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Highly Stable Pt—Ru Nanoparticles Supported on Three-Dimensional Cubic Ordered Mesoporous Carbon (Pt—Ru/CMK-8) as Promising Electrocatalysts for Methanol Oxidation

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ABSTRACT: The cost of the catalysts used in the direct methanol fuel cell 7 poses a challenge to its widespread use as an energy efficient and environment 8 friendly fuel conversion technology. In this study, two types of highly ordered 9 mesoporous carbon CMK-8 (I and II) with high surface area and 3-D 10 bicontinuous interpenetrating channels were synthesized and deposited with 11 Pt-Ru nanoparticles using the sodium borohydride reduction method. The 12 electrocatalytic capabilities for methanol oxidation were investigated using 13 cyclic voltammetry and chronoamperometry, and the results were compared 14 with that of Pt-Ru deposited on Vulcan XC-72 using the same prepara-15 tion method as well as with commercial Pt-Ru/C (E-TEK) catalyst. Pt-16 Ru/CMK-8-I synthesized by the method developed in this work revealed an 17 outstanding specific mass activity (487.9 mA/mg) and superior stability 18 compared with the other supports, thus substantiating its potential to reduce 19 the costs of DMFC catalysts. 20



1. INTRODUCTION

Energy, its widespread distribution, availability, and afford-23 ability has come to the foreground in developmental issues 24 worldwide as a result of the challenges confronting the use of 25 fossil fuels, namely, their rapid depletion and increasing environ-26 mental pollution.¹⁻³ The fuel cell, a fuel conversion technology, 27 is widely touted as having the potential to address these.^{4,5} The 28 direct methanol fuel cell operated with the electrochemical oxida-29 tion of methanol as fuel at the anode and the reduction of oxygen at 30 the cathode stands out among others because of its high conversion 31 efficiency, low pollution, low weight, and high power density.⁶ 32 Methanol also offers the advantage of easy storage, refuelling, and 33 transportation when compared with hydrogen-oxygen fuel cell.^{7,8} 34

However, one of the major challenges facing the market 35 competitiveness of direct methanol fuel cells is the cost of the 36 catalyst, mainly the platinum-ruthenium bimetallic alloy, which 37 has been discovered to be the most appropriate among other 38 options.⁹⁻¹³ This catalyst is very often dispersed on a conven-39 tional carbon support, which influences the catalytic activity through 40 metal support interaction.^{14–16} Hence, efforts are being channelled 41 toward obtaining a support material that simultaneously optimizes 42 the catalyst dispersion, loading, and electrocatalytic efficiency. 43

An ideal support-catalyst assembly should ensure facile 44 molecular transport of reactants and products, have good 45 electronic conductivity, and possess high surface reactivity; 46 these would enhance the molecular conversion.¹⁷ A highly 47 ordered mesoporous carbon (HOMC) with tunable pore 48 sizes, high surface area, large pore volume, and more narrow 49 pore size distribution lends itself to the foregoing merits.^{18–21} 50 In general, ordered mesoporous carbons, especially CMK-3, 51

have been used extensively as supports for direct methanol fuel cell catalysts.²²⁻²⁹

CMK-8 mesoporous carbons are unique because of their 3-D cubic *Ia3d* mesostructure, which consists of two interpenetrating continuous networks of chiral channels.³⁰ This is a replica of the mesoporous silica (KIT-6) hard template that follows the G-surface.³¹ Hence their structure is also referred to as bicontinuous gyroidal.

