

Методы получения наноструктур и наноматериалов

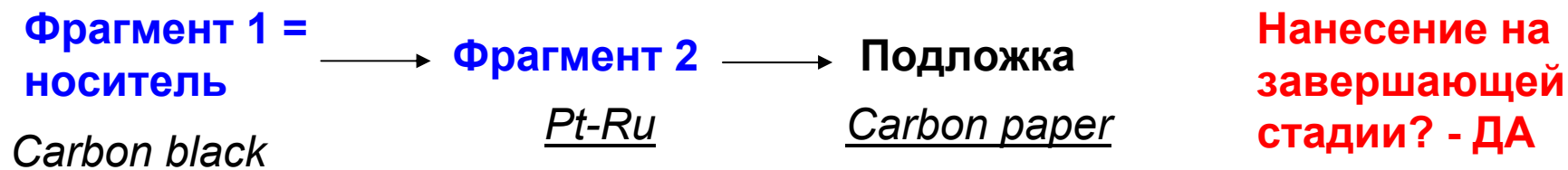
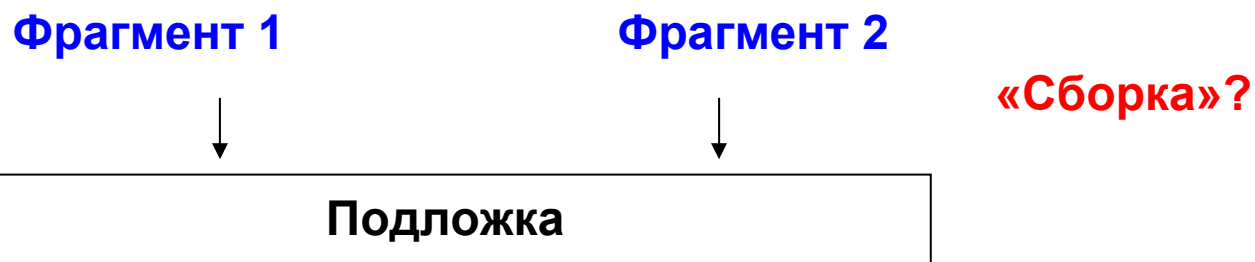
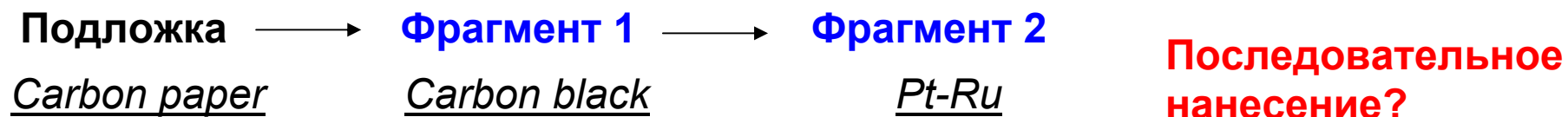
16 апреля 2011.

Общие принципы выбора оптимальной технологии материала с заданными свойствами и метрологических приемов, применяемых в ходе получения материала.

На примере оптимизации металлического катализатора на углеродном носителе.
По материалам работ Института катализа им. Г.К.Борескова СО РАН

<http://www.elch.chem.msu.ru/rus/prg415.htm>

«Технологические схемы» - детализация для катализаторов на носителях



Обеспечивает наибольшую равномерность распределения катализатора

Нанесение коллоидного Pt-Ru на сажу?

Более точно определены состав и размер частиц

Пропитка сажи солями Pt и Ru, затем химическое восстановление?

Более равномерно распределены частицы, не нужен стабилизатор


Выбор носителя (support)

В обсуждаемом примере - Сибунит

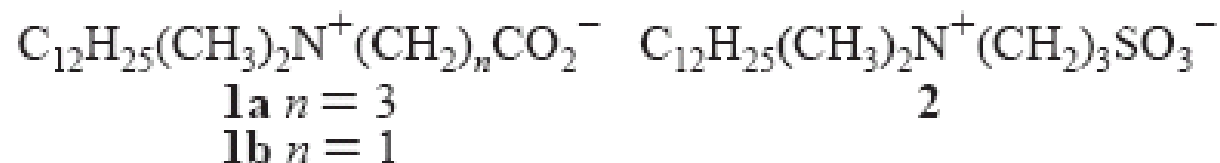
the Sibunit family which has recently shown its superiority over conventional Vulcan carbon.⁶² Sibunit carbons are produced by high temperature pyrolysis of hydrocarbons.⁶³ Their advantages are: (i) purity, (ii) uniform morphology of primary carbon globules (contrary to carbon blacks, in particular Vulcan⁶⁴), (iii) high electrical conductivity (of importance for fuel cell applications), (iv) high mechanical stability, and (v) corrosion resistance. The porosity (and thus the specific surface area) of Sibunit carbons may be purposely varied in a wide range from a small value to more than $500 \text{ m}^2 \text{ g}^{-1}$ depending on the extent of their activation. Various Sibunit

