

ABSTRACT
OF THE PRESENTATIONS ON THE 7TH ANNUAL DAY OF
NATIONAL CENTRE FOR CATALYSIS RESEARCH

28TH JULY (SUNDAY), 2013



PROGRAMME

(For the annual day on 28th July SUNDAY 2013)

Time	Presentation	Persons
8.45 to 9.00 a.m.	Inauguration	Prof. Krishnamurthy
9.00 to 9.15 a.m.	Presentation I	Ms.VijayShanthi
9.15 to 9.30 a.m.	Presentation II	Mr.P.Rajesh Kumar
9.30 to 9.45 am	Presentation III	Ms.V.Jeya Lakshmi
9.45 to 10.00 a.m.	Presentation IV	Prof Ramna
10.00to 10.15 a.m.	Tea Break	MsSelvi/ Saranya
10.15 to 11.00a.m.	Presentation: <i>Alternates to Pt for electrode applications</i>	B.Viswanathan
11.00to 11.15 a.m.	Concluding remarks	Prof S.Sivasanker

We wish to record our deep appreciation and gratefulness to all the members of NCCR for their continued support and also contributions to the overall growth of the centre. We are aware that our centre could do better and hope we will together be able to achieve greater heights in making NCCR an internationally recognized centre for learning and research.in the future

LIST OF PARTICIPANTS

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7th annual day

CONCLUDING REMARKS

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7th annual day

Understanding Chemical Information with Light and Electrons

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Experiments using coherent sources of light (lasers) and electrons (via electron microscopes) have contributed a great amount in how we think about chemical information (reactions). These sources have a theoretical basis that often seems in conflict with experiments. I will present three examples that illustrate the apparent conflict. The goal beyond the talk today is to resolve through cleverly designed experiments and good theory, aiming for greater information content.

7th anniversary

Innovative Silica Materials: Creating New Opportunities in Advanced Catalysis

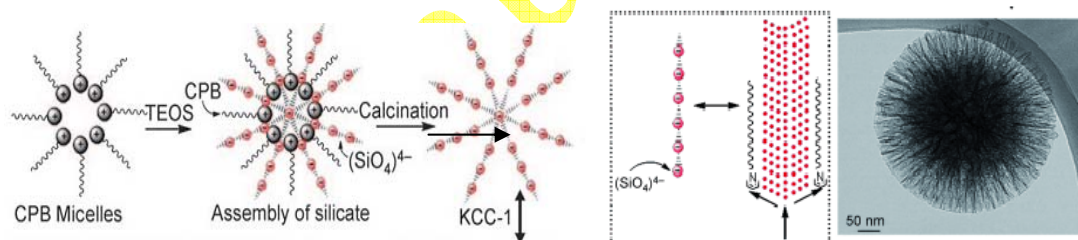
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“Necessity is the Mother of Invention”

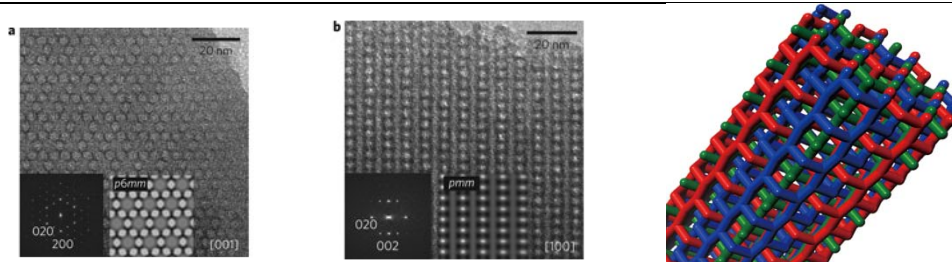
The realm of porous silica materials was extended after the emergence of Kresge's preparation of mesoporous silica materials M41S using surfactants as organizing agents¹. The effectiveness of a material as catalyst support relies on its well-ordered periodicity and interconnected pore systems which provides high accessibility to active sites, better diffusivity of reactant molecules. Apart from this, morphology of the material plays significant role in its activity. In quest of nanocatalysis, drug delivery, gas sensors and photonics, a wide range of silica materials with excellent morphologies such as fibrous (dendrimeric KCC-1¹, tricontinuous porous systems IBN-9²), hexagonal rod like (chiral silica³), spherical (core shells and hollow spheres), and inverse opal structured (3DOM silica⁴) etc., are synthesized. The structural capabilities of these innovative materials at the scale of a few nanometers can meet the demands of the growing applications.

In this context, design and functionality of few silica materials were illustrated in brief using examples from recent literature.