Merits of CMK-8 like other HOMC include extremely high surface area, well-defined pore size, high thermal stability, flexible framework composition, and intrinsic conductivity.^{30,32,33} Compared with other HOMCs like CMK-3, the unique highly branched intertwined 3-D channel network (nanoscale level) of CMK-8 is likely to provide more accessible entrances and channels as well as serve as a highly opened porous host with easy and direct access for guest species, this would result in a higher loading of electroactive species and also facilitate inclusion or diffusion throughout the pore channels without pore blockage.^{34,35} Another advantage of CMK-8 over other HOMCs is that it possesses a higher *Ia3d* symmetry that leads to a relatively isotropic graphitized structure with a higher conductivity; this enhances heterogeneous electron transfer more effectively.³⁶

In this study, we seek to exploit the aforementioned structural characteristics of CMK-8. By varying the mole ratio of starting reactants, two different types of highly ordered mesoporous silica KIT-6 were synthesized and used as hard template for synthesizing

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Figure 1. (a) Low-angle XRD patterns of CMK-8 and (b) N_2 adsorption–desorption isotherms of CMK-8-I and (c) CMK-8-II samples. (The inset shows their BJH pore size distributions.)

78two types of CMK-8 carbons (I and II) with different pore sizes;79Pt-Ru was deposited on the CMK-8 via the sodium borohydride80reduction method. The CMK-8 HOMCs were characterized by81means of N_2 -physisorption, X-ray diffraction (XRD), and trans-82mission electron microscopy (TEM). The electrochemical activity83and stability of the catalysts were explored using cyclic voltammetry84and chronoamperometry. The results when compared with that of

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Table 1.	Pore Characteristics	of the	Mesoporous	and V	Vulcan
XC 72R	Carbons				

carbon	BET surface area (m^2/g)	total pore volume (cm³/g)	pore size (nm)
Vulcan XC 72 R ^a	235	0.67	
mesoporous carbon CMK-8-I	1060	1.26	4.9
mesoporous carbon CMK-8-II	1149	1.48	3.2
^a From ref 32.			

both commercial (E-TEK) and in-house Pt-Ru/Vulcan XC-72R revealed the potential of CMK-8 as an excellent support material for Pt-Ru catalysts when used in methanol oxidation. To the best of our knowledge, this is the first application of CMK-8 HOMC in the development of catalysts for use in direct methanol fuel cells.

2. EXPERIMENTAL SECTION

2.1. Synthesis of Highly Ordered Mesoporous Silica and Carbon. The mesoporous silica was synthesized as follows.³⁵ Typically, 6 g of triblock copolymer, EO₂₀PO₇₀EO₂₀ (Pluronic P123, Sigma Aldrich) was dissolved in 217 g of deionized water and 11.628 g of 37 wt % conc. HCl (Sigma Aldrich) solution with stirring at 35 °C. After complete dissolution, 6 g of butanol was added at once with vigorous stirring. After 1 h of stirring, 12.9 g of tetraethylorthosilicate (TEOS, 98 wt %, Sigma Aldrich) was added at once to the homogeneous clear solution while still stirring. The mixture was left under vigorous and constant stirring for 24 h at 35 °C. Afterward, the mixture was placed in an oven at 100 °C and left for 24 h under static conditions (in a closed polypropylene bottle). The solid product obtained after hydrothermal treatment was filtered while hot and dried at 100 °C without washing. To complete the synthesis, we removed the template by extraction in an ethanol-HCl mixture; this was done by stirring the filtrate for 1 to 2 h in a mixture of 300-400 mL of ethanol with 20-30 mL of 37% conc. HCl, followed by calcination in air at 550 °C for 6 h. KIT-6 I and II were obtained by varying the mole ratio of reactants.

The mesoporous carbon was prepared using a slight modifica-112 tion of a reported procedure.³⁰ Typically, 1.25 g of sucrose (Sigma 113 Aldrich) and 0.14 g of H₂SO₄ (97 to 98 wt %, Sigma Aldrich) 114 were added to 5 g of deionized water. This was mixed with 1 g of 115 KIT-6 mesoporous silica. The mixture was dried in an oven at a 116 temperature of 100 °C for 6 h; the temperature was increased 117 to 160 °C and maintained for another 6 h. To the partially 118 decomposed sucrose was added a sucrose solution prepared 119 with 0.75 g sucrose and 0.08 g H₂SO₄ in 5 g of water. The 120 drying procedure was repeated at a ramp rate of 0.5 °C/min. 121 The carbon-silica composite was pyrolyzed in flowing nitrogen 122 at a temperature of 900 $^\circ C$ (N2 flow: 50 mL/min; heating 123 rate 2 °C/min) for 4 h. The carbon was recovered by dissolving 124 the silica template in 1 M ethanolic sodium hydroxide (50% 125 water-50% ethanol v/v), filtering, and washing with ethanol. 126 Finally, the resultant carbon was dried at 100 °C for 12 h. CMK-I 127 and II were obtained by using KIT-6 I and II as hard templates, 128 respectively. 129