Синтетическая процедура

Phys. Chem. Chem. Phys., 2007, 9, 5476–5489

PtRu/C catalysts were prepared using home-made pyrolytic carbon Sibunit 19P (Omsk, Russia, BET surface area $72 \text{ m}^2 \text{ g}^{-1}$) and for comparison Vulcan XC-72 (Cabot Corp., BET surface area $250 \text{ m}^2 \text{ g}^{-1}$). The Pt : Ru atomic ratio was equal to 1, while the overall metal percentage was varied from 5 to 60 wt%. Catalysts were synthesized *via* co-hydrolysis of RuCl_3 and H_2PtCl_6 under the action of $\text{Na}_2\text{CO}_3 + \text{HCOONa}$ in the presence of powdered carbon supports. Samples containing from 5 to 30% metal were prepared in one step and reduced with H_2 at 150 (1 hour) and then 200 °C (1 hour). 40, 50 and 60% samples were prepared in a step-wise manner in 2, 3 and 4 steps, respectively, with intermediate drying and reduction at 150 °C for 1 hour. For more details, the reader is referred to ref. 62. 

PtRu (1:1) catalysts were prepared by co-hydrolysis of chloride complexes of Ru^{III} and Pt^{IV} using a procedure similar to that described by Reetz and Koch [36]. The authors of Ref. [36] found that an addition of alkali to a solution of RuCl₃ + H₂PtCl₆ results in the formation of small colloidal particles of mixed metal oxides, and added organic surfactants in order to prevent their further growth and coagulation. Unlike them, we avoided an addition of organic ligands (which form a shell around metal particles and may thus influence their activities) but performed synthesis in the presence of carbon supports, assuming that the latter may act as a macroligands stabilising colloids of mixed metal oxides.

Бетаиновые стабилизаторы

Indeed, upon stirring an aqueous solution of PtCl_4 and carbobetaine **1a** (molar ratio, 1:4) in the presence of excess NaOH at 50 °C for 7 d, complete consumption of the yellow platinum salt was observed with formation of a deep red-brown colloidal solution of $\text{PtO}_2/\mathbf{1a}$ (eq 1). The reaction was monitored by UV-



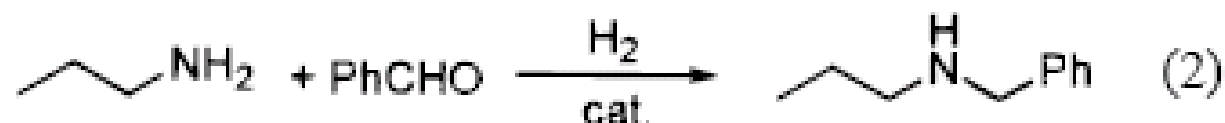
vis spectroscopy (disappearance of the PtCl_4 absorption at 250 nm and appearance of a plasmon absorption in the range 200–800 nm) and by transmission electron microscopy (TEM).

То есть борьба за полноту превращения требовала жестких условий, а значит – стабилизации малых частиц

Ref.36

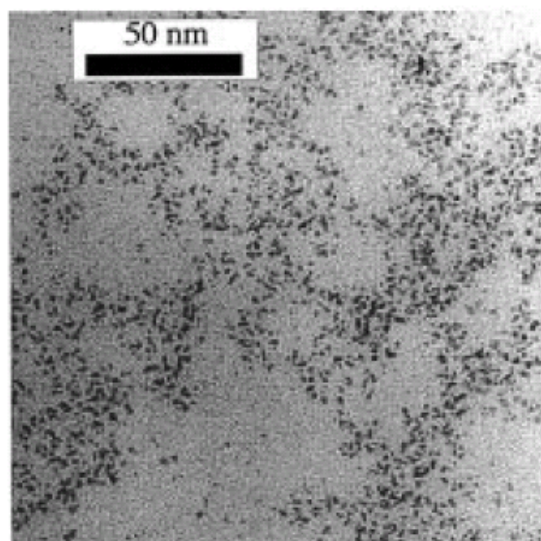
J. Am. Chem. Soc. **1999**, *121*, 7933–7934

activity, the reductive amination of benzaldehyde by *n*-propylamine was chosen as a model reaction (eq 2).

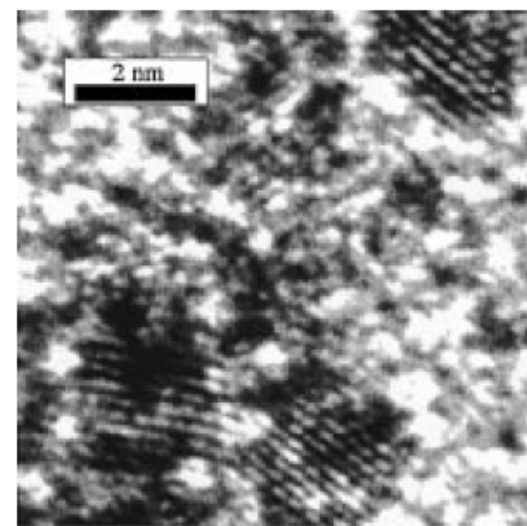


Using the new catalyst PtO₂/Al₂O₃, commercially available Pt/Al₂O₃ (5%),^{12c} and Adams catalyst,^{12d} reductive amination was carried out at a substrate-to-Pt ratio of 1000:1 in methanol as the solvent at room temperature and atmospheric pressure.

