



Influence of Chromium Carbide-Derived Carbon Support and Ceria Nanocrystals on Pt–CeO₂/C Catalysts for Fuel Cell Applications

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The influence of different synthesis parameters on CeO₂ and Pt nanoparticle (NP) deposition on Ketjenblack carbon (C(KB)) was examined. The Pt NP diameter (3.1–4.1 nm) was not influenced by CeO₂ synthesis parameters. The CeO₂ NPs synthesized using ultrasound sonication contribute to a better durability of the Pt–CeO₂/C against CO poisoning. In contrast, CeO₂ synthesized using the microwave heating method contributes to better methanol oxidation reaction (MOR) activity at low electrode potential. Synthesis parameters of CeO₂ and Pt NPs developed for the C(KB)-based catalysts were applied for C(Cr₃C₂)-based catalysts. The Pt NP diameter of C(Cr₃C₂)-based catalysts was slightly higher (7.2 nm) as some Pt NPs were agglomerated. The C(Cr₃C₂) support facilitates the MOR and CO stripping, especially in the case of the Pt/C on C(Cr₃C₂) support. The MOR activity at 0.85 V of Pt NPs on the C(Cr₃C₂) support is as good as the MOR activity for the best Pt–CeO₂ on the C(KB) support. The C(Cr₃C₂) support also improves the CO removal from the Pt surface. All the synthesized catalysts had better MOR activity than the commercial Pt/C (Vulcan) catalyst. The oxygen reduction reaction activity of Pt–CeO₂/C catalysts with higher CeO₂ content synthesized with the microwave heating method was very good.

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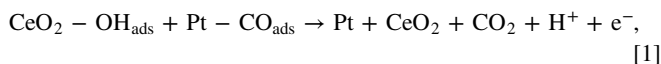
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Proton exchange membrane (PEM) hydrogen fuel cell (FC) is a promising technology for mobile vehicles with no carbon dioxide emission. However, the oxygen reduction reaction (ORR) at the cathode of PEM hydrogen FC is sluggish,^{1–3} impurities in gas poison the catalyst layer,^{4,5} especially the anode side, and hydrogen gas storage limits the interior space of mobile vehicles. Therefore, there is room for the development of PEM direct alcohol FC,⁶ PEM ammonia FC,⁷ PEM dimethyl ether FC,^{8,9} and PEM direct hydrazine FC.¹⁰ However, PEM direct methanol (DM) FC and PEM direct ethanol FC have received the most attention due to their high energy density per volume and the suitability of DMFC anode catalysts also for PEM hydrogen FC application. According to the report of Alternative Fuels Data Center, USA,¹¹ a gallon of methanol contains 50% equivalent energy amount of a gallon of gasoline, and this is 80% higher than that of liquid hydrogen. Nevertheless, DMFC also has its challenges for commercialization. The most serious issue is the activity and durability of anode catalyst for methanol oxidation reaction (MOR).⁶

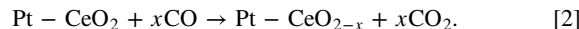
To improve the stability and electrochemical activity of the anode catalyst for DMFC, the combination of Pt and another metal or metal oxide should be used. The most common anode catalysts for PEMFC are the commercial PtRu/C catalysts.^{12–15} Nevertheless, the high cost of Ru prompts the demand to replace Ru with a different metal or metal oxide. Many studies on different types of Pt catalysts have been conducted, such as PtSn/C,¹⁶ PtCu alloy,¹⁷ Pt-Fe₂O₃,¹⁸ Pt-Ni/C,¹⁹ and PtCo/C.²⁰ The idea of using Pt coupled with a secondary metal or metal oxide is to weaken the bond between Pt and CO_{ads}, which deactivates the Pt active site.

Amongst choices for a secondary metal or metal oxide, cerium (IV) oxide (ceria) has gained a lot of interest due to its high oxygen storage capacity and high tolerance toward CO-like intermediates of MOR.^{21–24} In our previous study,²⁵ ceria particles were synthesized

by the modified solvothermal synthesis method using urea.²⁶ That synthesis method generated 30 μm grain-size flower-shaped ceria crystals, even if the ceria crystallite size was only 11 nm. However, even big grain-size CeO₂ particles contributed insignificantly to the catalytic synergistic effect of ceria at the Pt–CeO₂/C catalysts toward MOR as the most MOR active Pt–CeO₂/C in the previous study was barely higher than MOR activity of Pt/C synthesized using the same Pt deposition method. The removal of the poisoning CO_{ads} from the Pt surface can take place at the junctions between Pt and CeO₂, following the reactions (Eqs. 1 and 2):²⁷



and the oxidation of CO due to the fluorite structure of CeO₂ takes place parallel.



Therefore, the smaller CeO₂ crystals and better dispersion of CeO₂ can increase the CO oxidation rate and improve the stability of the Pt catalyst against the CO-like intermediates adsorption (blocking adsorption).

The parameters influencing the deposition of Pt nanoparticles (NPs) on the ceria-carbon support by the ethylene glycol (EG) reduction method were investigated in our previous study.²⁵ It was difficult to control the Pt deposition rate, e.g., control better the nucleation and growth of Pt NPs, in a one-pot synthesis using the combination of heating methods (ultrasound sonication, microwave radiation, and boiling). Therefore, in the previous study, the Pt NPs tended to agglomerate. Using only one heating method can simplify the synthesis method and enable better control of reaction parameters.

Although the role of catalytically active components (Pt and CeO₂) in a catalyst is important, the structure of carbon support affects the catalytic activity of the catalyst significantly.²⁸ The chromium carbide-derived carbon, noted as C(Cr₃C₂), synthesized

in our previous study²⁹ is an active material toward ORR in both acidic and alkaline environments due to its high number of active sites at the surface, large specific surface area, and unique micro-mesoporous structure. Therefore, it is a promising support material for MOR and ORR catalysts.

The influence of different carbon support materials and catalyst synthesis methods on the physical properties and electrochemical activity of MOR, CO oxidation and ORR activity on Pt–CeO₂/C was investigated in this study. The following hypotheses were set:

- If the Pt NP deposition method conditions are optimal, the deposition order of CeO₂ NPs, i.e., before the Pt NP deposition or co-deposition with Pt NPs and differences in the synthesis parameters of CeO₂ NPs, i.e., heating method, and Ce(NO₃)₃ concentrations do not influence the physical and electrochemical characteristics of Pt NPs deposited onto C(KB) support.
- The C(Cr₃C₂)-based catalysts are electrochemically more active toward MOR, CO stripping, and ORR if the same synthesis methods are used for the C(Cr₃C₂)-based and C(KB)-based catalysts to deposit Pt and CeO₂ NPs. The catalyst support influences the physical properties of Pt and CeO₂ NPs, such as particle size distribution (PSD), Pt dispersion, and the number of oxygen vacancies for CeO₂ NPs.

Experimental

Material synthesis.—*Synthesis of CeO₂-C and CeO₂ colloid.*—The first approach was to synthesize CeO₂/C, ceria-carbon, separately, and this material was used to deposit the Pt NPs later. In detail, the Ketjenblack carbon, C(KB), (FuelCellStore, Ketjenblack carbon EC-300J) was mixed with cerium (III) nitrate hexahydrate (Stream Chemicals, 99.9% - Ce) to synthesize the ceria-carbon material (11 wt% of CeO₂) using an ultrasound sonication bath. The 10 mol dm⁻³ NaOH solution was prepared from NaOH (Sigma-Aldrich, 99.99% metals basis, Semiconductor grade) and Milli-Q water (18.2 MΩcm at 25 °C). A suitable volume of 10 mol dm⁻³ NaOH was added to the EG (Lach-Ner, 99.98%) reaction solution to obtain the final concentration given in Table I. In order to synthesize 0.75 g of CeO₂/C material, a reaction volume was up to 197 cm³. Thereafter, the reaction was carried out in the ultrasound bath (Elmasonic P 30 H, at 37 kHz, 100% power) for 2 hours. After that, the reaction mixture was filtered and rinsed multiple times using Milli-Q water. The solid part was collected and dried at 100 °C and 50 mbar. This ceria-carbon material was used to synthesize the SL₂_Pt–CeO₂/C(KB). The specific synthesis parameters are given in Table I.

The second approach was to synthesize the CeO₂ colloid solution. The CeO₂ and Pt NPs were deposited onto the carbon support at the same time using the corresponding colloid solution. In detail, the colloidal ceria solution was synthesized using either ultrasound sonication³⁰ or microwave method²⁴ with appropriate NaOH concentration in EG solution. Cerium(III) nitrate was mixed with EG. A solution of 10 mol dm⁻³ NaOH was used to prepare the NaOH solution with the required concentration. A volume of 10 mol dm⁻³

NaOH in Milli-Q water was diluted in EG and added slowly into the reaction mixture to obtain the final concentration shown in Table I. As the concentrated NaOH solution was used for the synthesis, the volume percent of water was small and constant. The final volume for the synthesis mixture was 46.5 cm³. Then, the reaction mixture was either microwave or ultrasound-treated. The parameters applied are given in Table I. The reaction mixture was microwave-treated 78 s three times to complete the formation of CeO₂ colloid. The interval between each microwave heating was 30 minutes to cool down the solution to room temperature. The obtained solution was shaken well by hand and used to prepare Pt–CeO₂/C catalysts.

Synthesis of Pt colloid.—The following procedure was used in the typical synthesis of Pt colloid. Firstly, a stock Pt solution was prepared by dissolving 126 mg of H₂PtCl₆ · 6 H₂O in 1 cm³ of Milli-Q water. 200 cm³ of EG was transferred into a 500 cm³ synthesis flask. 10 mol dm⁻³ NaOH was prepared by dissolving the required NaOH amount in Milli-Q water. Then, 0.743 cm³ of 10 mol dm⁻³ NaOH was transferred into the synthesized flask. 0.846 cm³ of the stock Pt solution and 10 cm³ Milli-Q water were transferred into a small beaker. The synthesis flask was set up with the refluxing system and oil bath. The reaction solution was mixed well using the hot plate with a magnetic stirrer. The argon gas (AS Linde Gas, 99.9999%) was bubbled through the reaction solution. After bubbling with argon gas for 15 min, the diluted Pt solution was pumped slowly into the reaction mixture by using a syringe pump. Then, the syringe was rinsed three times using 22.4 cm³ of Milli-Q water. Therefore, the reaction mixture contained 200 cm³ of EG and 34 cm³ of water in total. The final concentration of the chemicals is given in Table II. The reaction mixture was heated up to 100 °C and was kept at this temperature for 2 hours. The dark brown solution formed was the Pt colloidal solution containing 40 mg of Pt.

Synthesis of Pt–CeO₂/C catalysts.—The C(KB) and a C(Cr₃C₂) synthesized at 900 °C²⁹ were used for the preparation of Pt–CeO₂/C and Pt/C materials. The C(Cr₃C₂) was ball-milled at 300 rpm for 45 minutes. Depending on the calculated amount of CeO₂ colloid in the previous step, carbon amount around 120–160 mg was weighed to synthesize corresponding 20 wt% Pt–CeO₂/C and Pt/C catalysts, e.g. 160 mg of carbon was used to synthesize 20 wt% Pt/C catalysts. Carbon was mixed well in a 50 cm³ mixture of EG and Milli-Q water before the ultrasound sonication for 10 minutes. After that, the carbon suspension and CeO₂ colloid mixture were transferred into the Pt colloid solution. In the case of SL₂_Pt–CeO₂/C(KB), the 160 mg of ceria-carbon mixture was transferred into the Pt colloid solution. The reaction mixture was stirred well using a magnetic stirrer during the NP deposition. A solution of 0.5 mol dm⁻³ H₂SO₄ was added dropwise until pH 5. The precipitation of Pt NPs onto the carbon support by controlling the pH of the solution has been used by many research groups.^{31,32} Thereafter, the reaction mixture was left for sedimentation for 30 minutes. The final step was to filter and dry the solid product received overnight in a vacuum oven at 100 °C and 50 mbar reduced pressure. For the comparison, the Vulcan XC-72 carbon, noted as C(Vulcan), and 20 wt% commercial Pt catalyst

Table I. The synthesis parameters and heating methods (microwave and ultrasound heating) applied for the preparation of CeO₂/C and colloidal CeO₂ mixture.

Material	Substrate	$C_{\text{Ce(NO}_3)_3}/$ mmol dm ⁻³	$C_{\text{NaOH}}/$ mol dm ⁻³	Microwave duration/ s	Ultrasound duration/ hour
ceria-carbon (for SL ₂ _Pt–CeO ₂ /C(KB))	C(KB)	2.5	1	—	2
colloidal ceria (for SL_Pt–CeO ₂ /C(KB))	—	2	0.1	—	2
colloidal ceria (for ML_Pt–CeO ₂ /C(KB))	—	2.5	0.1	234	—
colloidal ceria (for MH_Pt–CeO ₂ /C(KB))	—	5	0.1	234	—
colloidal ceria (for MH_Pt–CeO ₂ /C(Cr ₃ C ₂))	—	5	0.1	234	—

Notes. $C_{\text{Ce(NO}_3)_3}$ —the concentration of Ce(NO₃)₃ in the reaction mixture.
 C_{NaOH} —the concentration of NaOH in the reaction mixture

Table II. The parameters and methods applied for the synthesis of Pt–CeO₂/C(KB) and Pt–CeO₂/C(Cr₃C₂) materials.