2.2. Preparation of the Pt–Ru/CMK-8 Electrocatalyst. 130 Pt–Ru electrocatalysts were synthesized and deposited on 131 carbon supports by using a wet chemical reduction method. In 132 this work, carbon-supported Pt–Ru nanoparticle electrocatalyst 133

S. no.	electrocatalysts	particle size XRD (nm)	particle size TEM (nm)	metal loading (%)	elemental composition Pt:Ru (at %)
1	Pt-Ru/XC-72	4.64	4.0	19.28	Pt ₅₆ Ru ₄₄
2	Pt-Ru/C (E-TEK)	1.91	2.6	23.2	Pt ₅₃ Ru ₄₇
3	Pt-Ru/CMK-8-I	5.60	6.5	19.54	Pt ₅₇ Ru ₄₃
4	Pt-Ru/CMK-8-II	3.82	5.0	19.38	Pt55 Ru45

Table 2. Structural Parameters and Chemical Composition for Various Electrocatalysts



Figure 2. XRD Pattern of (a) Pt–Ru/CMK-8-I, (b) Pt–Ru/CMK-8-II, (c) Pt–Ru/XC-72 (prepared), and (d) Pt–Ru/C (E-TEK) catalyst.

with atomic ratio Pt/Ru (1:1) and 20 wt % of metal loading 134 (Pt-Ru) on carbon was prepared according to the following 135 procedure. Typically, the mesoporous carbon (40 mg) was ultra-136 sonically dispersed in a mixture of ultrapure water and isopropyl 137 alcohol (with a volume ratio of 1:1) for 20 min, after which a 138 desired amount of 0.01 M H₂PtCl₆ (3.4 mL) (Acros) and 0.01 M 139 RuCl₃ (4.4 mL) (Aldrich) was added. The mixture was stirred for 140 30 min. The pH value of the ink was adjusted by adding a drop 141 NaOH solution; then, its temperature increased to 80 °C. We 142 added 25 mL of 0.2 mol L^{-1} solution of sodium borohydride to the 143 ink drop by drop, and the bath was stirred for 1 h. (6.1 mg of 144 sodium borohydride dissolved in 5 mL of deionized water was 145 added to the ink. and the mixture was stirred for 1 h.) The mixture 146 was cooled, dried, and washed repeatedly with ultrapure water 147 (18.2 M $\cdot \Omega$ cm) to remove excess chlorides. The catalyst powder 148 was dried in an oven and stored. All chemicals used were of 149 analytical grade. The catalyst was denoted as Pt-Ru/CMK-8. 150

2.3. Characterization. Nitrogen sorption characterization of 151 the materials was conducted on a Micromeritics ASAP2010 152 surface area and pore size analyzer at 77.35 K. Powder XRD 153 was recorded on a PAN analytical X'Pert Pro MPD diffrac-154 tometer using Cu K α radiation. Morphology and microstructure 155 of the as-obtained samples were examined using a Tecnai G2 156 F20X-Twin MAT high-resolution TEM, operating at an accel-157 erating voltage of 200 keV. The metal loading of the catalysts was 158 accurately determined with an inductively coupled plasma atom-159 160 ic emission spectrometry (ICP-AES).