(12) (a) Aldrich, BET area: 155 m²/g. (b) Condea, BET area: 221 m²/g. (c) Heraeus, BET area: 20 m²/g. (d) Heraeus, BET area: 80 m²/g.



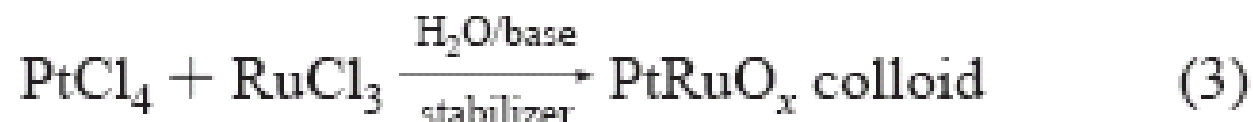
PtO₂



Ref.36

J. Am. Chem. Soc. **1999**, *121*, 7933–7934

Finally, preliminary experiments directed toward the preparation of water-soluble colloidal bimetallic oxides turned out to be successful. Upon stirring the aqueous solution of PtCl₄ and RuCl₃ (1:1 molar ratio) in the presence of sulfobetaine **2** and Na₂CO₃ at 80 °C for 18 h, a black colloidal solution was obtained (eq 3).



! не полное

! (XRD?)

! смесь!

Following purification by dialysis, the colloid was characterized by TEM, demonstrating the presence of 1.5 ± 0.4-nm-sized particles. Elemental analysis revealed 6.4% Pt and 4.0% Ru by weight, corresponding to a Pt:Ru molar ratio of about 1:1. Energy-dispersive X-ray (EDX) spot analysis proved the presence of both metals in individual nanoparticles. According to an XPS analysis,⁹ platinum occurs as Pt(II) and Pt(IV) in similar amounts in addition to Ru(IV). This means that Ru(III) reduces about 0.5 equiv of Pt(IV) to Pt(II) with formation of Ru(IV), as expected from the redox behavior of the two metals (Pt⁴⁺ + 2 Ru³⁺ → Pt²⁺ + 2 Ru⁴⁺).¹³ The PtRuO_x/2 colloid is stable for months in aqueous

By employing different ratios of the two metal precursors, the metal composition (Pt:Ru) of the colloids can be adjusted in the range from 1:4 to 4:1 on an optional basis. Moreover, if so desired, the colloidal Pt/Ru oxides can be converted into the corresponding zerovalent metal colloids by treating the aqueous colloidal solutions or the immobilized forms with H₂ at room temperature, while no significant changes in particle size or Pt/Ru composition occurred upon doing so.¹⁴

(14) The same procedure can be applied to the PtO₂ colloids.

Cited 31 times



Оптимизация оксидных коллоидных катализаторов



Получение металлических катализаторов «по аналогии»