Material	Substrate	$c_{\text{H}_2\text{PtCl}_6}/\text{mmol dm}^3$	$c_{\text{NaOH}}/\text{mmol dm}^3$	NaOH/Pt	Method
SL2_Pt–CeO ₂ /C(KB)	ceria-carbon	0.88	30	34	Two-step method
SL_Pt–CeO ₂ /C(KB)	C(KB)	1.5	80	55	Co-precipitation
ML_Pt–CeO ₂ /C(KB)	C(KB)	0.88	30	34	Co-precipitation
MH_Pt–CeO ₂ /C(KB)	C(KB)	0.88	30	34	Co-precipitation
Pt/C(KB)	C(KB)	0.88	30	34	Precipitation
MH_Pt–CeO ₂ /C(Cr ₃ C ₂)	C(Cr ₃ C ₂)	0.88	30	34	Co-precipitation
Pt/C(Cr ₃ C ₂)	C(Cr ₃ C ₂)	0.88	30	34	Precipitation

Notes. The Pt colloids were synthesized using the ethylene glycol reduction method:

- Two-step method—only Pt nanoparticles (NPs) were precipitated onto ceria-carbon synthesized separately from colloid
- Co-precipitation—Pt and CeO₂ NPs were co-precipitated onto the carbon support from colloid
- Precipitation—Pt NPs were precipitated onto carbon support from colloid

$c_{\text{H}_2\text{PtCl}_6}$ —concentration of H₂PtCl₆ in the reaction mixture for Pt colloid synthesis

c_{NaOH} —concentration of NaOH in the reaction mixture for Pt colloid synthesis

on Vulcan XC-72 carbon (from FuelCellStore), noted as Pt/C (Vulcan), were used.

Physical characterization.—Thermogravimetric analysis.—Thermogravimetric analysis (Fig. 1) was conducted using a NETZSCH STA449F3 system and an Al₂O₃ pan. The program was set to raise the temperature from 25 °C to 1000 °C with a heating rate of 10 °C min^{−1}. The experiment was conducted under gas streams of 10 cm³ min^{−1} O₂ (As Linde Gas, 99.999%) and 40 cm³ min^{−1} N₂ (As Linde Gas, 99.999%), respectively.

X-ray diffraction.—X-ray diffraction was conducted using a Bruker D8 Advance diffractometer with a Ni-filter CuK α radiation. A 0.6 mm wide parallel beam through a 2.5° Soller slit was used. After that, the diffracted radiation passed through another 2.5° Soller slit before reaching the LynxEye line detector system. The signal was recorded with the scanning step of 2 θ angle with 0.013° for each record. The total duration for each scanning step was 348 seconds. The fitting of the profile was conducted using the double Voigt approach method,³³ while the crystallite size estimation was conducted using the Topas software (version 6). An energy dispersive X-ray (EDX) handheld device (Tracer 5i) was used to analyze the elements in the studied samples.

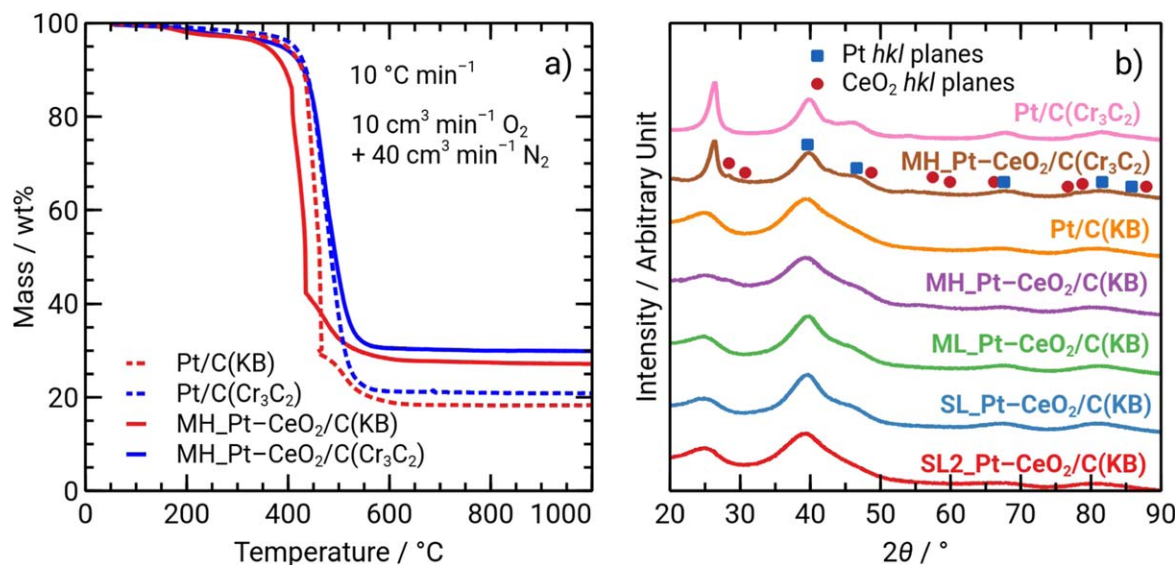
Raman spectroscopy.—Raman spectroscopy measurements were conducted using an argon laser (λ = 514 nm) coupled with a Renishaw InVia micro-Raman spectrometer. Twenty spots were measured to collect the excitation spectra for each material. The

laser power was 2 mW, and the collection time was 15 min for each spot. The average spectra are shown in Fig. 2.

Low-temperature nitrogen sorption.—The samples for low-temperature (at near 77 K) nitrogen sorption³⁴ were degassed at 100 °C and 13 μ bar for 24 h. The measurements were conducted using a 3Flex system (Micromeritics, USA). The pore-width distribution (PWD) and micro-mesoporosity data were estimated using the SAIEUS software³⁵ (version 2.02, Micromeritics, USA) and built-in function "Carbon-N2-77, 2D-NLDFT Heterogeneous Surface" based on the nonlocal density functional theory model for nitrogen sorption at porous carbon.³⁶ The other parameters such as the specific surface area (S_{DFT}), the mesopore surface area ($S_{\text{mesopores}}$), and the pore volume of total pores (V_{total}) and mesopores ($V_{\text{mesopores}}$) were estimated from the "Carbon-N2-77, 2D-NLDFT Heterogeneous Surface" modeling results.

Transmission electron microscopy.—A JEOL JEM-2100 device (JEOL GmbH, Eching, Germany) operated at an acceleration voltage of 200 kV was used to record the transmission electron microscopy (TEM) images. For the PSD analysis of Pt NPs, more than 200 Pt NPs were measured.

Microwave-plasma atomic emission spectrometry.—The microwave plasma atomic emission spectrometry (MP-AES) was conducted to analyze the Pt and CeO₂ content in the studied materials. 10–20 mg of samples were dissolved by sequentially adding 6 cm³ of 35% HCl (Carl Roth ROTIPURAN Supra) and 2 cm³ 69% HNO₃

**Figure 1.** Thermogravimetry results (a) and X-ray diffractograms (b) for materials studied.

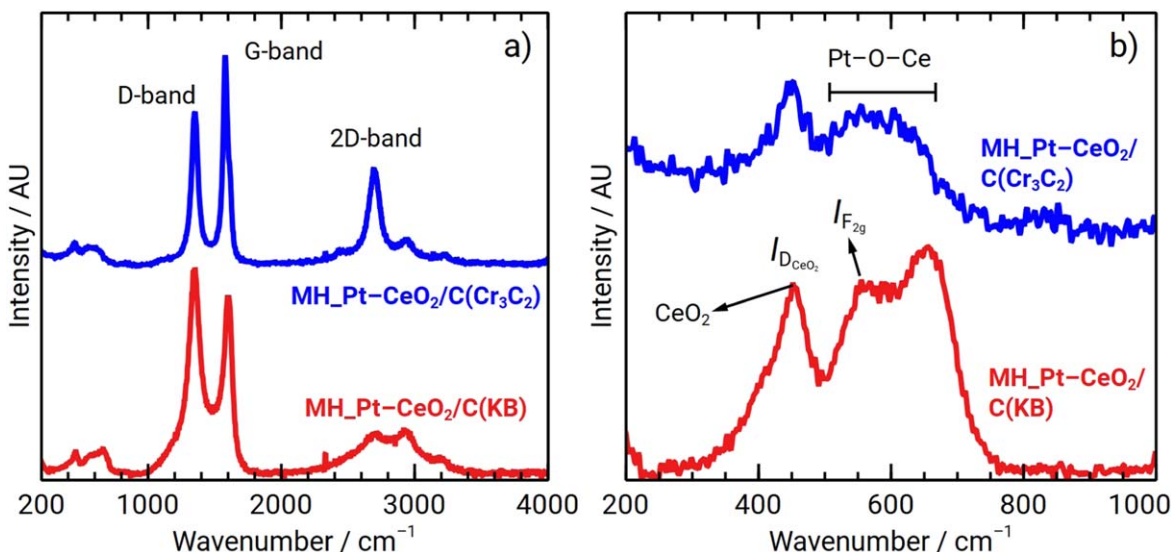


Figure 2. Raman spectra of selected materials (a) and magnification for the spectra below 1000 cm⁻¹ (b).

(Carl Roth ROTIPURAN Supra) into NXF100 digestion vessels (PTFE-TFM liner). After that, the digestion vessels were capped and heated for digestion using an Anton Paar Multiwave PRO microwave digestion system coupled with an 8N rotor. The digested samples were diluted using 1% HNO₃/1% HCl solution to a final dilution factor of 80 000 for the determination of CeO₂ and Pt contents. An Agilent 4210 MP-AES was calibrated using single-element Ce and Pt solutions before measuring Ce at 417.659 nm wavelength and Pt at 265.945 nm wavelength. The CeO₂ and Pt content was calculated back from the measured data of Ce and Pt in diluted samples.

Electrochemical measurements.—Basic setup and the conditioning of the electrodes.—Electrochemical characterization, MOR, and ORR studies were conducted using a three-electrode system in a 0.5 mol dm⁻³ H₂SO₄ and 0.1 mol dm⁻³ HClO₄ electrolyte solution, respectively. The reference electrode was a reversible hydrogen electrode (RHE), which was prepared in the corresponding electrolyte solution.³⁷ The RHE was connected to the cell via a Luggin capillary. The auxiliary electrode was a Pt net. The working electrode was the glassy carbon disk electrode (GCDE) covered by the catalyst.

The working electrode for all experiments was prepared by pipetting a 7 μL drop of catalyst suspension onto the GCDE (PINE Instrument Company, electrode diameter 5 mm) surface. The nominal concentration of Pt on GCDE surface was 18 μg_{Pt} cm⁻². The suspension was prepared by sonicating 4.9 mg of catalyst in a mixture of 1.33 cm³ Milli-Q water, 0.57 cm³ isopropanol (Sigma-Aldrich, >99%) and 41 μL of Nafion solution (5% solution, Sigma-Aldrich). The ionomer-to-carbon mass ratio was 0.5.

All the electrochemical measurements were conducted using the Autolab PGSTAT302N potentiostat and NOVA 1.11.2 software. Before the electrochemical measurements, the conditioning step was performed by scanning the working electrode potential from 0.025 V to 1.400 V at 0.5 V s⁻¹ and at 1600 rpm for 100 cycles in the corresponding electrolyte solution in an Ar atmosphere.

Electrochemically active surface area.—The electrochemical active surface area, ECSA, and Pt NP diameter, $d_{\text{Pt,ECSA}}$, estimations were conducted in 0.5 mol dm⁻³ H₂SO₄ or 0.1 mol dm⁻³ HClO₄ solution saturated with Ar. The potential was scanned from 0.06 V to 1.00 V at various scan rates from 0.01 to 0.40 V s⁻¹. The ECSA and $d_{\text{Pt,ECSA}}$ were determined using data collected and discussed in detail by Trasatti et al.³⁸

$$\text{ECSA}(\text{m}^2_{\text{Pt}}\text{g}^{-1}) = \frac{Q_{\text{H}_{\text{UDP}}}}{m_{\text{Pt}} \cdot Q_{\text{H}_{\text{UDP,ref}}}}, \quad [3]$$

where the $Q_{\text{H}_{\text{UDP,ref}}}$ is a reference value (2.10 C m⁻²) for the $Q_{\text{H}_{\text{UDP}}}$ process on a smooth polycrystalline Pt surface.³⁹ Assuming that the Pt NPs are spherical, the diameter of the Pt NPs, $d_{\text{Pt,ECSA}}$, can be estimated using the ECSA value.⁴⁰

$$d_{\text{Pt,ECSA}}(\text{nm}) = \frac{6}{\rho_{\text{Pt}} \cdot \text{ECSA} \cdot 10^9} \quad [4]$$

where $\rho_{\text{Pt}} = 21.45 \times 10^6 \text{ g m}^{-3}$ is bulk density of Pt.⁴¹

Methanol oxidation reaction measurements.—The MOR activity was measured in the solution of 0.5 mol dm⁻³ H₂SO₄ and 1 mol dm⁻³ CH₃OH saturated with Ar. During the cyclic voltammetry measurements (CV), the potential was scanned from 0.06 V to 1.26 V at 0.05 V s⁻¹ until the current-potential curves were stable (around 10 cycles). The potential range and electrode potential scan rate in CV measurement were selected to make the comparison of results with other authors more simple.^{12,16,17,42,43} The chronoamperometry experiments were performed at fixed potentials of 0.85 V for 60 min and 0.50 V for 30 min, respectively.