2.4. Electrochemical Measurements. Electrochemical mea surements were collected using a computer-controlled Gill
AC potentiostat (ACM Instruments, Cumbria, U.K.). A three electrode cell consisting of the glassy carbon (0.07 cm²) as



Figure 3. TEM images of (a) KIT-6 and (b-d) CMK-8 mesoporous carbon.

working electrode, Pt foil, and Ag/AgCl (saturated by KCl solution) electrodes as counter and reference electrodes, respectively, was used. All electrochemical experiments were carried out at room temperature in $0.5 \text{ M H}_2\text{SO}_4$ electrolyte. The electrolyte solution was purged with high pure nitrogen for 30 min prior to a series of voltammetric experiments.

2.5. Preparation of the Working Electrode. Glassy carbon electrode (0.07 cm^2) polished to a mirror finish with $0.05 \ \mu\text{m}$ alumina suspension and washed with water before each experiment has served as an underlying substrate of the working electrode. The electrodes for the electrochemical measurements were fabricated by dispersing 5 mg of Pt-Ru supported mesoporous carbon in 500 μ L of distilled water, and the dispersion to the glassy carbon electrode, and the solvent was evaporated. 179

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Figure 4. TEM images of (a,b) Pt-Ru/CMK-8-I, (c) Pt-Ru/CMK-8-II (d) Pt-Ru/XC-72 (prepared), and (e) Pt-Ru/C (E-TEK) catalyst.

The resulting film was covered with 5 μ L of Nafion to bind the particles on the substrate and it was evaporated, which results in Pt-Ru-supported mesoporous carbon. A solution of 1 M CH₃OH in 0.5 M H₂SO₄ was used to study the methanol oxidation activity.

185 3. RESULTS AND DISCUSSION

3.1. Characterization of the Mesoporous Carbon. The 186 porosimetric analysis of the 3-D mesoporous carbons gave the 187 results shown in Figure 1 and Table 1, where the data of Vulcan F1 188 T1 189 carbon are also reported for comparison. The nitrogen adsorp-190 tion isotherms of CMK-8-I and CMK-8-II and their correspond-191 ing BJH desorption pore size distribution are shown Figure 1. The isotherms of CMK-8-I and CMK-8-II are of type IV 192 according to the IUPAC classification and exhibit a sorption 193

hysteresis loop. Both of the samples exhibit a high degree of structural ordering with a narrow pore size distribution, as indicated by the steep capillary condensation step of the respective adsorption isotherm and the BJH pore size distribution (Figure 1b).

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The structural properties of synthesized ordered mesoporous carbon (CMK-8) are summarized in Table 1. The prepared CMK-8 with tailored pore sizes possesses the pore diameters of 3.1 and 4.9 nm. The pore diameter of CMK-8-I is larger than CMK-8-II, which reflects the influence of pore diameter of their parent mesoporous silica. CMK-8-I and CMK-8-II possess pores with diameters of about 3.1 and 4.9 nm (Table 1), high BET surface areas of 1060 and 1149 m² g⁻¹, and large pore volumes of 1.46 and 2.0 cm³ g⁻¹, respectively (Table 1).

From the XRD pattern of CMK-8-I and -II (Figure 4b), a highintensity Bragg peak and one shoulder peak, which can be

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Figure 5. Cyclic voltammograms of (a) Pt-Ru/XC-72, (b) Pt-Ru/C (E-TEK), (c) Pt-Ru/CMK-8-II, and (d) Pt-Ru/CMK-8 -I in 0.5 M H_2SO_4 at 50 mV, 25 °C.

indexed as (211) and (220), are characteristics of a typical pattern for *Ia3d* mesostructure,^{37,38} a confirmation that the particles possess a highly ordered structure.

3.2. Physicochemical Characterization of the Electrocatalysts. Metal atomic composition (Pt/Ru, atomic ratio) and weight percent of the electrocatalysts were determined by ICP and are shown in Table 2. It is found that the actual metal loadings of various catalysts agree well with their theoretical metal loadings, demonstrating that the deposition of metals on CMK-8 support was successful.