Ref.62

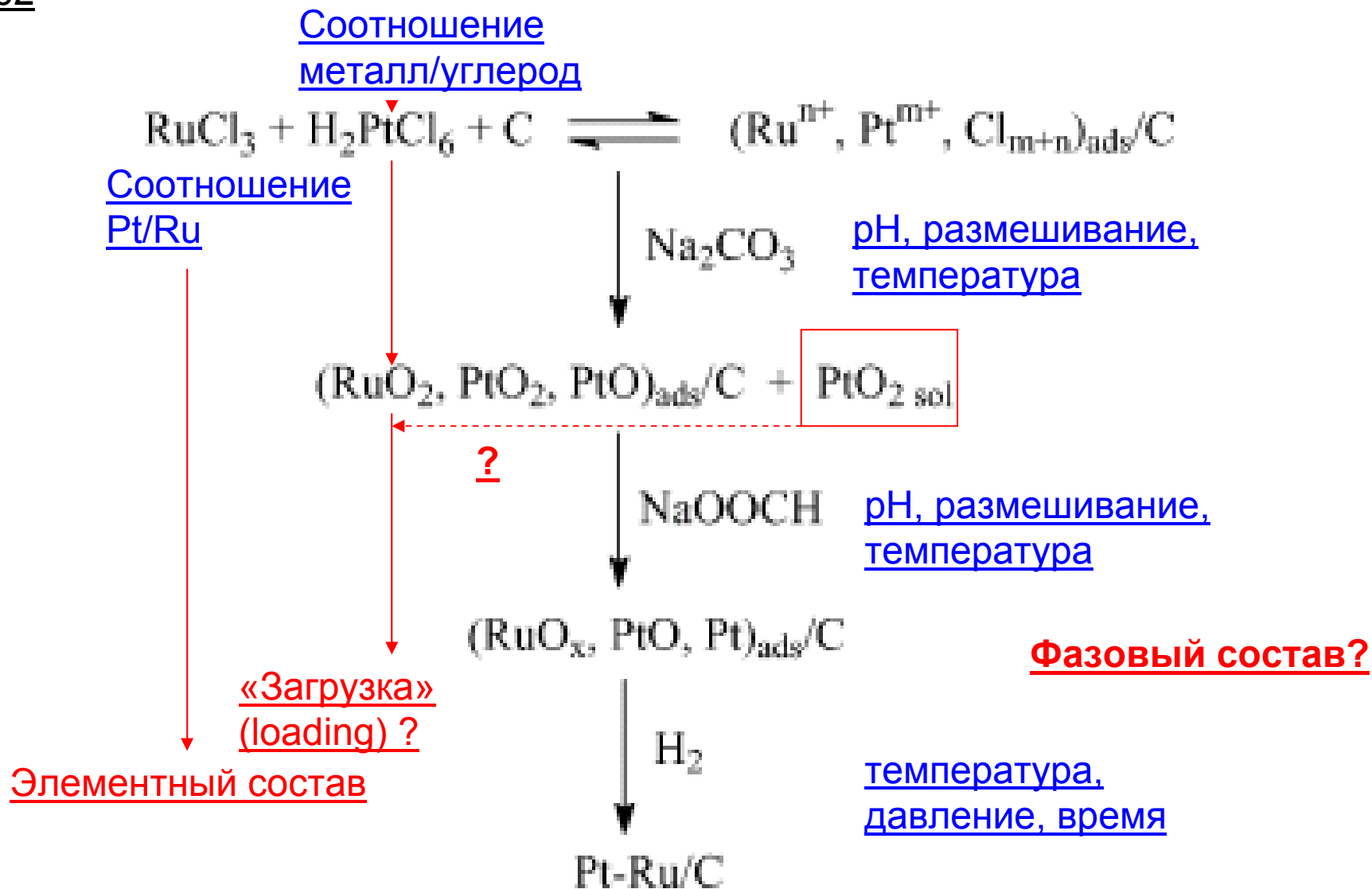
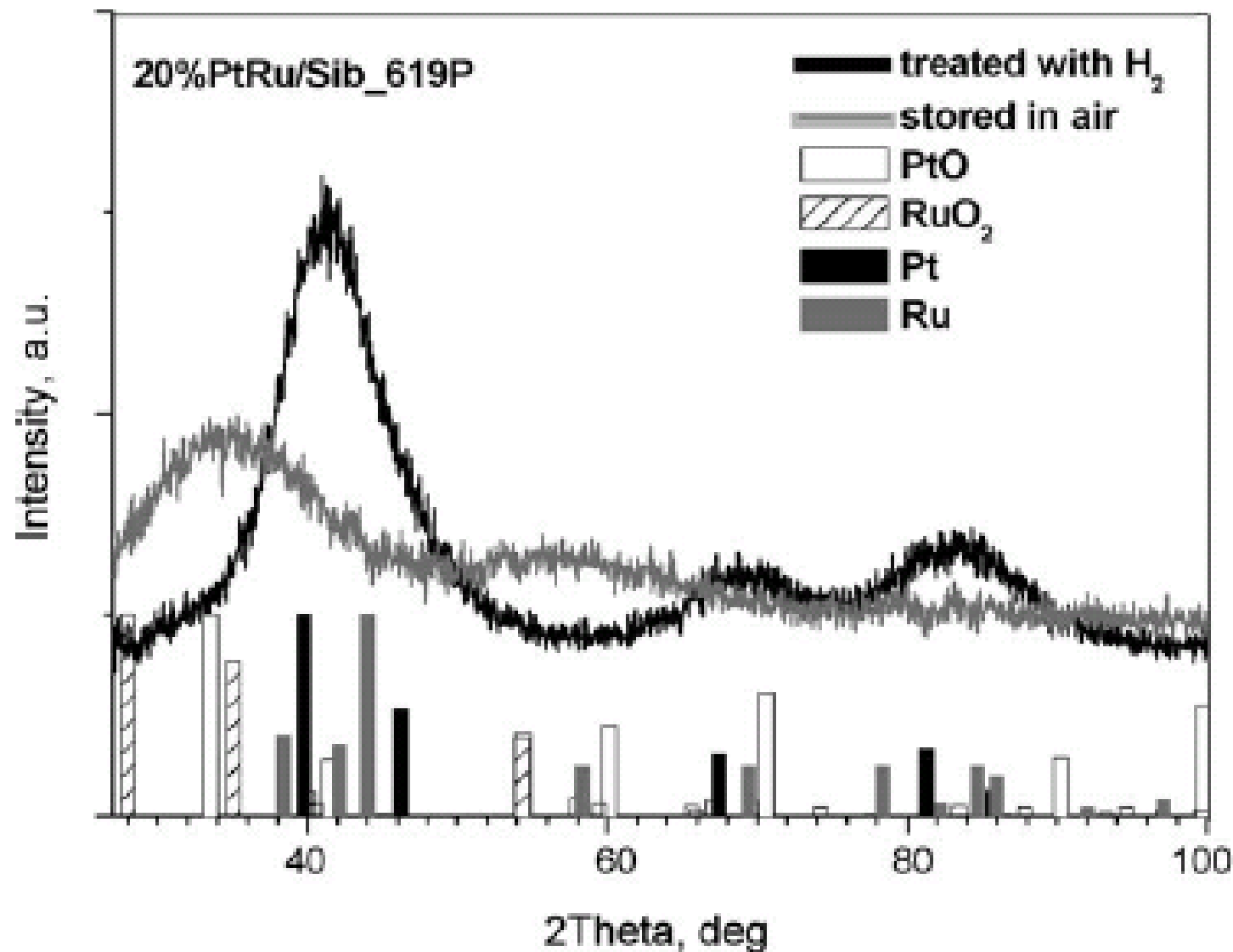