Oxygen reduction reaction measurements.—The ORR activity was measured in 0.1 mol dm⁻³ HClO₄, which was prepared from 70% HClO₄ (99.999%, redistilled, Sigma-Aldrich) and Milli-Q water. The rotating disk electrode (RDE) measurements were conducted from 0.01 to 1.00 V at 0.02 V s⁻¹ and 1600 rpm. The background current was established as the electrolyte was saturated with Ar gas. The measurement current was collected in the electrolyte saturated with O₂. The measurement current was corrected with the background current before proceeding with further calculations. During the measurements, the potential was corrected with the ohmic drop potential.

CO stripping measurements.—The CO oxidation measurements were conducted in 0.1 mol dm⁻³ HClO₄ solution after the conditioning step. The solution was bubbled with argon gas for 10 min while the working electrode potential was kept at 0.05 V (400 rpm). After that, the gas flow was switched to CO gas for 10 min. Finally, the argon gas was introduced again for another 10 min before the CO oxidation. Five CV cycles were measured within the range from 0.05

Table III. Physical characterization results of catalysts studied.

Material	Residual mass / wt%	Pt wt%	CeO ₂ wt%	$d_{\text{Pt,TEM}}/\text{nm}$	$d_{\text{Pt,XRD}}/\text{nm}$	$d_{\text{CeO}_2,\text{XRD}}/\text{nm}$	$I_{\text{D}_{\text{CeO}_2}}/I_{\text{F}_{2g}}$
SL2_Pt–CeO ₂ /C(KB)	23	23	0.3	3.6 ± 1.5	1.1	1.0	—
SL_Pt–CeO ₂ /C(KB)	25	22	0.3	4.1 ± 1.4	1.0	0.7	—
ML_Pt–CeO ₂ /C(KB)	20	23	0.3	3.1 ± 0.9	0.9	1.0	—
MH_Pt–CeO ₂ /C(KB)	27	23	5.1	3.4 ± 1.1	0.7	0.7	1.02
Pt/C(KB)	18	21	—	3.3 ± 1.2	1.4	—	—
MH_Pt–CeO ₂ /C(Cr ₃ C ₂)	30	22	7.4	7.2 ± 3.8	0.9	5.1	1.18
Pt/C(Cr ₃ C ₂)	21	20	—	7.2 ± 3.8	1.5	—	—
Pt/C(Vulcan)	—	16 ^a	—	24.3 ± 19.1	5.7 ^a	—	—

Notes. Residual mass –residual mass from thermogravimetric analysis

Pt wt% –Pt weight percent estimated from the microwave-plasma atomic emission spectroscopy results

CeO₂ wt% –CeO₂ weight percent estimated from the microwave-plasma atomic emission spectroscopy results

$d_{\text{Pt,TEM}} = \frac{\sum_{i=1}^n d_i^3}{\sum_{i=1}^n d_i^2}$ –volume to area diameter of Pt nanoparticles estimated from more than 200 Pt particles in transmission electron microscopy images,

St.Dev. = $\left(\frac{1}{n-1} \times \sum_{i=1}^n (x_i - \bar{x})^2\right)^{1/2}$ 51,64

$d_{\text{Pt,XRD}}$ –the crystallite size of Pt from XRD results

$d_{\text{CeO}_2,\text{XRD}}$ –the crystallite size of CeO₂ from XRD resultsa Data is from Prits et al.⁶⁵

Table IV. Electrochemically active surface area and Pt dissolution results of studied materials.

Material	$c_{\text{Pt}}/\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$	ECSA _{H₂SO₄} ^a / $\text{m}_{\text{Pt}}^2\text{g}_{\text{Pt}}^{-1}$	ECSA _{HClO₄} ^b / $\text{m}_{\text{Pt}}^2\text{g}_{\text{Pt}}^{-1}$	ECSA _{CO} ^c / $\text{m}_{\text{Pt}}^2\text{g}_{\text{Pt}}^{-1}$	$d_{\text{Pt,ECSA}}/\text{nm}$
SL2_Pt–CeO ₂ /C(KB)	14.4 ± 1.4	88 ± 5	112 ± 10	109 ± 13	2.5 ± 0.2
SL_Pt–CeO ₂ /C(KB)	13.7 ± 0.5	76 ± 12	101 ± 4	—	2.7 ± 0.1
ML_Pt–CeO ₂ /C(KB)	14.9 ± 0.2	89 ± 1	—	—	—
MH_Pt–CeO ₂ /C(KB)	14.1 ± 1.7	79 ± 12	99 ± 18	106 ± 2	2.9 ± 0.4
Pt/C(KB)	13.0 ± 0.4	82 ± 1	109 ± 16	115 ± 2	2.6 ± 0.5
MH_Pt–CeO ₂ /C(Cr ₃ C ₂)	14.5 ± 0.3	54 ± 3	71 ± 7	72 ± 5	3.9 ± 0.4
Pt/C(Cr ₃ C ₂)	12.5 ± 2.2	71 ± 4	89 ± 9	97 ± 13	3.1 ± 0.3
Pt/C(Vulcan)	18 [*]	17 ± 1 [*]	20 ± 3	—	17 ± 2

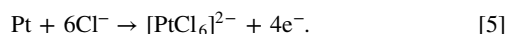
c_{Pt} –Pt concentration on the electrode surface estimated from Pt dissolution results. The nominal c_{Pt} is 18 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$ and the averaged c_{Pt} estimated from all materials is 13.9 ± 3.2 $\mu\text{g}_{\text{Pt}}\text{cm}^{-2}$.

$d_{\text{Pt,ECSA}}$ –volume to area diameter of Pt nanoparticles estimated from ECSA results in 0.1 mol dm^{−3} HClO₄ solution.

^{*}Data is from Prits et al.⁶⁵ a) ECSA estimated from the hydrogen underpotential deposition in 0.5 mol dm^{−3} H₂SO₄. b) ECSA estimated from the hydrogen underpotential deposition in 0.1 mol dm^{−3} HClO₄. c) ECSA estimated from the CO stripping in 0.1 mol dm^{−3} HClO₄.

V to 1.00 V, at the scan rate of 20 mV s^{−1} (0 rpm), and the argon gas was flowing above the solution.⁴⁴ The last CV cycle was used as the baseline to correct for the background charges during the calculation of ECSA from CO oxidation peaks, ECSA_{CO}. The ECSA_{CO} was estimated in the potential range from 0.4 to 1.0 V using the reference charge of 420 $\mu\text{C cm}_{\text{Pt}}^{-2}$ for Pt-based catalyst.⁴⁵

Pt dissolution measurements.—The Pt dissolution experiment was performed in 6 mol dm^{−3} HCl aqueous solution, which was prepared from concentrated HCl (Sigma-Aldrich, 36.5%–38%, Analytical specification Pr. Eur.), using a three-electrode system. The reference electrode was the Ag|AgCl saturated KCl electrode (Ag|AgCl), the auxiliary electrode was the carbon fiber electrode, and the working electrode was the GCDE covered by a drop of the catalyst. The potentials for these experiments are reported against the Ag|AgCl electrode. Six cyclic voltammograms were measured from 0.45 V to 0.95 V vs. Ag|AgCl at 0.5 mV s^{−1} to collect the Pt dissolution data.^{24,46} The background data were collected using the same electrode after the dissolution was conducted. The apparent Pt dissolution charge values used were corrected with background charge (for Pt free system) to estimate the Pt content on the electrode surface. In detail, the Pt dissolution in the potential region from 0.45 to 0.95 V corresponds to the oxidation of Pt⁰ to Pt⁴⁺.⁴⁶



The concentration of Pt on the electrode surface, c_{Pt} , was calculated using Faraday law and following the equation below:

$$c_{\text{Pt}}(\mu\text{g}_{\text{Pt}}\text{cm}^{-2}) = \frac{Q_{\text{corr.}} \times M_{\text{Pt}} \times 10^6}{nFA_{\text{electrode}}} \quad [6]$$

where $Q_{\text{corr.}}$ (C) is the charge corresponding to Pt dissolution, F is Faraday constant (96485 C mol^{−1}), n is the number of electrons transferred (4 e[−]), M_{Pt} is the atomic mass of Pt (195 g mol^{−1}), and $A_{\text{electrode}}$ is electrode surface area (0.196 cm²).

Results and Discussions

The structure of catalyst supports and catalysts.—The total mass fraction of Pt and CeO₂ in catalysts was determined from the TGA residual mass values. Data are given in Table III, and selected TGA curves are demonstrated in Fig. 1a. The Pt and CeO₂ contents estimated from MP-AES (see Table III) can be used for the interpretation of the electrochemical activity of studied materials. Although after microwave digestion, there was no precipitate in vessels with samples SL2_Pt–CeO₂/C(KB) and Pt/C(KB), vessels with samples SL_Pt–CeO₂/C(KB) and MH_Pt–CeO₂/C(KB) contained a small amount of precipitate. There was even more precipitate in the vessels with samples ML_Pt–CeO₂/C(KB), MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂). The incomplete dissolution of samples could cause an underestimation of elements in the samples. The Pt wt% estimated from MP-AES results (Table III) is slightly over 20 wt% for all materials. This indicates that Pt from the materials was dissolved completely because the nominal Pt wt% for the synthesis was 20. The Pt content from the MP-AES seems to be slightly overestimated as the Pt content

should be equal to or smaller than the TGA residual mass in the case of ML_Pt–CeO₂/C(KB) and Pt/C(KB) catalysts. Due to the similar synthesis parameters and methods of the MH_Pt–CeO₂/C(KB) and MH_Pt–CeO₂/C(Cr₃C₂) materials (see Tables I and II), the composition of these two materials is very similar. However, the CeO₂ contents (Table III) of these two materials are slightly underestimated based on the TGA residual mass and Pt content. This underestimation issue is also problematic in the case of quantitative determination of small CeO₂ wt% in SL₂_Pt–CeO₂/C(KB), SL_Pt–CeO₂/C(KB), and ML_Pt–CeO₂/C(KB) materials, however, it is still useful to confirm the presence of such small CeO₂ amount in these materials.

The c_{Pt} in Table IV reflects the actual amount of Pt in the catalyst deposited onto GCDE calculated from the Pt electrochemical dissolution experiment as shown in Eq. 5.⁴⁶ This c_{Pt} was used to estimate the electrochemical activity of materials. By using this c_{Pt} for ECSA and mass activity calculations, the uncertainty of pipetting and the homogeneity of catalyst suspension were taken into account. However, the c_{Pt} was slightly lower ($13.9 \pm 3.2 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$) than the nominal $18 \mu\text{g}_{\text{Pt}} \text{cm}^{-2}$ for the reasons mentioned above.

The diffractograms in Fig. 1b reveal that the structure of catalysts reflects also the structure of the carbon precursors. The peaks of Pt and CeO₂ are broad, and the intensity of the peaks is low. Therefore, the crystallite size of Pt and CeO₂ particles is small. The Pt peaks at 2θ angles at 40°, 46°, 68°, 82° and 86° corresponded to Pt hkl planes (111), (200), (311), (331) and (222), respectively.⁴⁷ The diffraction peaks for the CeO₂ phase are somewhat unclear because the CeO₂ is amorphous. However, the modeling results revealed the presence of CeO₂ phase at 2θ angles at 29°, 33°, 47°, 56°, 59°, 69°, 77°, 79° and 88°, which correspond to the planes (111), (200), (220), (311), (222), (400), (331), (420) and (422), respectively and is in agreement with Zhang et al.³⁰ The EDX data confirmed the presence of Ce in materials studied. Although Pt crystallite size, $d_{\text{Pt,XRD}}$, was similar and around 1 nm, $d_{\text{Pt,XRD}}$ was somewhat influenced by the carbon support properties. The $d_{\text{Pt,XRD}}$ values for MH_Pt–CeO₂/C(KB) and Pt/C(KB) materials were slightly smaller than $d_{\text{Pt,XRD}}$ values for MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) materials, respectively. The CeO₂ crystallite size, $d_{\text{CeO}_2,\text{XRD}}$, of MH_Pt–CeO₂/C(KB) was smaller than that of MH_Pt–CeO₂/C(Cr₃C₂). Thus, the structure of the catalyst prepared by the coprecipitation method was influenced by carbon materials, e.g., the CeO₂ crystallite size of the MH_Pt–CeO₂/C(Cr₃C₂) catalyst is 5 times higher than that for the CeO₂ NPs of the C(KB)-based catalysts (see Table III). However, the different parameters for Ce colloid synthesis, such as ultrasound, microwave, and chemical concentrations, did not affect the crystallite

size of CeO₂ within the PtCe–C(KB) catalysts as the average crystallite size of CeO₂ NPs for all C(KB)-based catalysts is 0.8 ± 0.2 nm.