Figure 2 shows the XRD profiles (a) Pt-Ru/CMK-8 -I and F2 220 (b) Pt-Ru/CMK-8-II catalyst. The crystalline structure of the 221 metal in the nanoparticles is revealed by all XRD patterns, which 222 clearly show diffraction peaks that can be indexed to four main 223 characteristic reflections of the face-centered cubic (fcc) crystal-224 line Pt, namely, (1 1 1), (2 0 0), (2 2 0), and (3 1 1).^{27,29} In the 225 XRD analysis for the Pt-Ru/CMK-8 samples, no distinct peak 226 indicating the presence of elemental Ru, RuO₂ or amorphous 227 phases is observed. These results imply that for all catalysts 228 prepared in this study, Ru is incorporated in the Pt fcc structure. 229 Yet another possibility could be that metallic Ru is not detected 230 because the intensities of its reflections are much smaller than 231 those of the Pt. 232

In the work by Chu and Gilman, it was observed that at 233 atomic % Pt/Ru 48:52 wide-angle XRD reveals only the reflec-234 tion pattern characteristics of platinum; however, at Pt/Ru 27:73, 235 the characteristic patterns for platinum and ruthenium were 236 revealed. The implication is that when Ru is present at an almost 237 equal or lesser amount relative to Pt, a good alloy is obtained, 238 but when there is a wide difference in their relative amounts, 239 a separate Ru phase can be identified.^{29,39,41}Table 2 summarizes 240 the average particle sizes of the catalysts calculated from the 241 Pt $(2\ 2\ 0)$ peak by the Scherrer formula 242

$$d(\text{\AA}) = k\lambda/\beta\cos\theta$$

where k is a coefficient (0.9), λ is the wavelength of X-ray used (1.54056 A°), β is the full width at half-maximum, and θ is the angle at position of peak maximum. 243 244 245

The synthesized mesoporous carbons with the small pore size 246 and large pore size were utilized for Pt-Ru deposition. These 247 ordered 3-D mesoporous carbon substrates should favor catalyst 248 dispersion and three-phase contact among Pt-Ru, Nafion 249 ionomers, and reactants; they have a surface area higher than 250 that of Vulcan, and, more importantly, a higher fraction of this 251 area is in the mesoporous region. The strong porous structure 252 and high surface area give better dispersion of the catalyst. 253

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Figure 6. Cyclic voltammograms of (a) Pt-Ru/XC-72, (b) Pt-Ru/C (E-TEK), (c) Pt-Ru/CMK-8-II, and (d) Pt-Ru/CMK-8-I in 0.5 M H_2SO_4 and 1 mol dm⁻³ methanol at 50 mV.

To examine the immobilization of Pt-Ru nanoparticles on 254 mesoporous carbon, we carried out TEM measurements of the 255 prepared catalysts. Typical TEM images of the Pt-Ru/CMK-8-I 256 and Pt-Ru/CMK-8-II catalysts (Figure 4) show an average 257 particle size of 6.5 and 5.0 nm for Pt-Ru/CMK-8-I and Pt-258 Ru/CMK-8-II, respectively. Therefore, the values of the mean 259 particle size obtained from XRD are slightly lower than that 260 obtained from TEM analysis. It can be seen from the TEM image 261 262 that Pt-Ru particles dispersion is still very uniform and agglomeration was not observed despite the fact that the particle size 263 somewhat increases upon increasing the Pore diameter. The 264 TEM images in Figure 3 and 4 also reveal the highly ordered F3 265 structure of the mesoporous carbon. Large domains of ordered F4 266 pores can be seen on the micrograph, especially the lateral view, 267 which shows the parallel arrangement of the ordered pores. This 2.68 also reveals that the catalyst deposition process did not alter the 269 ordered structure of the support. 270

Having been assembled with Pt—Ru nanoparticles, the surface morphology of CMK-8 has not been remarkably changed, and Pt—Ru nanoparticles are clearly observed on the external surface of the host, detected as black spots (Figure 4C). It implies that Pt—Ru nanoparticles have been well-dispersed in the 3-D CMK-8-I mesoporous carbon. Another aspect to be examined is the comparison between the two CMK-8 supported Pt—Ru catalysts despite the fact that two Pt–Ru/CMK-8 catalysts exhibited different electrochemically active surface area and methanol oxidation activity. As described in previous sections, the pore structures of two CMK-8 supports and sizes of catalyst particles supported on CMK-8 were not very similar. The mesoporous carbon with large pore diameter exhibits better dispersion of Pt–Ru particle size with small particle size than small pore-size-supported Pt–Ru catalysts. Because of its better dispersion and small particle size, Pt–Ru/CMK-8-I exhibits better performance than Pt–Ru/CMK-8-II.