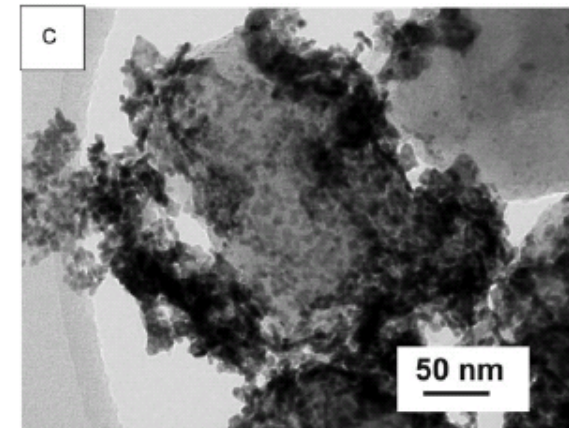
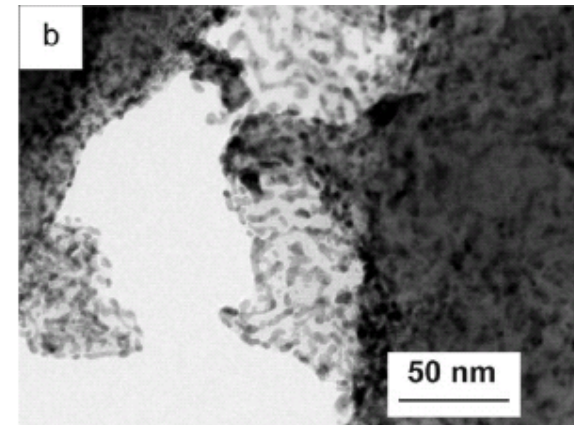