The Raman spectra for the materials studied are given in Fig. 2a, and reveal the carbon structure at higher wavenumbers (above 1000 cm^{−1}). The D-band (1358 cm^{−1}) and G-band (1583 cm^{−1}) shapes indicate that both C(KB) and C(Cr₃C₂) are generally amorphous as the ratio of peak intensities is $I_{\text{D}}/I_{\text{G}}$ around 1.15 and 0.74, respectively. In spite of that, the sharp peak at 2D-band (2704 cm^{−1}) for the MH_Pt–CeO₂/C(Cr₃C₂) material indicates that the support C(Cr₃C₂) is between the second and the third stage of graphitization and C(Cr₃C₂) is a nanocrystalline graphite.²⁹ This result agrees well with the XRD results as the C(002) peaks of MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) at the 2θ angle of 26° are sharper compared to the C(KB) based materials. In the region below 1000 cm^{−1}, the sharp F_{2g} peak at 451 cm^{−1} and the broad peak around 600 cm^{−1} (Fig. 2b) indicate the presence of Pt–CeO₂^{48,49} at the MH_Pt–CeO₂/C(KB) and MH_Pt–CeO₂/C(Cr₃C₂) surfaces. The peak at F_{2g} is red-shifted compared to the same peak for pure CeO₂ crystals expressed at 466 cm^{−1}. This redshift indicates the smaller grain-size of CeO₂ crystal.⁴⁹ The broad peak around (600 cm^{−1}) is the overlap of two peaks: the asymmetry of Pt–O–Ce linkage (550 cm^{−1}) and the symmetry linkage for Pt–O–Ce (690 cm^{−1}). The stretching mode of CeO₂ (D_{CeO₂}) at (550 cm^{−1}) was used to evaluate the oxygen vacancies. The higher intensity ratio of $I_{\text{D}_{\text{CeO}_2}}/I_{\text{F}_{2g}}$ indicates a higher number of oxygen vacancies⁵⁰ for MH_Pt–CeO₂/C(Cr₃C₂) than that for MH_Pt–CeO₂/C(KB) (see Table III). The spectra below 1000 cm^{−1} indicate that our CeO₂ NPs are small and well-dispersed on the carbon surface.

The porosity of Pt–CeO₂/C materials is inherited from the carbon precursors (Fig. 3a). The total pore volume, V_{total} , values for Pt–CeO₂/C and Pt/C catalysts (Table V) are reduced compared to the V_{total} of carbon precursors. C(KB) and C(Cr₃C₂) have two regions in PWD. The first PWD maxima is around 0.8 nm, and the second PWD maxima region is from 2 nm to 10 nm. Therefore, both carbon materials have a micro-mesoporous structure. However, the fraction of mesopores, $V_{\text{mesopores}}/V_{\text{total}}$, for C(Cr₃C₂) is higher than that of C(KB). Besides, the $V_{\text{mesopores}}/V_{\text{total}}$ ratio for catalysts remains close to that of carbon precursors. Thus, based on the TEM images, Pt and CeO₂ NPs were deposited evenly on the carbon surface. The V_{total} is proportional to the percentage of C(KB) in Pt–CeO₂/C(KB) and Pt/C(KB) catalysts (Fig. 3b). There is a weaker correlation between the V_{total} and the percentage of C(Cr₃C₂).

The TEM results (Fig. 4) demonstrate that the Pt NPs are very well dispersed on the C(KB)-based materials (a-c, f, and h) as C(KB) has a

Table V. Low-temperature nitrogen sorption results estimated from “Carbon-N2-77, 2D-NLDFT Heterogeneous Surface” modeling data for materials studied.

Material	$S_{\text{DFT}}/\text{m}^2 \text{g}^{-1}$	$S_{\text{mesopores}}/\text{m}^2 \text{g}^{-1}$	$V_{\text{total}}/\text{cm}^3 \text{g}^{-1}$	$V_{\text{mesopores}}/\text{cm}^3 \text{g}^{-1}$	$V_{\text{mesopores}}/V_{\text{total}}$
SL ₂ _Pt–CeO ₂ /C(KB)	458	138	0.53	0.39	0.73
SL_Pt–CeO ₂ /C(KB)	440	142	0.53	0.39	0.74
ML_Pt–CeO ₂ /C(KB)	516	151	0.59	0.42	0.71
MH_Pt–CeO ₂ /C(KB)	460	128	0.52	0.36	0.70
Pt/C(KB)	508	149	0.59	0.42	0.71
C(KB)	730	202	0.78	0.54	0.70
MH_Pt–CeO ₂ /C(Cr ₃ C ₂)	103	49	0.17	0.15	0.84
Pt/C(Cr ₃ C ₂)	104	47	0.17	0.15	0.85
C(Cr ₃ C ₂)	213	101	0.34	0.29	0.86
Pt/C(Vulcan) ^a	180	73	0.41	0.36	0.88
C(Vulcan) ^b	242	93	0.83	0.77	0.93

S_{DFT} —specific surface area from modeling data

$S_{\text{mesopores}}$ —surface area of mesopores estimated from modeling data

V_{total} —total pore volumes estimated from modeling data

$V_{\text{mesopores}}$ —the volume of mesopores estimated from modeling data^a) Data is taken and derived from the results of Prits et al.⁶⁵ b) Data is taken and derived from the results of Valk et al.²⁴ Data is estimated by using BET and t-plot methods.

relatively high S_{DFT} value (around $730 \text{ m}^2 \text{ g}^{-1}$, see Table V). The Pt PSD patterns of these materials are similar, with the most particle counts around 2.5 nm. The number averaged diameter of Pt NPs is close for these materials, ranging from 2.5 ± 0.9 to 3.3 ± 1.1 nm. Almost no agglomerates can be detected. Therefore, the synthesis method for Pt deposition on C(KB)-based materials was repeatable, even if the synthesis methods for CeO_2 particles were different in each case. The $\text{Ce}(\text{NO}_3)_3$ concentration used during the CeO_2 synthesis does not influence the Pt deposition if Pt PSD of the $\text{MH_Pt-CeO}_2/\text{C(KB)}$ catalyst is compared to other $\text{Pt-CeO}_2/\text{C(KB)}$ catalysts (see Fig. 4).

In the case of $\text{C}(\text{Cr}_3\text{C}_2)$ -based materials (Figs. 4e and 4g), the Pt NPs are slightly agglomerated due to the lower S_{DFT} value of $\text{C}(\text{Cr}_3\text{C}_2)$ (around $213 \text{ m}^2 \text{ g}^{-1}$, see Table V). However, the diameter of most Pt particles ranges from 2 to 4 nm. The Pt PSD patterns of $\text{MH_Pt-CeO}_2/\text{C}(\text{Cr}_3\text{C}_2)$ and $\text{Pt/C}(\text{Cr}_3\text{C}_2)$ materials are surprisingly similar, and the averaged diameter of Pt NPs is around 4.3 ± 2.3 nm. This confirmed the success of the Pt deposition method on $\text{C}(\text{Cr}_3\text{C}_2)$ -based materials. In comparison with commercial Vulcan carbon support, which has a similar S_{DFT} value (around $243 \text{ m}^2 \text{ g}^{-1}$),²⁴ the commercial Pt/C(Vulcan) is extensively agglomerated with diverse particle sizes, and most of the Pt particles distributed around 5–7 nm (Fig. 4d). The volume to area diameter of Pt NPs,⁵¹ $d_{\text{Pt,TEM}}$, (see Table III) was calculated to compare it with the diameter calculated from the ECSA values in the electrochemical measurement, which is also volume to area diameter.³⁸ The details of the Pt surface area based on the $d_{\text{Pt,TEM}}$ values will be discussed later with ECSA results.

The contact of Pt and CeO_2 particles is spotted on both C(KB) and $\text{C}(\text{Cr}_3\text{C}_2)$ -based materials, and this is demonstrated for $\text{MH_Pt-CeO}_2/\text{C(KB)}$ and $\text{MH_Pt-CeO}_2/\text{C}(\text{Cr}_3\text{C}_2)$ materials in Fig. 5. This agrees with the results of MP-AES and Raman spectroscopy, which indicate the presence and contact of the CeO_2 and Pt particles, respectively. The coprecipitation of Pt and CeO_2 on $\text{C}(\text{Cr}_3\text{C}_2)$ caused the formation of some big Pt- CeO_2 clusters (up to 22.4 nm), in which both Pt and CeO_2 phases can be found. The interplanar spacing of Pt lattice fringes is found in all materials around $2.25 \pm 0.05 \text{ \AA}$, corresponding to the Pt (111) plane.⁵² The CeO_2 (111) plane was also detected with the interplanar spacing around 0.33 nm (see Fig. 5).^{52,53}

The dispersion of Pt NPs was evaluated via the ECSA estimation from CV data measured in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ and $0.1 \text{ mol dm}^{-3} \text{HClO}_4$ aqueous solution, so-called $\text{ECSA}_{\text{H}_2\text{SO}_4}$ and $\text{ECSA}_{\text{HClO}_4}$, respectively, given in Table IV. The Pt wt% was estimated using the Pt dissolution curves in Fig. 6a.

The $\text{ECSA}_{\text{HClO}_4}$ is higher (about 1.3 times) than $\text{ECSA}_{\text{H}_2\text{SO}_4}$ for the same catalyst material. In a review by Marković et al.⁵⁴, the sensitive structure of Pt toward the adsorption of bisulfate anion at three different planes (111), (100), and (110) of Pt has been pointed out. This specific adsorption of bisulfate anions on the Pt surface reduces the ORR activity in the H_2SO_4 solution. Thus, the specific adsorption blocks the initial adsorption of other chemical species on the Pt surface; however, this adsorption behavior does not change the ORR pathway. This type of specific adsorption does not occur in the HClO_4 electrolyte. The specific adsorption of bisulfate anions explains the lower $\text{ECSA}_{\text{H}_2\text{SO}_4}$ compared to the $\text{ECSA}_{\text{HClO}_4}$ due to the deactivation of some Pt sites. The ECSA is smaller for $\text{MH_Pt-CeO}_2/\text{C}(\text{Cr}_3\text{C}_2)$ and $\text{Pt/C}(\text{Cr}_3\text{C}_2)$ catalysts compared to that for $\text{MH_Pt-CeO}_2/\text{C(KB)}$ and Pt/C(KB) catalysts, respectively. Therefore, Pt NPs were probably dispersed more homogeneously on the C(KB) support based on TEM measurement results given in Fig. 4. Besides, for the materials studied, the $\text{ECSA}_{\text{H}_2\text{SO}_4}$ and $\text{ECSA}_{\text{HClO}_4}$ were high compared to other studies.^{2,16,22,55} The ECSA_{CO} values (see Table IV) are comparable with $\text{ECSA}_{\text{HClO}_4}$ values. A similar result was also observed by Schulenburg et al.⁴⁵ A particle diameter of spherical Pt NPs, $d_{\text{Pt,ECSA}}$,³⁸ calculated from $\text{ECSA}_{\text{HClO}_4}$ is from 2 nm to 4 nm. These values could be compared with the same parameter calculated from TEM data ($d_{\text{Pt,TEM}}$). The particle diameter of the Pt NPs estimated from TEM images is slightly higher (especially for $\text{C}(\text{Cr}_3\text{C}_2)$ -supported catalysts, see Tables III and IV). This can be caused, e.g., by the over-estimation of the Pt NP agglomeration and inaccuracies with the estimation of the Pt NP's border.^{38,51}

CV data obtained in $0.5 \text{ mol dm}^{-3} \text{H}_2\text{SO}_4$ are given in Fig. 6b and are presented as gravimetric capacitance curves (C, E curves). The capacitance curves (Fig. 6b) for the $\text{MH_Pt-CeO}_2/\text{C}(\text{Cr}_3\text{C}_2)$ and $\text{Pt/C}(\text{Cr}_3\text{C}_2)$ overlap in the potential region of the electrical double layer, EDL (from 0.4 V to 0.7 V). The very small difference of S_{DFT} between $\text{MH_Pt-CeO}_2/\text{C}(\text{Cr}_3\text{C}_2)$ and $\text{Pt/C}(\text{Cr}_3\text{C}_2)$ materials in Table V agrees well with these data. The accessible surface area also influences the capacitance values in EDL region for $\text{Pt-CeO}_2/\text{C(KB)}$ and Pt/C(KB) materials. For the $\text{SL_Pt-CeO}_2/\text{C(KB)}$ material, which has the smallest S_{DFT} (Table V) amongst catalysts on C(KB), the micropores were probably blocked during the coprecipitation of Pt and CeO_2 NPs. In comparison amongst $\text{Pt-CeO}_2/\text{C(KB)}$ materials, the S_{DFT} and the capacitance in the EDL potential region decreases in the same order: $\text{ML_Pt-CeO}_2/\text{C(KB)} > \text{SL}_2\text{-Pt-CeO}_2/\text{C(KB)} \geq \text{MH_Pt-CeO}_2/\text{C(KB)} > \text{SL_Pt-CeO}_2/\text{C(KB)}$.