3.3. Electrochemical Characterization of the Electrocatalysts. Figure 5 shows the cyclic voltammograms of Pt-Ru/ XC-72 and Pt-Ru/CMK-8 in 0.5 M H_2SO_4 solution at 290 50 mV $\ensuremath{\mathrm{s}^{-1}}$ in a potential window of -0.2 to 1.0 V versus 291 Ag/AgCl. The charges and currents associated with the hydrogen 292 adsorption/desorption regions of Pt-Ru/CMK-8 electrodes 293 were almost larger than the Pt-Ru/XC-72 electrodes. Hence 294 it could be understood that the mesoporous carbon support 295 influences the active surface area. It is well-documented that 296 currents for the formation and oxidation of adsorbed hydrogen 297 atoms are proportional to the active surface area of metal. 298

3.4. Evaluation of Methanol Electro-Oxidation Activity of Composite Materials. The electrocatalytic activities of the Pt-Ru/CMK-8 catalysts for methanol oxidation reaction were 301

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317 318 with those reported in the literature.^{42,43} The catalyst prepared from CMK-8-II, showed very low current density for methanol electrooxidation compared with Pt-Ru/CMK-8-I. The catalyst prepared from the CMK-8-I support, which had lower surface area and larger Figure 7 shows the current density of methanol oxidation increases progressively with the increase in the number of potential cyclic scanning, and the peak current density reaches

stable values after 20 cycles. The enhancement in the oxidation current observed with 3-D mesoporous carbon (CMK-8) support is indicative of the important role it plays in promoting the methanol oxidation, as a result of its unique structure (CMK-8), which also allows for rapid diffusion and thus oxidation of methanol. Therefore, the well-interconnected nanopore array



Figure 7. Cyclic voltammogram of Pt-Ru/CMK-8-I catalyst in 0.5 M H_2SO_4 and 1 mol dm⁻³ methanol at 50 mV (20 scans), 25 °C.

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of 3-D mesoporous carbon is the main influencing factor for the significant improved electrocatalytic activity

Table 3 shows the values of electrocatalytic activity of the 321 T3 prepared catalysts. Table 3 also gives a comparison of the 322 catalytic activity for all Pt-Ru/CMK-8 catalysts in terms of 323 forward anodic peak potential for methanol oxidation and the 324 ratio of the forward anodic peak current (I_f) to the backward 325 anodic peak current (I_b) to indicate the catalytic performance. 326 The ratio of $I_{\rm f}$ to $I_{\rm b}$ can be used to describe the tolerance of 327 catalysts to the accumulation of carbonaceous species.³²A high 328 $I_{\rm f}/I_{\rm b}$ ratio implies a very efficient oxidation of methanol to carbon 329 dioxide during the anodic scan and the removal of poisoning 330 species from the surface of the catalyst. In contrast, a low $I_{\rm f}/I_{\rm b}$ 331 ratio implies the reverse. The I_f/I_b ratio is generally used to 332 evaluate the CO-poisoning tolerance of the catalysts. The $I_{\rm f}/I_{\rm b}$ 333 values shown in Table 3 demonstrate the fact that the tolerance 334 of the Pt-Ru/CMK-8-I is greatly enhanced. Pt-Ru/CMK-8-I 335 catalysts exhibit higher I_f/I_b ratio than the Pt-Ru/C highlight-336 ing their strongly reduced poisoning and hence improved stabil-337 ity.³² The lower stability of Pt-Ru/C catalysts compared with 338 that of Pt-Ru/CMK-8-I catalysts is further confirmed by the 339 chronoamperometric studies. 340