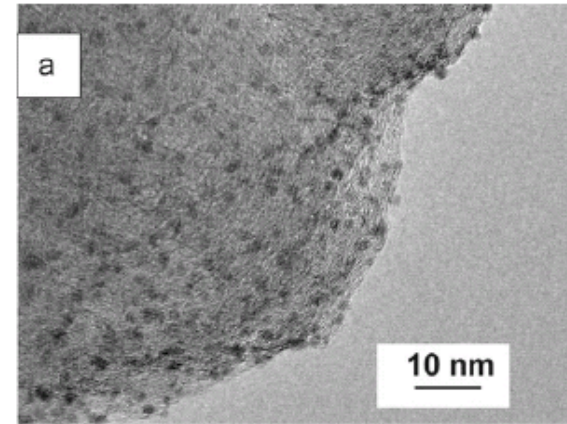
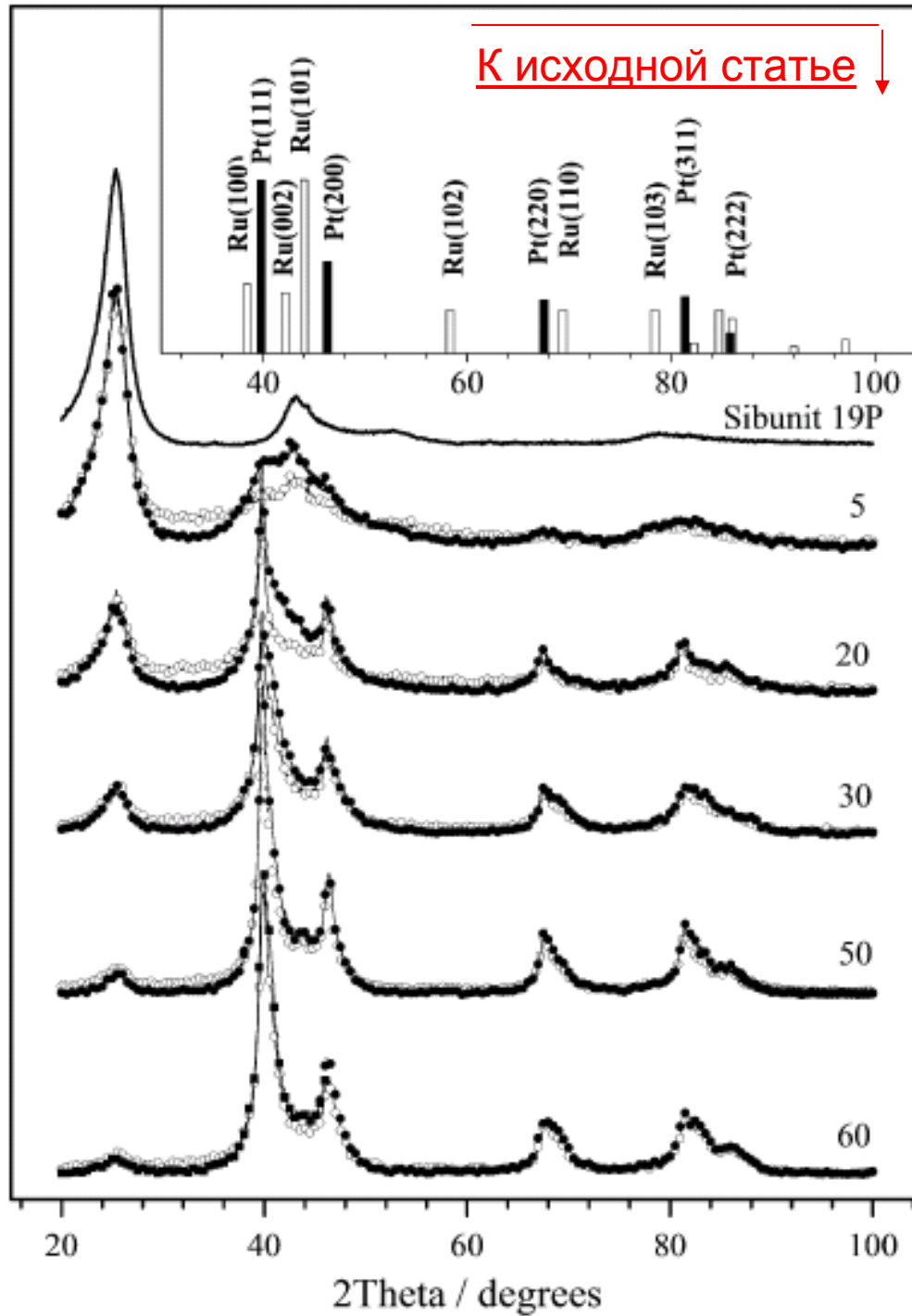