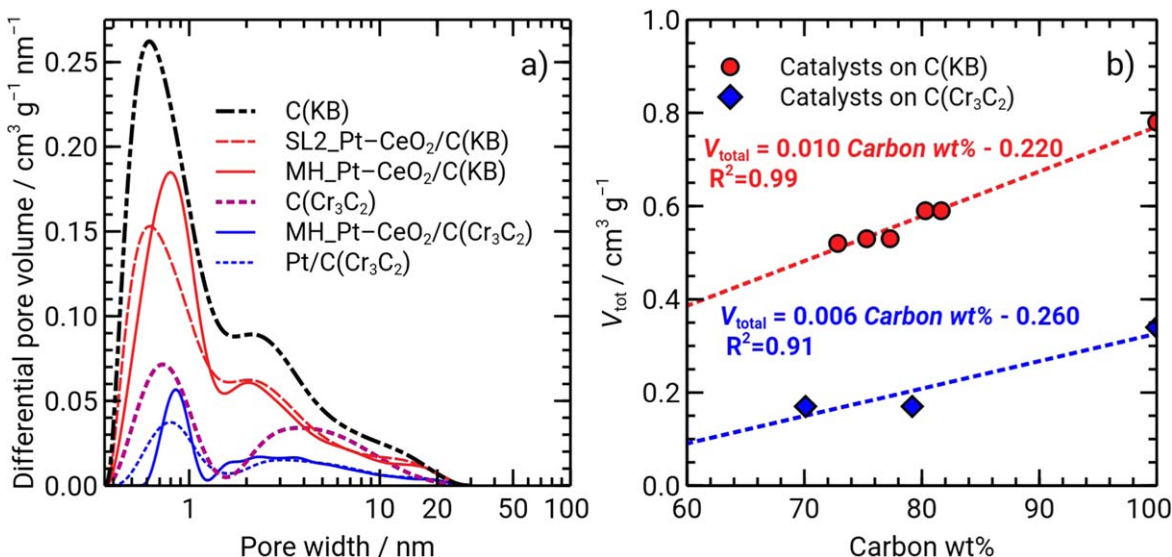


Figure 3. The pore-size distribution for the materials studied (a) and the correlation between the total pore volume and carbon percentage in the catalyst (b).

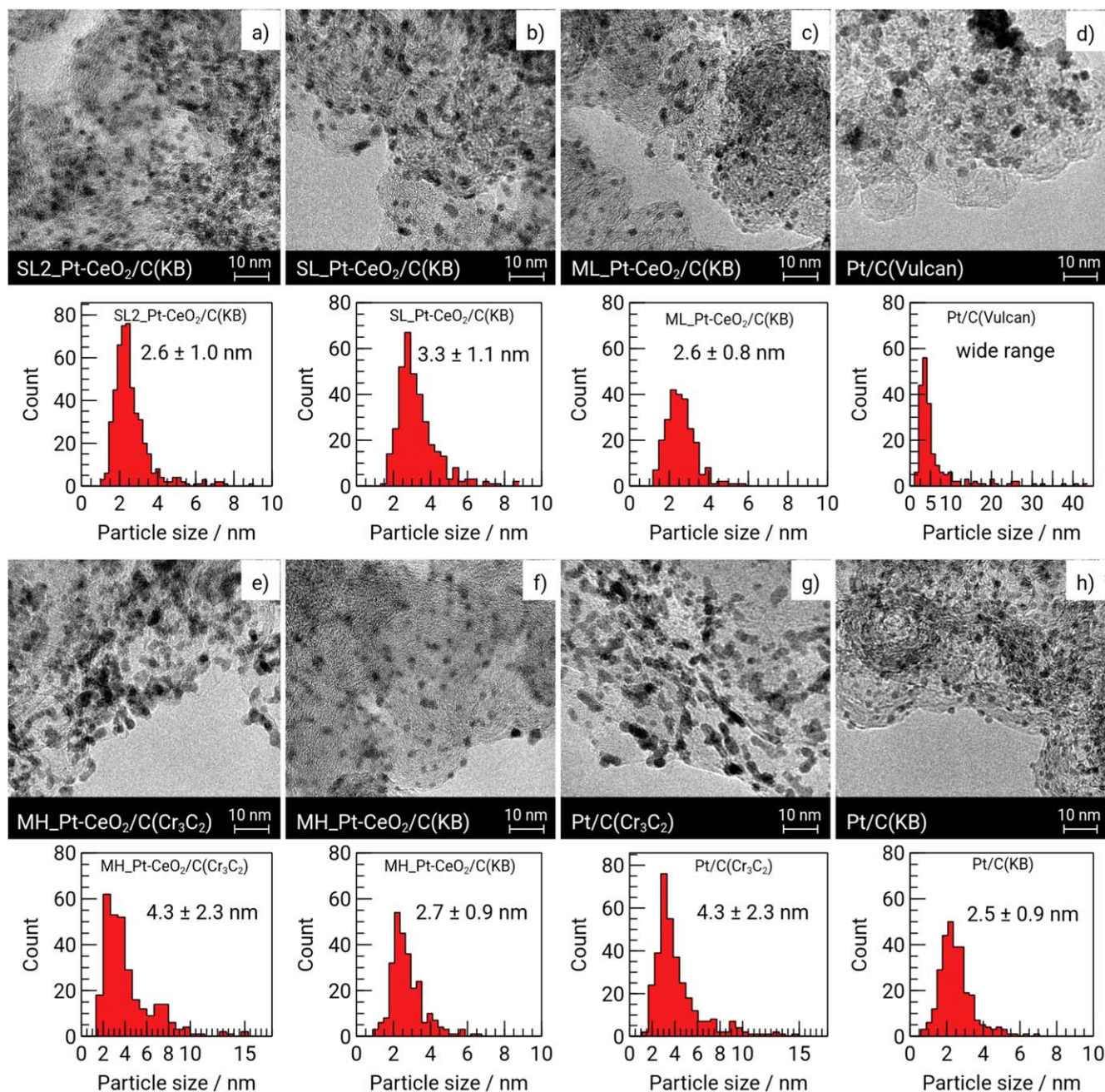


Figure 4. The dispersion of Pt nanoparticles on Pt–CeO₂/C and Pt/C materials. The histogram of the Pt particle diameter of the corresponding material, estimated by measuring more than 200 particles, is placed under the transmission electron microscopy image. The averaged diameter of Pt nanoparticles is estimated for each material.

Methanol oxidation reaction.—The MOR pathway on different electrode materials has been studied by many authors.^{56–58} It is generally agreed that the MOR begins at electrode potential 0.4 V and is limited by the adsorption rate of methanol on the metal/metal oxide surface. The methanol adsorption in the potential region from 0.4 to 0.6 V deactivates Pt sites, especially at the potential more positive than 0.5 V, where the formation of formate takes place.⁵⁶ The adsorption of OH groups starts faster at the potentials more positive than 0.6 V and initiates the oxidation of CO_{ads} to CO₂ (see Eqs. 1 and 2). The anodic peaks around 0.85 V correspond to the fastest oxidation process rate of CO_{ads} to CO₂.

The CV measurement (Fig. 7a) in the mixture of 0.5 mol dm^{−3} H₂SO₄ and 1 mol dm^{−3} CH₃OH was used to evaluate the fastest MOR rate using mass activity at the anodic peak potential, $i_{ap,CV}$. Besides, the CA measurements at different fixed potentials (0.50 V and

0.85 V) were conducted in the same mixture to investigate the short-time stability of the materials in the highly poisonous conditions (at 0.50 V) and under the conditions where the MOR rate is the highest (at 0.85 V), respectively, data is demonstrated in Figs. 7b and 7c. The stable mass activities at the end of CA measurement at the fixed potentials 0.50 V and 0.85 V are noted as $i_{CA @0.50 V}$ and $i_{CA @0.85 V}$, respectively. The MOR results have been compiled in Table VI.

The physical characteristics of Pt–CeO₂/C(KB) catalysts, such as dispersion of Pt NPs, Pt crystallite size, $d_{Pt,TEM}$, and porosity (see Tables III and V), are very similar. The difference due to the synthesis conditions of CeO₂ NPs (see Table I) is most pronounced in the MOR activity. Firstly, although the ultrasound sonication applied for the SL2_Pt–CeO₂/C(KB) and SL_Pt–CeO₂/C(KB) catalysts, the MOR peak mass activity, $i_{ap,CV}$, of the SL2_Pt–CeO₂/C(KB) (516 ± 30 A g_{Pt}^{−1}) is higher than that of the SL_Pt–CeO₂/C(KB) (415 ± 44

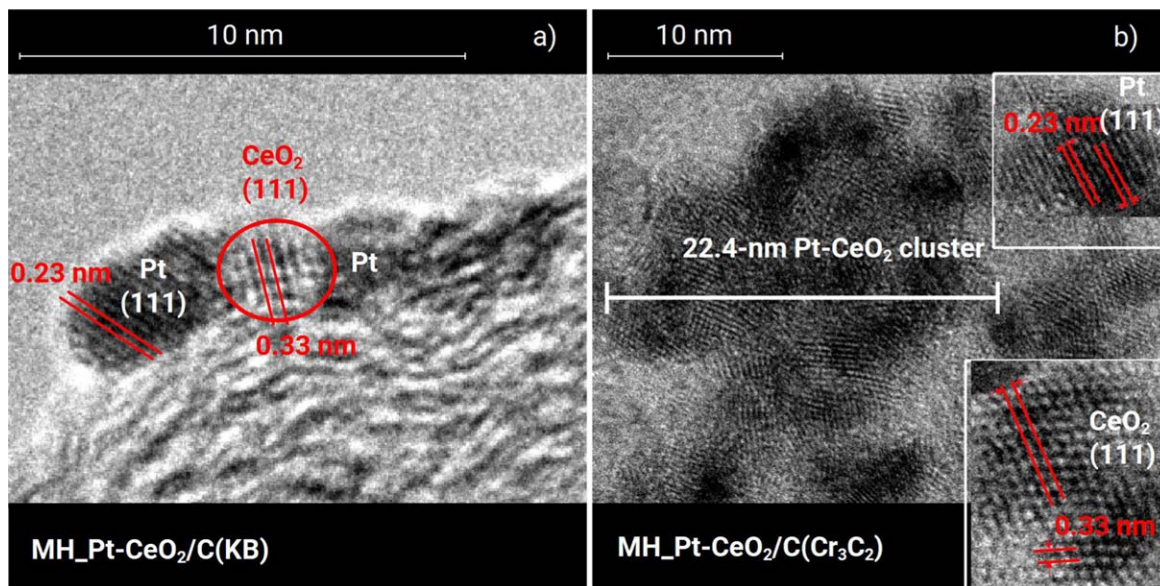


Figure 5. The Pt and CeO₂ nanoparticles of Pt–CeO₂/C catalysts deposited onto different carbon materials are demonstrated. The inserts in part b illustrate the lattice fringes of Pt (111) and CeO₂ (111) of the MH_Pt–CeO₂/C(Cr₃C₂) material.

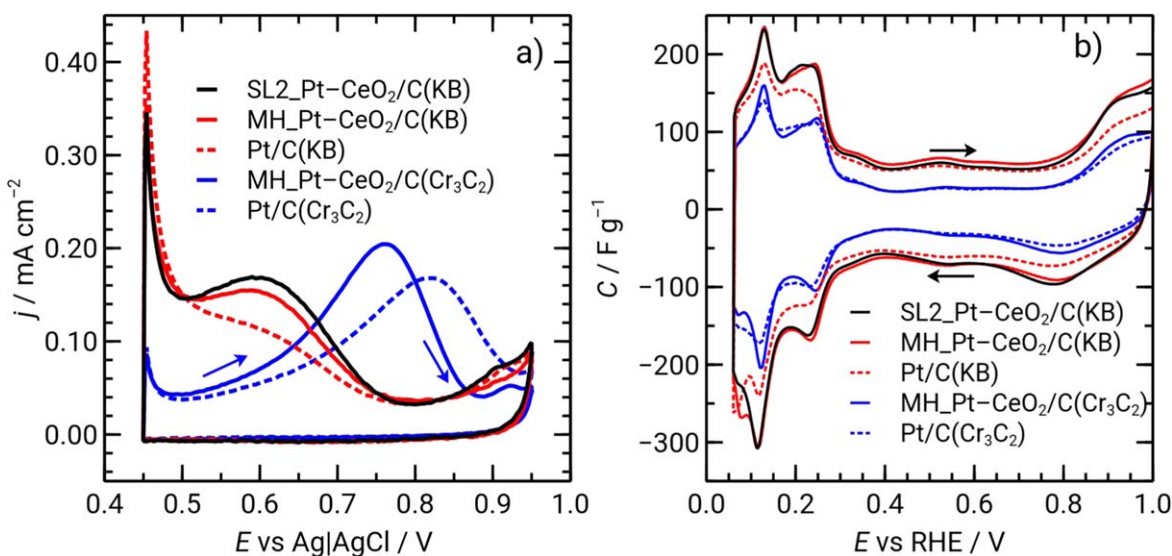


Figure 6. Pt dissolution curves in 6 mol dm^{−3} HCl at 0.5 V s^{−1} (a) and gravimetric capacitance curves calculated from cyclic voltammetric data in 0.5 mol dm^{−3} H₂SO₄ at 100 m V s^{−1} (b).

