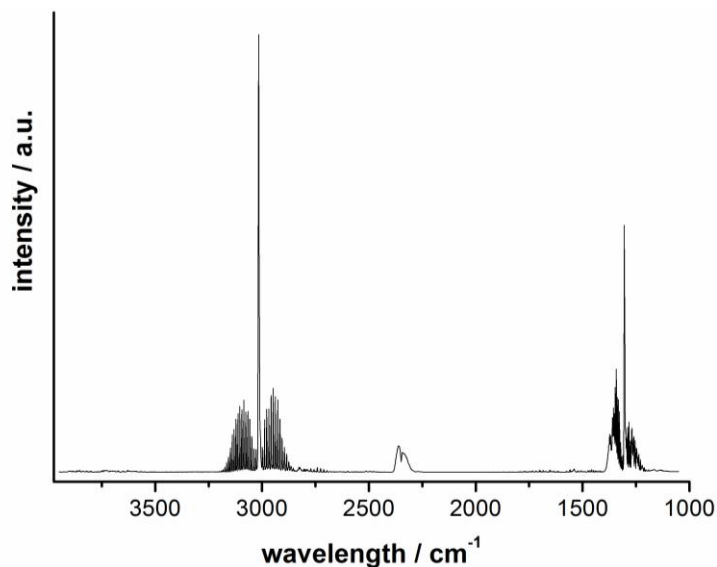
### Scanning Electron Microscopy



**Figure 5S** SEM images of biomass-derived nitrogen-doped carbon material (*i.e.* *ExLOB-900*).



## Gas phase analysis



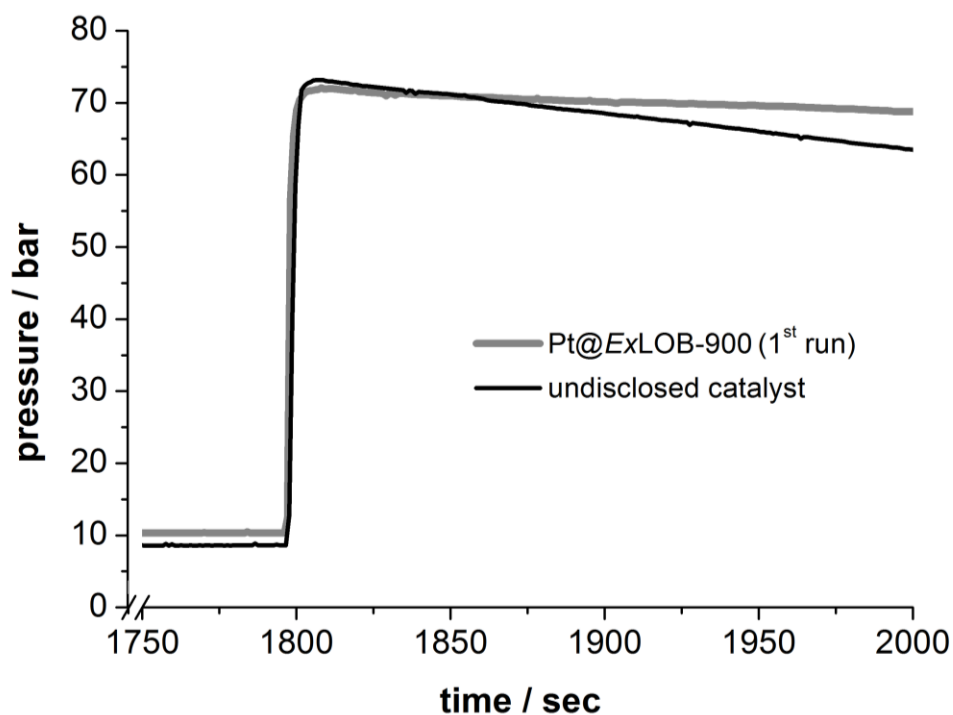
**Figure 6S** Typical gas phase FT-IR spectrum after reaction.

## Additional catalytic data for determination of reaction rates

**Table 4S** Additional catalytic data for determination of turnover frequencies (TOFs) in a modified autoclave set-up as described before (*Experimental Details*).