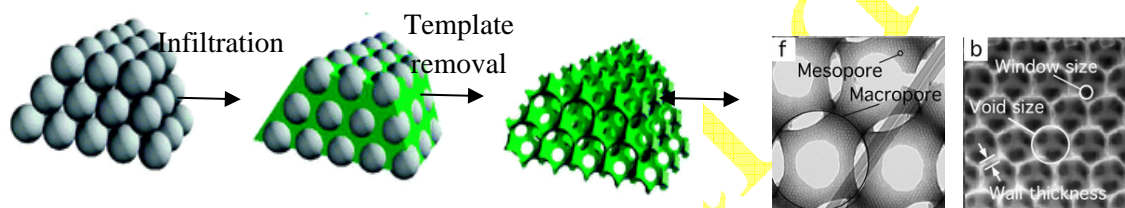
- (a) **Fibrous silica spheres (KCC-1):** These dendrimeric silica fibres show high activity in surface organometallic chemistry (SOMC)¹. These are way better than porous silica. Since the pore blocking effects are absent, the available active sites are considerably more.



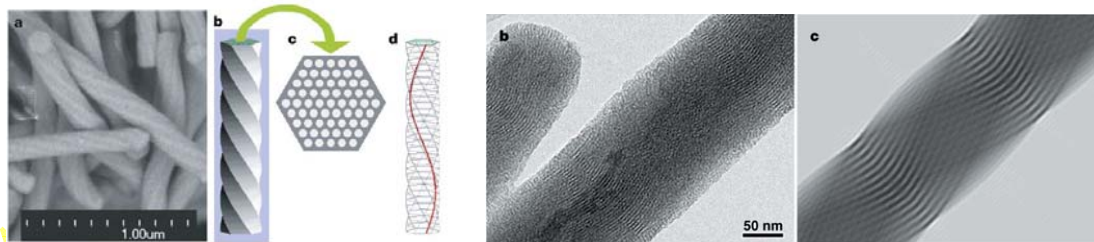
- (b) **Tricontinuous mesoporous silica (IBN-9)²:** IBN-9 has the most complex pore and is the first representation of an H-minimal surface in a real material. Its 3D hexagonal mesopores ($P6_3/mcm$), with a tri-continuous pore system leads to better diffusivity and hence reactivity.



(c) **3D ordered macroporous (3DOM) materials or inverse opals**⁴: Negative replicas that are obtained from the colloidal crystal template (CCT) are called inverse opals. They have numerous applications, both for the optical properties (photonic crystals) and in nanocatalysis because of their three-dimensionally interconnected pore system.



(d) **Chiral mesoporous silica**: Enantiomerically pure mesoporous materials with twisted hexagonal rod-like morphology were synthesized using amino and quaternary amino silanes. Its shape selectivity and enantioselectivity are significant in manufacturing of enantiomerically pure chemicals and pharmaceuticals³.



These innovative materials with unprecedented morphologies, high stabilities, good physical and chemical properties made a valuable contribution to the field of catalysis, pharmaceuticals, etc. Using these materials as supports, yet much ideal catalysts can be prepared precisely.

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7th annual day

Sodium Tantalate based Catalysts for Photocatalytic Reduction of Carbon dioxide by Water

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Introduction:

Carbon dioxide has increased in the atmosphere from fossil fuel use in industry and transportation, manufacture of cement, building air conditioning and deforestation. With a global radiative forcing of 1.74 W.m^{-2} , CO_2 is the largest contributor among well-mixed long-lived greenhouse gases, accounting for more than 63% of the total. The photo reduction of CO_2 by water to yield hydrocarbons (methane, methanol etc.) is the major applications that have triggered intense research efforts in photo catalysis [1-2]. Photo catalytic reduction (PCR) of CO_2 , involving multi-electron transfer steps, is highly complex and difficult one [3]. It consists of two steps that proceed simultaneously, splitting of water to yield hydrogen and reduction of CO_2 to hydrocarbons and has the potential to emerge as alternative energy source to fossil fuels [4-6]. Design of effective catalysts for such a complex process holds the key for its viability. Among the vast majority of active photocatalysts, perovskite type compounds, such as SrTiO_3 , $\text{K}_2\text{La}_2\text{Ti}_3\text{O}_{10}$, NaTaO_3 , $\text{RbNdTa}_2\text{O}_7$, $\text{La}_2\text{Ti}_2\text{O}_7$ and $\text{Sr}_3\text{Ti}_2\text{O}_7$ have been proven to be active for water splitting. Splitting of water is the primary step in the PCR of CO_2 by water. Hence these compounds have the potential to catalyze PCR as well. Unfortunately, their practical applications have been restricted to the ultraviolet region due to their large band gaps, which occupies only about 4% of the whole solar spectrum. In recent years, doping on a semiconductor with a wide band gap to extend the optical absorption edge is one of the effective strategies for developing photo catalysts active in the visible region. Amongst the various mixed oxides, NaTaO_3 modified with lanthanum and NiO as co-catalyst, displays maximum activity for hydrogen production [7] by splitting of water with very high quantum efficiency of 56% with UV radiation (270nm). So, In this study, we have chosen $\text{NaTaO}_3\text{:La}$, and its modified versions with various metal (Pt, Ag, Pd, Au) and metal oxides (NiO, CuO), co-catalysts for CO_2 reduction under UV-visible light region.