A g_{Pt}^{−1}). However, the MOR activity of these two materials at 0.85 V is comparable (200 ± 10 and 188 ± 27 A g_{Pt}^{−1}, respectively), according to the $i_{CA @ 0.85 \text{ V}}$ parameter, which more adequately reflects the MOR activity in the high current density region. The difference between the SL₂_Pt–CeO₂/C(KB) and SL_Pt–CeO₂/C(KB) catalyst is visible in the MOR durability parameter $i_{CA @ 0.85 \text{ V}}/i_{ap,CV}$ (0.39 and 0.45, respectively, see Table VI). Thus, the co-precipitation of CeO₂ and Pt colloids forms the Pt–CeO₂ NPs with better MOR durability. The ultrasound sonication method is more effective than the microwave heating method for the deposition of CeO₂ colloid simultaneously with Pt if the SL₂_Pt–CeO₂/C(KB) and ML_Pt–CeO₂/C(KB) materials are selected for the comparison. All the MOR parameters of the SL_Pt–CeO₂/C(KB) catalyst are higher than that of the ML_Pt–CeO₂/C(KB) catalyst, except for the $i_{CA @ 0.50 \text{ V}}$ parameter. As indicated by the TGA residual mass (20 wt%) and the Pt content (23 wt%) from the MP-AES measurement of the ML_Pt–CeO₂/C(KB) catalyst, this material has very low CeO₂

content. This too low CeO₂ content in ML_Pt–CeO₂/C(KB) catalyst may be the cause for the low MOR activity. Therefore, to establish the effect of CeO₂ content on MOR activity, the MH_Pt–CeO₂/C(KB) was synthesized using the same method as for the ML_Pt–CeO₂/C(KB) catalyst, but with higher Ce(NO₃)₃ concentration (5 mM, see Table I) in the synthesis solution. As a result, the $i_{CA @ 0.85 \text{ V}}$ value of the MH_Pt–CeO₂/C(KB) catalyst (193 ± 22 A g_{Pt}^{−1}) is as high as that of SL_Pt–CeO₂/C(KB) catalyst (188 ± 27 A g_{Pt}^{−1}). However, the $i_{CA @ 0.50 \text{ V}}$ (0.86 ± 0.09 A g_{Pt}^{−1}) of the MH_Pt–CeO₂/C(KB) catalyst is the highest amongst the Pt–CeO₂/C(KB) catalysts. At the same time, the durability parameter, which characterizes the resistivity against CO poisoning, is the lowest ($i_{CA @ 0.85 \text{ V}}/i_{ap,CV} = 0.33$). Although the resistance of the MH_Pt–CeO₂/C(KB) against CO poisoning is low, this material exhibits high MOR activity at both working potentials (0.85 and 0.50 V). Thus, the microwave heating method for CeO₂ colloid synthesis with high Ce(NO₃)₃ concentration is promising. In the

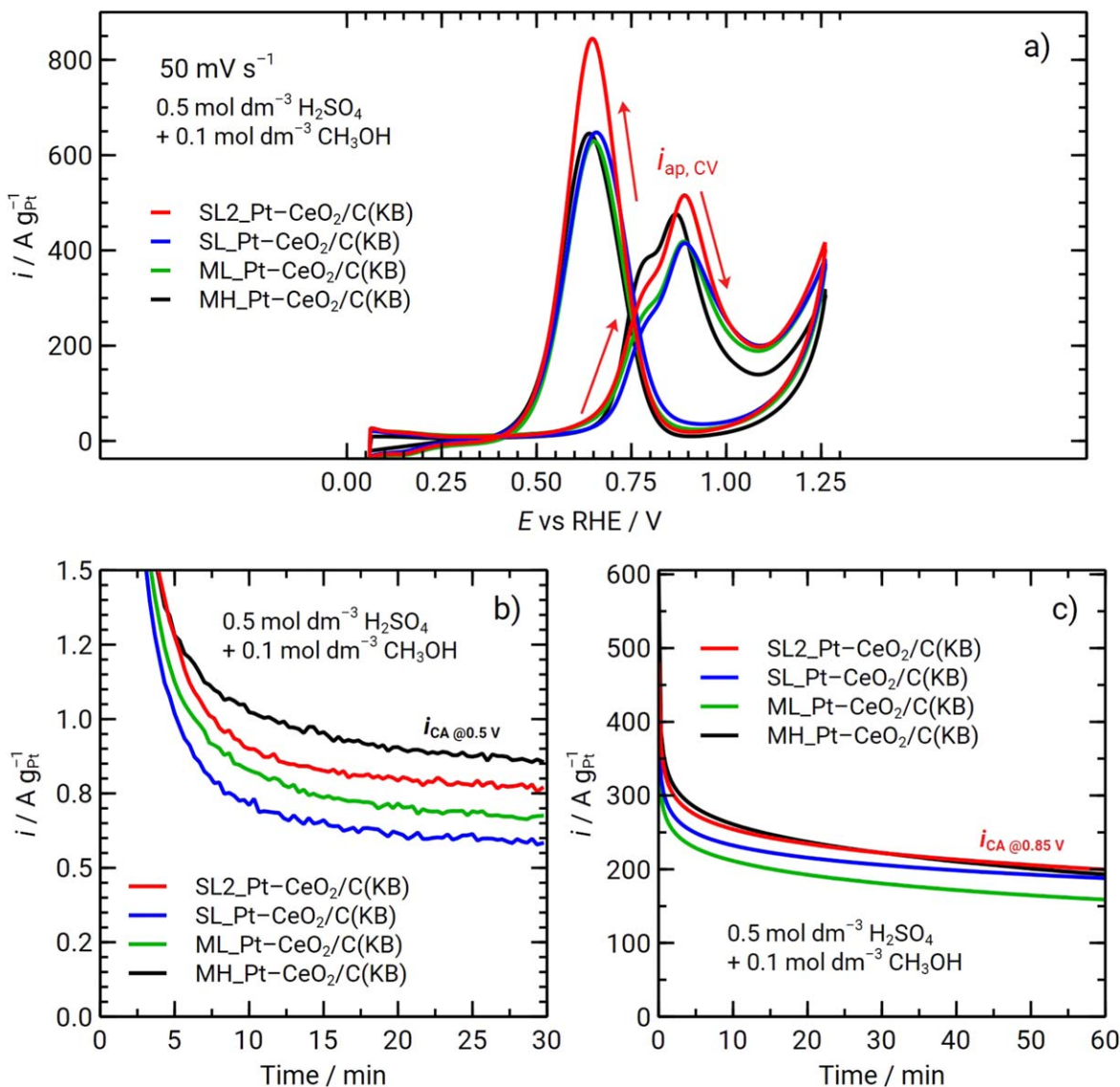


Figure 7. The comparison of methanol oxidation activity for Pt–CeO₂/C(KB)-based catalysts synthesized in different conditions investigated in the mixture of 0.5 mol dm^{−3} H₂SO₄ and 1 mol dm^{−3} CH₃OH saturated with argon. The cyclic voltammetry data at 50 mV s^{−1} is shown in part (a); and chronoamperometric curves at 0.50 V in part (b) and at 0.85 V in part (c).

Table VI. Methanol oxidation reaction parameters for the catalysts synthesized. Measurements were conducted in the mixture of 0.5 mol dm^{−3} H₂SO₄ and 1 mol dm^{−3} CH₃OH saturated with argon.

Material	$i_{ap,CV}/A\ g_{Pt}^{-1}$	$i_{CA\ @0.85\ V}/A\ g_{Pt}^{-1}$	$i_{CA\ @0.5\ V}/A\ g_{Pt}^{-1}$	$i_{CA\ @0.85\ V}/i_{ap,CV}$
SL2_Pt–CeO ₂ /C(KB)	516 ± 30	200 ± 10	0.77 ± 0.09	0.39
SL_Pt–CeO ₂ /C(KB)	415 ± 44	188 ± 27	0.58 ± 0.13	0.45
ML_Pt–CeO ₂ /C(KB)	419 ± 1	159 ± 3	0.68 ± 0.01	0.38
MH_Pt–CeO ₂ /C(KB)	579 ± 39	193 ± 22	0.86 ± 0.09	0.33
Pt/C(KB)	434 ± 11	135 ± 8	0.66 ± 0.01	0.31
MH_Pt–CeO ₂ /C(Cr ₃ C ₂)	543 ± 24	201 ± 16	0.76 ± 0.05	0.37
Pt/C(Cr ₃ C ₂)	476 ± 19	216 ± 17	0.66 ± 0.01	0.45
Pt/C(Vulcan)	178 ± 11 ^a	—	0.07 ± 0.03 ^a	—

$i_{ap,CV}$ —the mass activity from cyclic voltammetry at the anodic peak (at 50 mV s^{−1})

$i_{CA\ @0.85\ V}$ —the stable mass activity from chronoamperometry at 0.85 V after 60 minutes

$i_{CA\ @0.5\ V}$ —the stable mass activity from chronoamperometry at 0.50 V after 30 minutes^a) Data from Prits et al.⁶⁵

literature,^{22,27} if the CeO₂ wt% in the Pt–CeO₂/C catalyst is either too low or too high, the MOR activity of the catalyst is reduced. Although the MOR activity depends on the synthesis methods, the optimal

CeO₂ wt% of Pt–CeO₂/C varies around 10–20 wt%.^{22,27} MOR parameters of Pt–CeO₂/C(KB) catalysts are higher than those of the Pt/C(KB) catalyst and are much higher than those of the MOR of

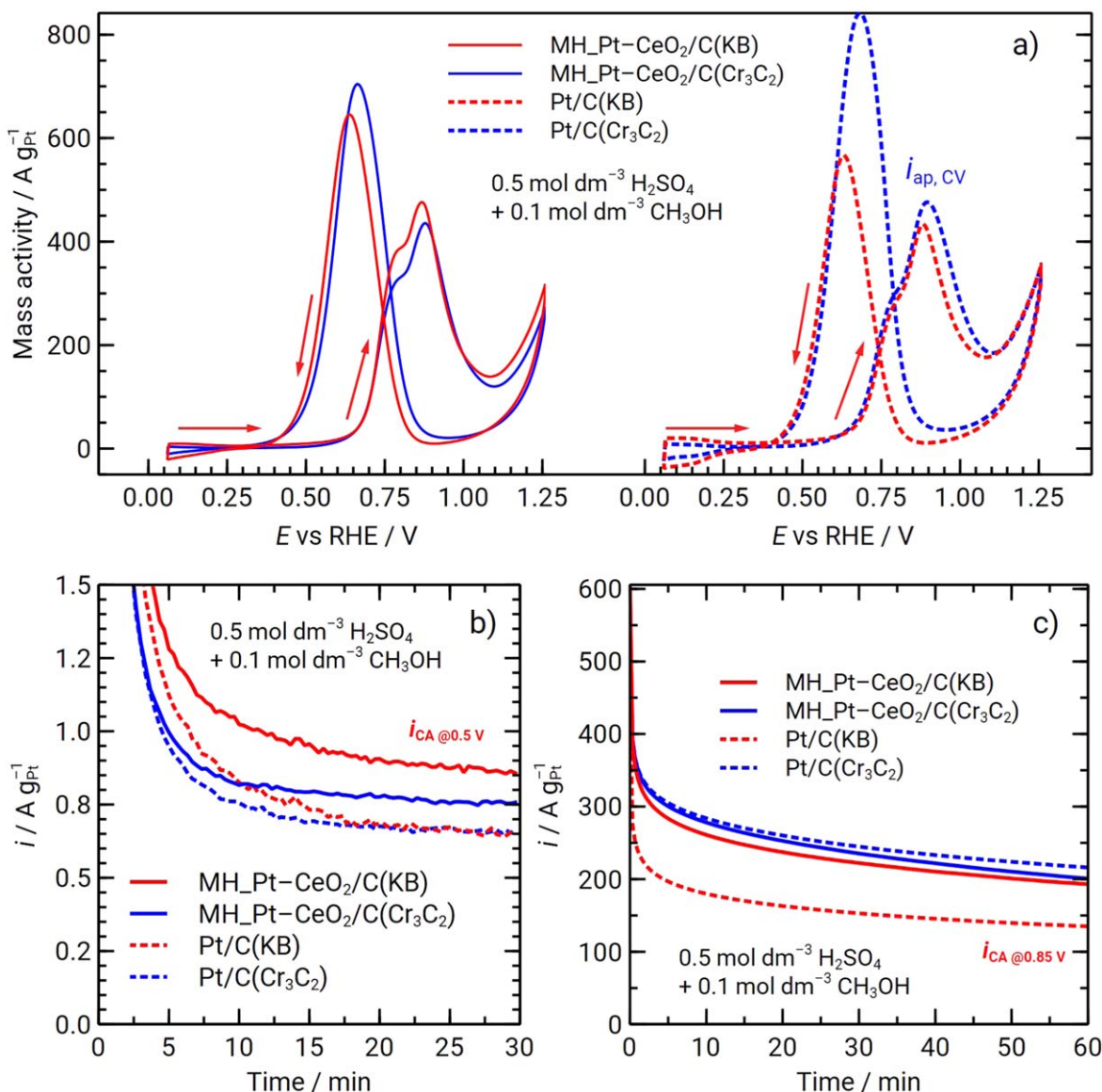


Figure 8. The comparison of methanol oxidation activity for catalysts deposited on C(KB) and C(Cr₃C₂) carbon support using the same synthesis conditions investigated in the mixture of 0.5 mol dm⁻³ H₂SO₄ and 1 mol dm⁻³ CH₃OH saturated with argon. The cyclic voltammery data at 50 mV s⁻¹ is shown in part (a); and chronoamperometric curves at 0.50 V in part (b) and at 0.85 V in part (c).

commercial Pt/C(Vulcan) (see Table VI). The low MOR activity of the Pt/C(Vulcan) catalyst is at least partly due to the low ECSA values ($\leq 20 \text{ m}^2 \text{ g}_{\text{Pt}}^{-1}$, see Table IV).