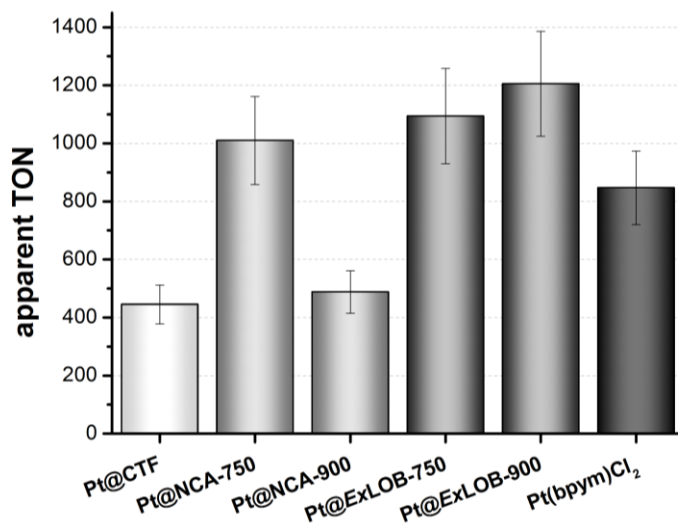
entry	catalyst	mass catalyst (mg)	Pt loading (wt.%)	produced methanol after hydrolysis (mol)	TOF (h <sup>-1</sup> ) <sup>a</sup>	TOF (h <sup>-1</sup> ) <sup>b</sup>
1	Pt@CTF	40	5.41	0.00129	174	233
2	Pt(bpym)Cl <sub>2</sub>	4.8	45.99	0.00441	912	779
3	Pt@ExLOB-900 (1 <sup>st</sup> run)	40	5.55	0.00698	2074	1227
4	Pt@ExLOB-900 (2 <sup>nd</sup> run)	16	6.01	0.00374	1938	1516
5	Pt@ExLOB-900 (3 <sup>rd</sup> run)	5.5	5.97	0.00152	1826	1802
6	Pt@ExLOB-900 (fresh catalyst)	5.5	5,55	0.00417	7020	5332

<sup>a</sup> Determined from pressure drop from 69 to 67.5 bar; <sup>b</sup> Determined from the amount of methanol produced within 30 minutes.

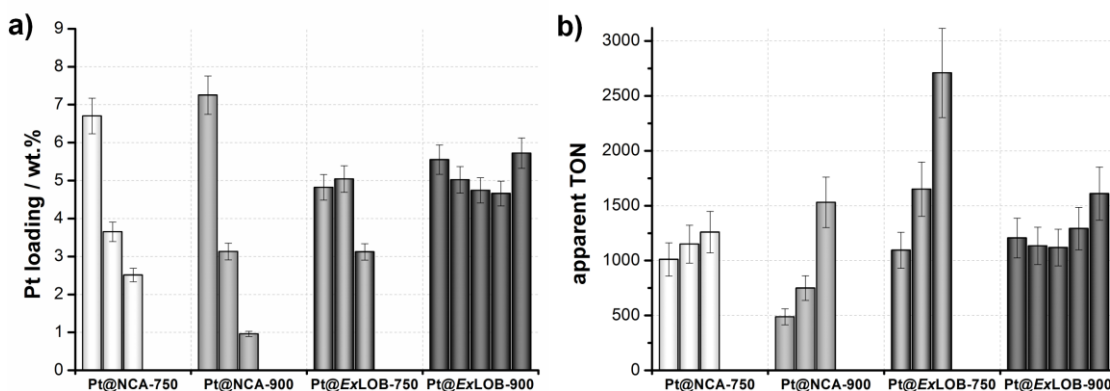


**Figure 7S** Pressure-time plots for Pt@ExLOB-900 (1<sup>st</sup> run) and a novel catalyst, the exact nature can not be disclosed yet due to a patenting process, which is still ongoing. The data clearly show that the novel catalyst achieves significant higher conversion of methane under the same reaction conditions indicated by the measured pressure drops. In particular, Pt@ExLOB-900 achieved a pressure drop rate of 0.9 bar min<sup>-1</sup> and the undisclosed catalyst a pressure drop rate of 3.0 bar min<sup>-1</sup>. The substantial difference in pressure drop rates clearly excludes the presence of mass transfer limitation of methane into the reaction solvent in the case of Pt@ExLOB-900.

### Additional results from screening for novel catalytic materials



**Figure 8S** Comparison of different catalytic materials tested in a simple batch-type autoclave set-up as mentioned above (*Experimental Details*). Apparent turnover number (TON) was calculated from the ratio of produced methanol and platinum content of the catalyst prior to reaction determined by elemental analysis.



**Figure 9S** Recycling experiments of novel catalytic materials in a batch-type autoclave set-up (three runs each or five runs for Pt@ExLOB-900, respectively): a) Pt loading prior to experiment run. b) Achieved apparent turnover numbers within reaction time.