Fig. 1. Schematic representation of the catalyst synthesis.



Уже нет проблемы смеси оксидов – только полноты восстановления до металла.
Размер частиц регулируется пористостью носителя.

Фазовый состав и микроскопия



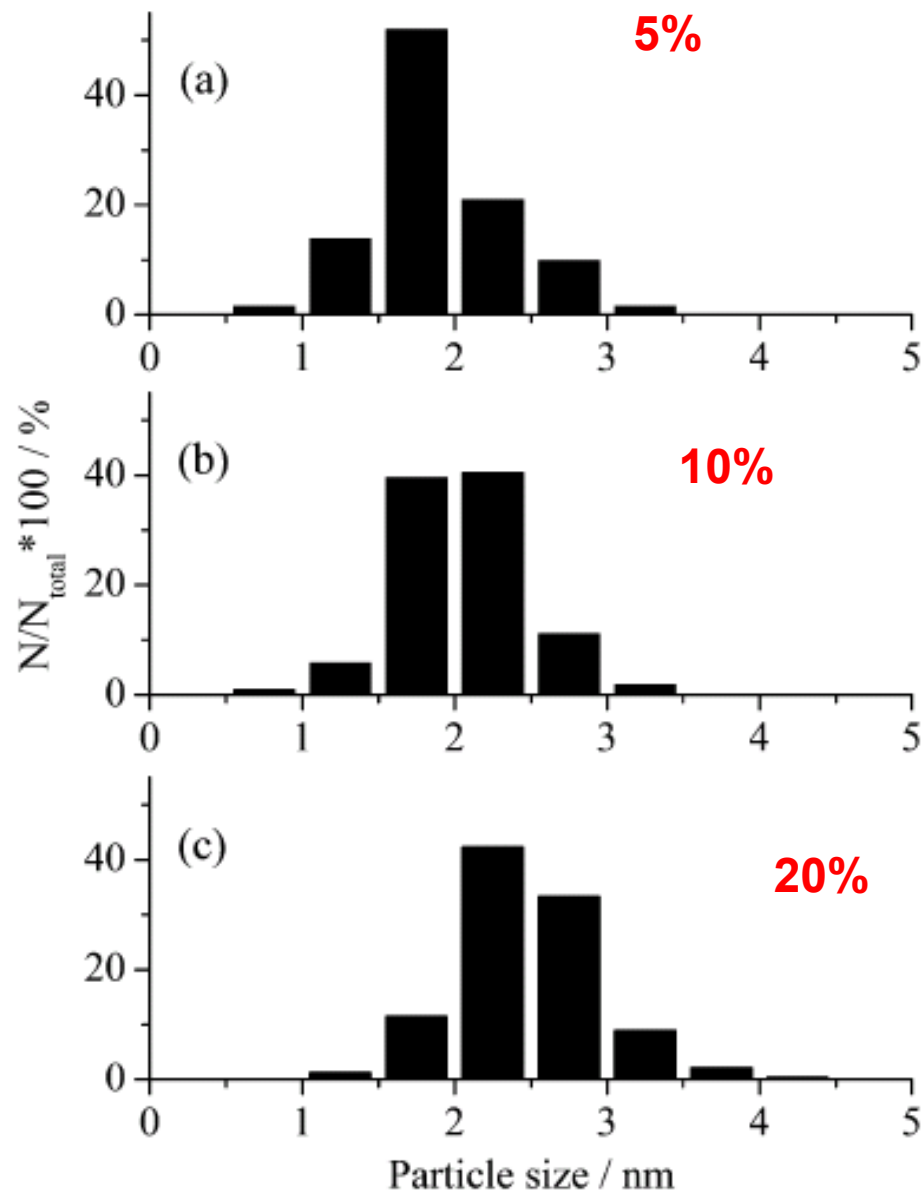
Грубая оценка дисперсности металла

$$A_{\text{chem}} = \frac{6000 \cdot D}{\rho}$$

Table 1 Metal dispersion D^a and specific surface areas calculated via gas phase CO chemisorption (A_{chem}) and electrochemical CO oxidation (A_{EC})

% PtRu	D	$A_{\text{chem}}/\text{m}^2 \text{ g}^{-1}$	$A_{\text{EC}}^b/\text{m}^2 \text{ g}^{-1}$	
5	0.59	190	165	152
10	0.36	117	85	—
20	0.28	91	88	—
30	0.16	54	49	58
40	0.17	55	43	—
50	0.11	36	—	—
60	0.10	33	28	37

^a Metal dispersion is calculated from the gas phase CO chemisorption data. ^b The results of two independent sets of measurements are given.

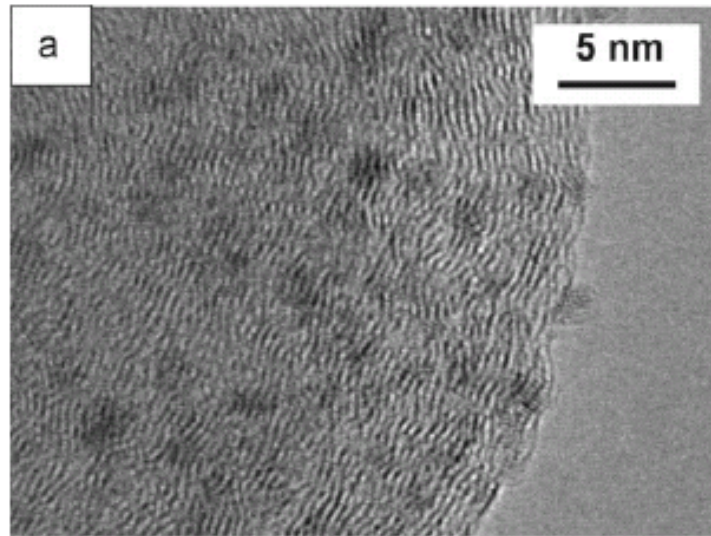


Статистически достоверное число частиц для построения размерных распределений из данных TEM?