Although the physical characteristics of C(Cr₃C₂)-based and C(KB)-based catalysts are different (see Tables III and V), the MOR activity of the MH_Pt-CeO₂/C(Cr₃C₂) and MH_Pt-CeO₂/C(KB) catalysts is similar at the peak potential (0.85 V): $i_{\text{ap,CV}}$ values are 543 ± 24 and $579 \pm 39 \text{ A g}_{\text{Pt}}^{-1}$, respectively, and $i_{\text{CA}@0.85 \text{ V}}$ values are 201 ± 16 and $193 \pm 22 \text{ A g}_{\text{Pt}}^{-1}$, respectively (see Table VI and Fig. 8). In Fig. 8b, the $i_{\text{CA}@0.50 \text{ V}}$ value of the MH_Pt-CeO₂/C(KB) catalyst ($0.86 \pm 0.09 \text{ A g}_{\text{Pt}}^{-1}$) is slightly higher than that of the MH_Pt-CeO₂/C(Cr₃C₂) catalyst ($0.76 \pm 0.05 \text{ A g}_{\text{Pt}}^{-1}$), while the $i_{\text{CA}@0.50 \text{ V}}$ values for the Pt/C(Cr₃C₂) and Pt/C(KB) catalysts both are the same ($0.66 \pm 0.01 \text{ A g}_{\text{Pt}}^{-1}$). This reflects somewhat that the durability and short-term performance of the MH_Pt-CeO₂/C(KB) catalyst at low potential (0.50 V) are better. However, the durability of C(Cr₃C₂)-based catalysts for MOR oxidation is much better than that of C(KB)-based catalysts

when comparing $i_{\text{CA}@0.85 \text{ V}}/i_{\text{ap,CV}}$ values, e.g. MH_Pt-CeO₂/C(Cr₃C₂) (0.37) versus MH_Pt-CeO₂/C(KB) (0.33), and Pt/C(Cr₃C₂) (0.45) vs. Pt/C(KB) (0.31). Thus, the C(Cr₃C₂) support enhances the durability of both Pt-CeO₂/C and Pt/C catalysts against CO poisoning compared to catalysts deposited on C(KB) support under the same synthesis conditions.

The MOR activities of the Pt/C(KB) and Pt/C(Cr₃C₂) catalysts are 2–3 times higher than that of the Pt/C(Vulcan) catalyst ($i_{\text{ap,CV}}=210$ and $i_{\text{CA}@0.50 \text{ V}}=0.21 \text{ A g}_{\text{Pt}}^{-1}$) although the specific surface area of the commercial Pt/C(Vulcan) catalyst is comparable with the S_{DFT} values of the MH_Pt-CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) catalysts (see Table V). The MOR activity of the Pt/C(Cr₃C₂) catalyst in this study was as high as that of the most active Pt-CeO₂/C(Vulcan or Ketjenblack) catalyst in our previous studies.^{24,25} This enhancement is due to the improvement of Pt deposition method and the unique structure of C(Cr₃C₂) support. Compared to the work of Wang et al.,⁵⁹ the MOR activity on the Pt/C(Cr₃C₂) catalyst is higher than that on Pt catalysts deposited on both ordered mesoporous carbon (OMC) and WC-supported OMC materials.

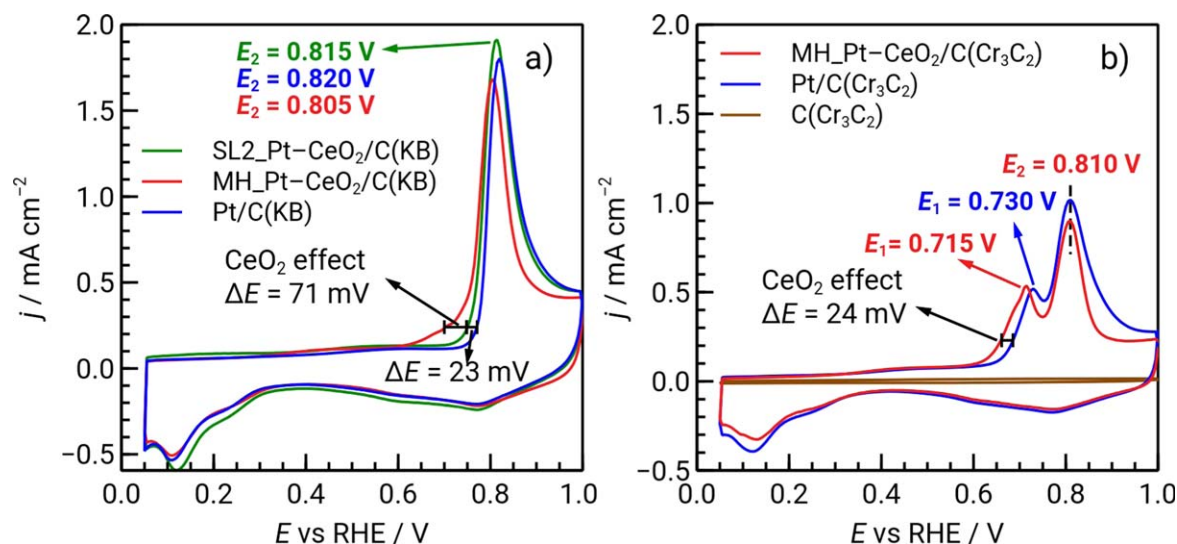


Figure 9. The CO stripping voltammograms of C(KB)-based (a) and C(Cr₃C₂)-based (b) catalysts in 0.1 mol dm⁻³ HClO₄ saturated with CO (during the stripping the argon gas was flowing above the solution) (20 mV s⁻¹).

CO stripping.—The CO oxidation measurements (Fig. 9) were conducted to examine the synergistic effect of Pt coupled with CeO₂ for the studied catalysts. For the C(KB)-based catalysts (see Fig. 9a), the CO oxidation peak potential value increases in the following order MH_Pt–CeO₂/C(KB) (0.805 V) < SL2_Pt–CeO₂/C(KB) (0.815 V) < Pt/C(KB) (0.820 V). The same catalytic effect could also be observed in the potential region from 0.6 to 0.8 V (see Fig. 9a), i.e., the overpotential of CO oxidation is lower for Pt–CeO₂/C-based materials and is proportional to the content of CeO₂. Therefore, the CO oxidation activity decreases in the opposite order MH_Pt–CeO₂/C(KB) > SL2_Pt–CeO₂/C(KB) > Pt/C(KB). It is obvious that the SL2_Pt–CeO₂/C(KB) catalyst possesses slightly higher CO oxidation activity than that of the Pt/C(KB) catalyst due to the trace amount of CeO₂. Therefore, the co-catalytic effect of Pt–CeO₂ is well observed in this case.

In the case of C(Cr₃C₂)-based catalysts, the CO stripping peak splits into two peaks at potential E_1 (around 0.715–0.730 V) and E_2 (at 0.810 V). The CO oxidation charge under the first peak E_1 is 40% and 24% of the total charges for the MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) catalysts, respectively. According to Yuan et al.,⁵² in the case of Pt–CeO₂/C(CNT), the splitting of the CO stripping peak can be caused by the participation of the hydroxyl groups on

the CeO₂ surface on the CO oxidation, and the water adsorption is more favorable on Pt–CeO₂ surface, even at low potentials, i.e. around 0.63 V.⁵² This phenomenon has also been observed for Pt–CeO₂/C and PtRu catalysts before.^{52,60} However, the presence of the CO oxidation peak splitting for the Pt/C(Cr₃C₂) points out the fact that, in our case, this is the synergistic influence of C(Cr₃C₂) support surface and Pt. The C(Cr₃C₂) alone is not able to oxidize CO (see Fig. 9b). Nevertheless, if active sites on C(Cr₃C₂) support are coupled with the Pt NPs, these sites enhance the CO oxidation on the Pt NPs. As our C(Cr₃C₂) possesses a trace amount of chromium,²⁹ the chromium NPs covered by carbon layers can be a part of the active site. The CO oxidation activity of the MH_Pt–CeO₂/C(Cr₃C₂) catalyst is slightly higher than that of the Pt/C(Cr₃C₂) catalyst, as the E_1 values are 0.715 and 0.730 V, respectively. Therefore, the CeO₂ alone does contribute to overall CO oxidation activity. The CO oxidation peak potential E_2 values of the MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) catalysts are smaller than the E_2 values of the SL2_Pt–CeO₂/C(KB) and Pt/C(KB) catalysts (see Fig. 9). Moreover, the current density values of the MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) catalysts in the potential region from 0.68 to 0.73 V are higher than that of the MH_Pt–CeO₂/C(KB) catalyst. This indicates the CO oxidation for

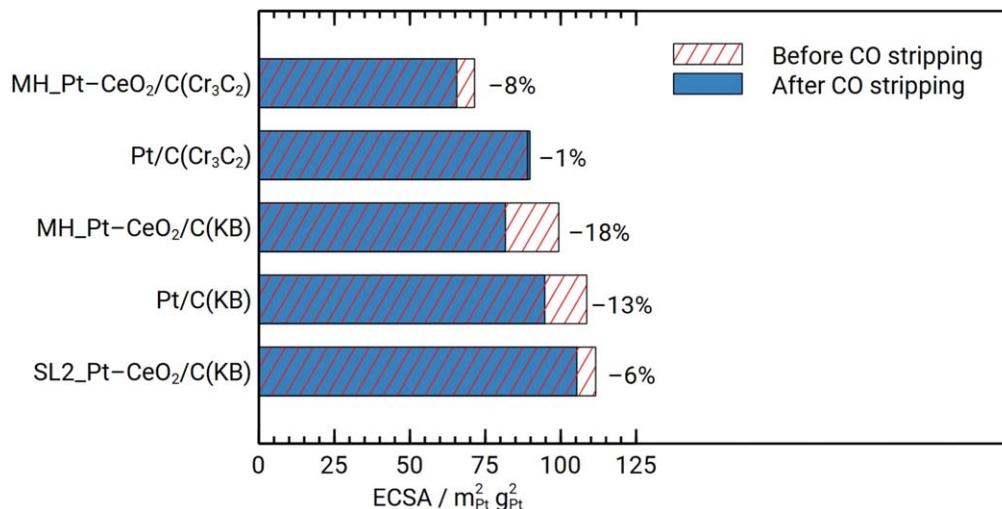


Figure 10. The electrochemically active surface area of Pt nanoparticles estimated from cyclic voltammetry data in 0.1 mol dm⁻³ HClO₄ before and after CO stripping measurements.

Table VII. Oxygen reduction reaction parameters for the selected catalysts. Measurements were conducted in 0.1 mol dm⁻³ HClO₄ solution saturated with oxygen.

Material	MA @0.9 V/A g _{Pt} ⁻¹	SA @0.9 V/A m _{Pt} ⁻²
SL_Pt-CeO ₂ /C(KB)	199 ± 14	2.0 ± 0.1
MH_Pt-CeO ₂ /C(KB)	357 ± 72	3.3 ± 0.2
Pt/C(KB)	234 ± 36	2.0 ± 0.2
MH_Pt-CeO ₂ /C(Cr ₃ C ₂)	288 ± 1	4.0 ± 0.1
Pt/C(Cr ₃ C ₂)	192 ± 16	2.3 ± 0.1
Pt/C(Vulcan)	176 ± 27	8.9 ± 0.4

MA @0.9 V—the mass activity at 0.9 V vs. reversible hydrogen electrode (RHE) estimated from the kinetic current density

SA @0.9 V—the specific activity at 0.9 V vs. RHE

the C(Cr₃C₂)-based catalysts starts at less positive potentials and is more aggressive.