The forward anodic peak current density of the methanol 341 oxidation catalysts increased in the order Pt-Ru/C < Pt-342 Ru/CMK-8-II < Pt-Ru/C (E-TEK) < Pt-Ru/CMK-8-I. 343 As can be seen from Table 3, the Pt-Ru/CMK-8-I catalyst 344 showed the highest I_f/I_b ratio of 3.3, suggesting an improved 345 tolerance to carbonaceous species poisoning. One possi-346 ble reason for the high current density is that faradaic currents 347 associated with kinetic-controlled electrochemical events 348 have been reported to be sensitive to the real accessible 349 surface area of the electrode rather than to its geometric 350 area. Roughness factors of the electrode, that is, the ratio of 351 real surface area to the geometric surface area, is bigger for 352 the electrode based on CMK-8-I due to the presence of 353 denser and ordered mesopores. Therefore, highly enlarged 354 electrode areas boost the faradaic currents of the sluggish 355 reaction.44,45 356

Table 3. Comparison of the Electrocatalytic Activity of the Prepared Catalysts for Methanol Oxidation

S. no.	electrocatalysts	onset potential (V)	anodic peak potential (V)	$I_{\rm f}/I_{\rm b}$ ratio	specific activity $(mA cm^{-2})^a$	mass activity $(mA mg^{-1})^b$
1	Pt-Ru/XC-72	0.45	0.66	1.05	31.11	167.5
2	Pt-Ru/C (E-TEK)	0.18	0.68	1.88	69.64	375.0
3	Pt-Ru/CMK-8-II	0.21	0.72	2.25	59.29	319.2
4	Pt-Ru/CMK-8-I	0.17	0.77	3.3	90.6	487.9
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Current density normalized to electrode geometrical area. ^o Activity per milligram Pt.

Table 7. Evaluation of Stability of Methanol Electro-Oxidation on Various Electrode Materia	Table 4.	Evaluation of Stab	lity of Methanol Ele	ctro-Oxidation on V	'arious Electrode Material
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		stability at 500 mV			stability at 600 mV			stability at 700 mV		
S no	electrocatalysts	cu (mA	rrent $rrent$ $rrent$ 3600 s	% decrease in activity after 3600 s	cu (mA 300 s	$cm^{-2})d$	% decrease in activity after 3600 s	(m. 300 s	4 Cm^{-2}	% decrease in activity after 3600 s
3. 110.	electrocatalysis	300 \$	3000 \$		300 \$	3000 \$		300 \$	3000 \$	
1	Pt-Ru/XC-72	21.3	15.8	25.8	18.6	13.5	50.7	7.37	4.2	43.0
2	Pt-Ru/C (E-TEK)	51.8	32.9	36.4	38.8	27.4	29.4	13.7	8.2	40.1
3	Pt-Ru/CMK-8-II	25.2	20.7	19.6	30.9	21.6	30.1	12	6.9	42.5
4	Pt-Ru/CMK-8-I	45.2	36.6	19.0	47.4	35.1	26.0	24.5	13.8	43.7



Figure 8. Chronoamperometric response recorded at different potentials (a) 500, (b) 600, and (c) 700 mV (vs Ag/AgCl) of various catalysts for methanol electro-oxidation in nitrogen saturated 0.5 mol dm⁻³ $\rm H_2SO_4$ and 1 mol dm⁻³ methanol at 25 °C.

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It was discovered that Pt-Ru/CMK-8-I with the largest pore 357 diameter showed a significantly higher performance than that of 358 Pt-Ru/CMK-8-II (small pore) and Pt-Ru/C (E-TEK). The 359 higher performance of Pt-Ru-supported 3-D mesoporous car-360 bon (CMK-8-I) support is mainly due to the fact that the large 361 pore diameter makes it easier for the smaller Pt-Ru nanoparti-362 cles to access the pores inside the channels and limits the 363 agglomeration of the particles both in the pore entrance and 364 on the porous surface of the support. The lower performance of 365 the CMK-8-II is mainly due to its smaller pore diameter, which 366 might be blocked by the bigger platinum nanoparticles, thus 367 resulting in a reduced electrocatalytic performance. However, it 368 should be pointed out that it is not the Pt-Ru particle size but 369 the mass transfer that plays a major role for the improved 370 electrocatalytic activity. These results reveal that not only the 371 particle size of the Pt-Ru on the surface of the mesoporous 372 carbon support but also the textural parameters of the mesopor-373 ous carbon support materials are highly critical for electrocata-374 lytic activity. 375