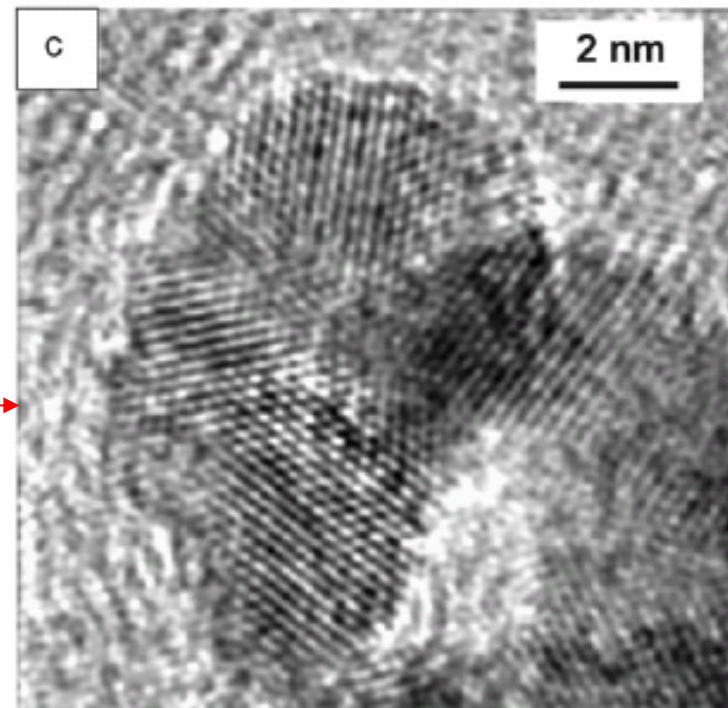
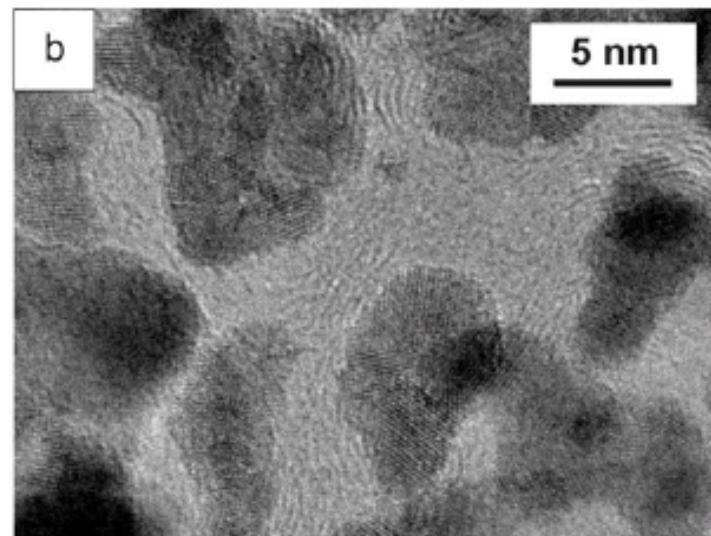
Зависит от ширины распределения и однородности материала

С XRD надо сопоставлять среднemasовые, а не среднечисленные распределения!!!

Fig. 11 Particle size distributions calculated from TEM for 5%PtRu/Sibunit (a), 10%PtRu/Sibunit (b) and 20%PtRu/Sibunit (c).



5% - одиночные



50% - блочные

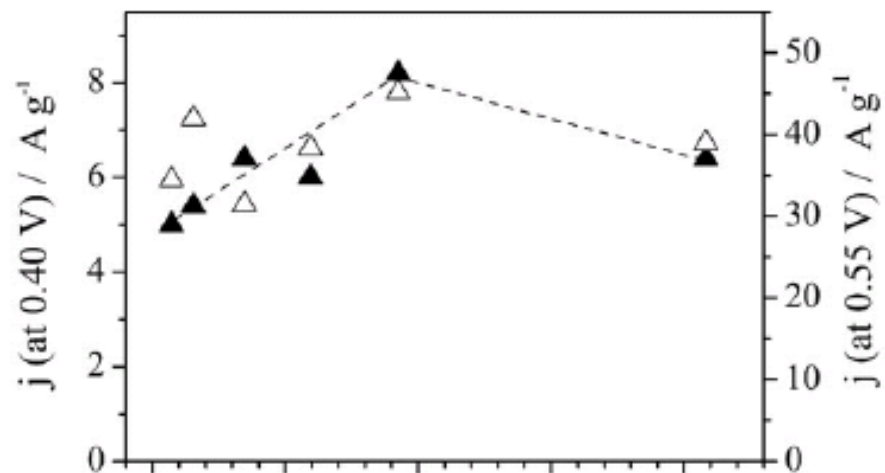
Иммобилизация на подложке – модельная система

. Work-
ing electrodes were obtained by pipetting 20 μl of an aqueous suspension containing 1.5 mg ml^{-1} of PtRu/C sample (no Nafion) on a polycrystalline gold foil (cleaned with aqua regia and annealed in a hydrogen flame). The films obtained after drying were mechanically stable, and showed reproducible cyclic voltammograms (CVs).

Это тоже loading! – катализатора, а не металла

Иммобилизация на подложке – модельное устройство

Homemade PtRu (1:1) catalysts supported on Sibunit carbons and on Vulcan XC-72, as well as commercial 20%PtRu(1:1)/Vulcan XC-72 catalyst from E-TEK, were used for the preparation of the anode. Pt/Vulcan (40 wt.%, E-TEK, Alpha Aesar) was utilised as the cathode catalyst. In order to make a MEA, a suspension of the catalyst powder, Nafion[®] solution (Dupont), and isopropanol were treated in an ultrasonicator. The ink was sprayed onto porous carbon backing layers (Toray paper from E-TEK, TGPH 060, no wet proofing), held at 110 °C. The 1.2 cm² patches of the Toray paper comprising sprayed catalyst layers were then cut and hot pressed with the Nafion[®] 117 membrane in between at 140 °C for 5 min at a pressure of 826 Ncm⁻². In order to keep the thickness of the anode electrocatalyst layer constant, we kept the amount of the catalyst powder (metal + carbon) around 1.5 mg cm⁻² for all carbon supports.



Сопоставление функциональных характеристик – активность в расчете на массу и истинную поверхность