In addition, the difference in ECSA_{HClO₄} values (see Fig. 10) measured before and after the CO stripping indicates the ability of Pt NPs to avoid CO poisonings. The SL₂Pt-CeO₂/C(KB), MH_Pt-CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) catalysts are more resistant to CO poisoning as the ECSA_{HClO₄} values are reduced less than 10% after the CO stripping measurement. The ECSA_{HClO₄} values of MH_Pt-CeO₂/C(KB) and Pt/C(KB) were reduced 18% and 13%, respectively. This parameter correlates with the $i_{CA} @0.85 \text{ V}/i_{ap,CV}$ parameter of MOR measurement. This observation is slightly surprising if one compares it with the $i_{CA} @0.50 \text{ V}$ parameter for the synthesized catalysts. Since the MH_Pt-CeO₂/C(KB) is the best MOR catalyst amongst all catalysts according to the CA measurement in the methanol solution at 0.5 V (see Figs. 7 and 8), the drastic decrease of ECSA_{HClO₄} after CO stripping is surprising. As the transformation of CO_{ads} on Pt surface to CO₂ starts at potentials more positive than 0.6 V⁵⁸ when the water adsorption is fast enough to provide OH_{ads} for the oxidation reaction (according to the MOR mechanism, see Fig. S1),⁶¹ the higher MOR activity of MH_Pt-CeO₂/C(KB) at 0.5 V with lower capacity to resist CO poisoning indicates that the MOR oxidation at some Pt-CeO₂ NPs of MH_Pt-CeO₂/C(KB) probably proceeds with the formic acid route and bypasses the formation of CO from the formaldehyde route, or the catalyst is able to oxidize the CO_{ads} (in the formaldehyde route)

with a fast water adsorption rate at Pt-CeO₂ surface (see Fig. S1). This phenomenon can be important for the MH_Pt-CeO₂/C(Cr₃C₂) catalyst if the $i_{CA} @0.50 \text{ V}$ and ECSA_{HClO₄} values (after CO stripping) of this material are compared with the same values of the Pt/C(Cr₃C₂) catalyst.

Oxygen reduction reaction.—Five materials, which were SL_Pt-CeO₂/C(KB), MH_Pt-CeO₂/C(KB), Pt/C(KB), MH_Pt-CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂), were selected to investigate the ORR activity (Fig. 11). The RDE results of ORR were analyzed following the classical Koutecký-Levich equation.^{62,63}

$$\frac{1}{j_c} = \frac{1}{j_k} + \frac{1}{j_d}, \quad [7]$$

where j_c is current density corrected with the background current density, j_k is the kinetic current density, and j_d is the diffusion step current density. The ORR was evaluated using mass activity (MA) and specific activity (SA) at 0.9 V vs. RHE, and the results are given in Table VII. The MA and SA values were calculated using Eqs 8 and 9, respectively.

$$MA = \frac{i_{k,0.9V}}{m_{Pt}}, \quad [8]$$

where $i_{k,0.9 \text{ V}}$ is the kinetic current at 0.9 V vs. RHE and m_{Pt} is the mass of Pt on the electrode surface.

$$SA = \frac{MA}{ECSA_{HClO_4}}. \quad [9]$$

The ORR can be influenced dramatically by the quality of the catalyst layer on the electrode surface. The j_c - E curves (Fig. 11a) have nice limiting plateaus, and the value of limiting current density is close to the theoretical value. Therefore, these thin film RDE data can be used to evaluate ORR kinetic parameters. The electrode surface was covered evenly with the catalyst layer based on the optical microscopy data (the insert in Fig. 11b).

Based on data given in Table VII, the MH_Pt-CeO₂/C(KB) and MH_Pt-CeO₂/C(Cr₃C₂) catalysts have higher ORR activity toward the ORR activity due to the higher CeO₂ content, i.e. MA values (357 ± 72 and 288 ± 1 A g_{Pt}⁻¹, respectively), and SA values (3.3 ± 0.2

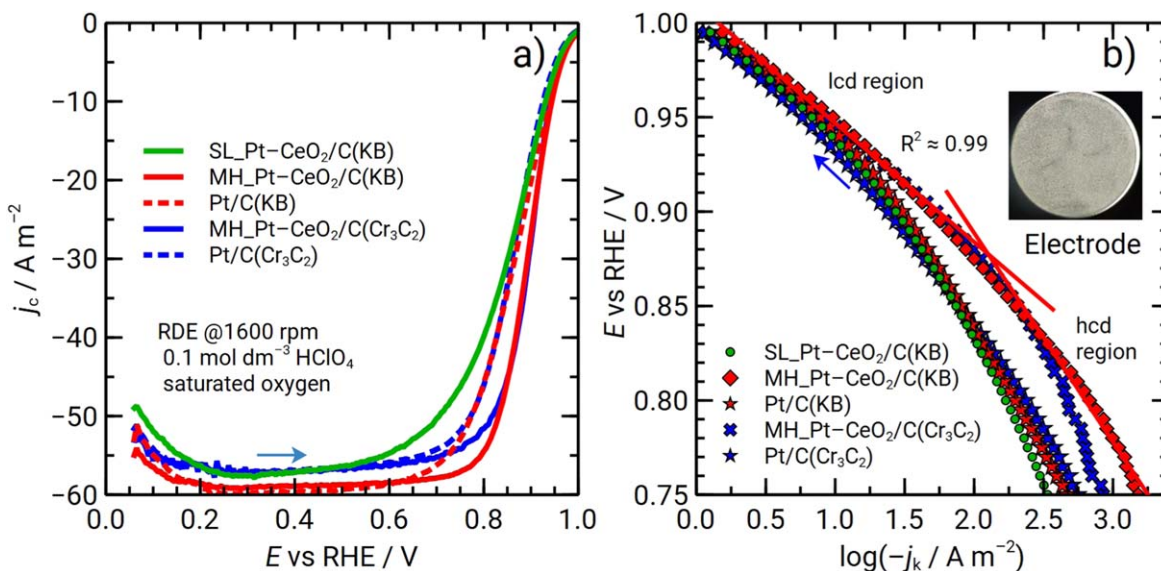


Figure 11. The rotating disk electrode (RDE) results (anodic potential sweep) are given in part (a), and the Tafel-like plots for selected materials are presented in part (b). The RDE measurements were conducted at 1600 rpm and 20 mV s⁻¹ in 0.1 mol dm⁻³ HClO₄ saturated with O₂. Insert: the optical microscopy image of the electrode surface uniformly covered with the catalyst layer.

and $4.0 \pm 0.1 \text{ A m}_{\text{Pt}}^{-2}$) are higher than for other catalysts synthesized. Thus, the ORR activity of these two materials is very comparable (see Fig. 11). The SL_Pt–CeO₂/C(KB) catalyst is only as active toward the ORR as the Pt/C catalysts, including the commercial Pt/C(Vulcan), given in Table VII due to low CeO₂ content. The average MA of all three Pt/C catalysts is $201 \pm 56 \text{ A g}_{\text{Pt}}^{-1}$. The Tafel slope of catalysts under study is 57–73 mV in the low current density region and about two times higher in the high current density region. A more detailed analysis of the ORR kinetics of catalysts is given in the supplementary material (see Table S1).

In comparison with Pt catalysts on different carbon support materials, the Pt/C(KB) has higher ORR kinetic currents than Pt/C(Cr₃C₂) when the oxygen dissociative pathway is dominant (Fig. 11b). Otherwise, when the associative pathway is dominant, the ORR of Pt/C(Cr₃C₂) is obviously faster than that of Pt/C(KB) in the mixed kinetic region (Fig. 11).

The ORR activity of the Pt/C(Cr₃C₂) catalyst investigated in this study is comparable to the ORR activity of the Pt/C(Mo₂C) and Pt/C(D-glucose derived carbon) catalysts.^{1,3} The MH_Pt–CeO₂/C(KB) and MH_Pt–CeO₂/C(Cr₃C₂) catalysts are more active than other PtC(carbide-derived carbon) catalysts. Our Pt–CeO₂/C catalysts can be compared with the catalysts synthesized by Lu et al.⁵⁰ The ORR activity established for our Pt–CeO₂/C catalysts is better than that of the Pt–CeO₂/C(nitrogen doped carbon) catalysts, which have approximately the same CeO₂ content. However, the Pt–CeO₂/C catalyst of Lu et al., which has higher CeO₂ content, has higher activity toward the ORR.

Conclusions

The CeO₂ synthesis parameters such as heating method, NaOH and Ce(NO₃)₃ concentrations do not influence the physical properties of Pt and CeO₂ NPs such as crystallite sizes (around 1 nm), Pt dispersion, and Pt volume to area-averaged diameter (3.1 to 4.1 nm). All the synthesized catalysts are micro-mesoporous, and the pores are not clogged during the deposition of NPs. However, the electrochemical activity of MOR, CO stripping, and ORR is influenced by synthesis parameters. The SL_Pt–CeO₂/C(KB) catalyst, for which the CeO₂ colloid was synthesized using ultrasound sonication, possesses good durability against CO poisoning with high $i_{\text{CA}} @ 0.85 \text{ V}/i_{\text{ap,CV}}$ value (0.45). The MH_Pt–CeO₂/C(KB) catalyst, for which the CeO₂ colloid was synthesized using microwave radiation, has the highest MOR activity ($i_{\text{CA}} @ 0.85 \text{ V} = 193 \pm 22 \text{ A g}_{\text{Pt}}^{-1}$ and $i_{\text{CA}} @ 0.50 \text{ V} = 0.86 \pm 0.9 \text{ A g}_{\text{Pt}}^{-1}$). Increasing the CeO₂ content in the C(KB)-based catalysts reduces the CO oxidation overpotential. However, the ability to remove CO from the Pt surface is worse in the case of C(KB)-based catalysts, with a significant decrease for the ECSA_{HClO₄} values of the MH_Pt–CeO₂/C(KB) and Pt/C(KB) catalysts (18% and 13%, respectively) after the CO stripping. The ORR activity is better if microwave heating is used to synthesize the CeO₂ colloid because the ORR activity of the MH_Pt–CeO₂/C(KB) catalyst is higher than that of the SL_Pt–CeO₂/C(KB) catalyst.

The physical characterization confirmed the difference in the properties of Pt and CeO₂ NPs if the same synthesis methods were applied for the deposition of Pt and CeO₂ NPs on the C(Cr₃C₂) and C(KB) carbon. For C(Cr₃C₂)-based catalysts, the crystallite size of Pt is slightly higher, and the crystallite size of CeO₂ is about five times higher than that of C(KB)-based catalysts. The Pt NPs are somewhat agglomerated in the case of C(Cr₃C₂)-based materials. The $d_{\text{Pt,TEM}}$ is $7.2 \pm 3.8 \text{ nm}$ for the MH_Pt–CeO₂/C(Cr₃C₂) and Pt/C(Cr₃C₂) catalysts. The Pt–CeO₂ clusters formed of several particles with a diameter up to 22.4 nm) are observed on the MH_Pt–CeO₂/C(Cr₃C₂) material, while the clusters of Pt–CeO₂ on the MH_Pt–CeO₂/C(KB) are formed from only 2–3 particles. The number of oxygen vacancies of the CeO₂ for the MH_Pt–CeO₂/C(Cr₃C₂) catalyst is higher than that for the

MH_Pt–CeO₂/C(KB) catalyst. According to Raman and TEM results, Pt and CeO₂ NPs have good contact in both materials. The C(Cr₃C₂) support material enhances the durability of Pt–CeO₂/C and Pt/C materials against CO poisoning. The MOR at 0.85 V ($i_{\text{CA}} @ 0.85 \text{ V}$) of MH_Pt–CeO₂/C(Cr₃C₂) catalyst is comparable with that of MH_Pt–CeO₂/C(KB). However, in comparison with the MH_Pt–CeO₂/C(KB) catalyst, the MH_Pt–CeO₂/C(Cr₃C₂) has higher durability against CO poisoning ($i_{\text{CA}} @ 0.85 \text{ V}/i_{\text{ap,CV}} = 0.37$) and higher ability to remove CO from Pt surface as the ECSA_{HClO₄} value was reduced only 8% after CO stripping. The Pt–CeO₂ catalyst NPs deposited on both carbon support materials can, to some extent, either oxidize the methanol by the reaction routes that bypass the formation of CO_{ads} or facilitate the water adsorption on the Pt–CeO₂ surface. The ORR activity of the catalysts on C(Cr₃C₂) and C(KB) is comparable (Table VII and Fig. 11).

All the synthesized catalysts had better MOR activity than the commercial Pt/C(Vulcan) catalyst.

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