3.5. Chronoamperometric Studies. To compare the longterm performance of the Pt–Ru/CMK-8 catalysts toward methanol oxidation reaction, the catalysts were biased at potentials between 0.5 and 0.7 V, and changes in the oxidation current with time were recorded. Figure 8 shows the chronoamperometric response recorded for 1 mol dm⁻³ methanol in 0.5 mol dm⁻³ H₂SO₄ at room temperature. Recording of the current transient was then performed at 0.5, 0.6, or 0.7 V, which was maintained for 3600 s.

It is clear from Figure 8 that despite the initial high current 385 density there is a constant decay in the current with respect to 386 time for all catalysts, possibly suggesting catalyst poisoning by 387 chemisorbed carbonaceous species formed during the oxidation 388 of methanol.³¹ For the Pt-Ru/CMK-8-I catalyst (Figure 8), 389 although there is a gradual decay for a period of 20 min, the 390 current appears to be quite stable afterward, suggesting the better 391 tolerance of the Pt-Ru/CMK-8-I catalyst. The Pt-Ru/CMK-8-I 392 electrode not only showed higher initial activity but also was 393 fairly stable within the time period of the experiment. Figure 8 394 indicates that the Pt-Ru/CMK-8-I catalyst exhibits better 395 performance for methanol electro-oxidation than the Pt-396 Ru/C (E-TEK) and Pt-Ru/CMK-8-II catalyst for all applied 397 potentials. The comparison of the 3-D mesoporous carbon-based 398 electrodes polarized at +0.5, +0.6, and +0.7 V clearly suggests that 399 the Pt-Ru/CMK-8-I deactivates faster when the electrode is 400 polarized at +0.7 V. The stability Pt-Ru/CMK-8-I electrode is 401 better compared with that of Pt-Ru/C (E-TEK) at +0.7 V 402 (Table 4). However, Pt-Ru/CMK-8-I not only showed initial 403 higher activity but also was comparatively more stable than the 404 Pt-Ru/C (E-TEK) electrode when polarized at +0.7 V. These 405 suggest that in addition to improving the utilization of catalytic 406 particles, 3-D carbon (CMK-8) support also enhances stability. 407

4. CONCLUSIONS

In this study, we have developed a new strategy for the 409 synthesis of Pt-Ru supported catalysts using CMK-8, a HOMC 410 as support. The effect of pore size on the electrochemical 411 performance of the anode was also investigated. As a result of 412 the smaller particle size and better dispersion, the Pt-Ru/CMK-413 8-I electrocatalyst displayed better performance in the direct 414 electro-oxidation of methanol than the Pt-Ru/CMK-8-II, Pt-415 Ru/C (E-TEK), and Pt-Ru/XC-72 electrocatalysts. In addition 416

The Journal of Physical Chemistry C

to improving electrochemical activity and boosting the tolerance 417 418 of the catalyst to carbonaceous species, Pt/Ru supported on CMK-8-I also had the best stability compared with the other 419 catalysts. It is worth noting that the outstanding mass activity of 420 Pt-Ru/CMK-8-I clearly puts it forward as a candidate support in 42.1 the bid to reduce the cost of catalysts in DMFCs. The excellent 422 423 features of CMK-8 could be ascribed to the following factors: 424 relatively larger mesopores, large surface area, and the cubic Ia3d 425 symmetry with interconnected nanopores that greatly enhanced mass transfer. Further work would be carried out to investigate 426 the possibility of improving the merits of Pt-Ru/CMK-8 by 427 making use of a better catalyst preparation method. 428

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