Experimental Section:

NaTaO_3 and 2.0% (w/w) lanthanum promoted catalysts were prepared by hydrothermal route [8]. To prepare NaTaO_3 , 0.6 g of NaOH dissolved in 20 ml of water (0.75M) and 0.442 g of Ta_2O_5 were added into a Teflon lined stainless steel autoclave. After hydrothermal treatment at 140°C for 12 hours, the precipitate was collected, washed with deionized water and ethanol and finally several times with water and dried at 80°C for 5 hours. La modified NaTaO_3 was prepared by the same procedure, by adding 0.0065 g of La_2O_3 along with NaOH and Ta_2O_5 in the autoclave. NiO (0.2% w/w) as co-catalyst was loaded on to synthesized $\text{NaTaO}_3\text{:La}$ powder by wet impregnation from an aqueous solution of Ni $(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$, drying at 100°C followed by calcination in air at 270°C for 2 hours. Loading of La & NiO was based on the optimization study carried out by Kato et.al.[7]. Similarly, 1Wt% CuO (as $\text{Cu}(\text{NO}_3)_2$), 1Wt% Ag (as AgNO_3), 1Wt% Pd (as PdCl_2), 0.15 w/w% Pt (as H_2PtCl_6) and 1.0 w/w% Au (as HAuCl_4) were loaded onto synthesized $\text{NaTaO}_3\text{:La}$ powder by wet impregnation and dried. Pt, Au, Pd salts were reduced in hydrogen at 450°C & 200°C respectively prior to use.

X-ray diffraction (XRD), UV-vis. Diffuse reflectance spectroscopy (DRS) techniques are used to investigate the structural and photo-physical properties of the prepared catalysts. Photo-catalytic efficiency of the catalysts (dispersed in aqueous NaOH solution of 0.2M) were evaluated for photoreduction of carbon dioxide with water using 77W Hg lamp, in UV visible region (300-700 nm) in batch mode. Products formed in liquid and gaseous phases were analysed by gas chromatography. Appropriate blank experiments were carried out to ensure that the measured hydrocarbon products originate only from the CO₂ dissolved in aqueous NaOH.

Results and discussions

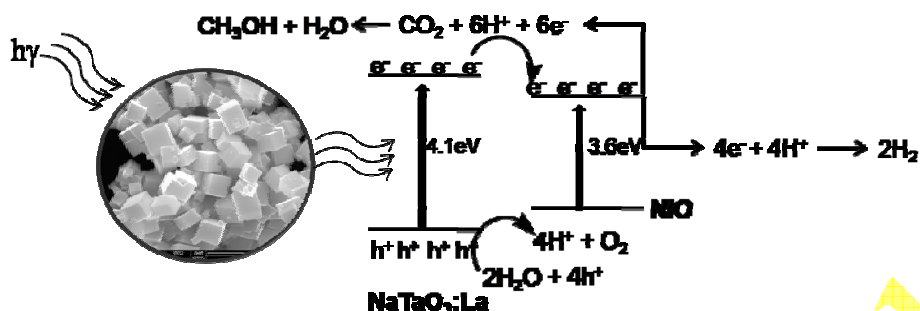
XRD patterns of all the catalysts showed characteristic d-lines that can be attributed to NaTaO₃ phase (JCPDS- 25-0863) and no diffraction peaks due to the raw material Ta₂O₅ was found. Addition of La and co-catalysts like, NiO, Pt & Au, being 2% maximum, did not result in any significant change in the XRD pattern of the parent material. However, as reported in literature [9] substitution of Na⁺ (1.39Å) by La³⁺ (1.36Å in octahedral co-ordination) in the lattice of NaTaO₃ resulted in small shift in d-lines. Diffuse reflectance spectra for NaTaO₃ based catalysts recorded, with respect to pure NaTaO₃ all the modified materials display small shifts in band gap values towards visible region.

Table 1: Product profile for photo catalytic reduction of CO₂ by water on various metal doped NaTaO₃:La

Catalyst	Products formed after 20hrs of Irradiation (µmol/g)						Con. (%)
	CH ₄	C ₂ H ₆	CH ₃ OH	CH ₃ CHO	C ₂ H ₅ OH	Total CO ₂ consumed	
NaTaO ₃	0.3	0.12	245.6	12.9	52.2	376.4	0.53
NiO/NaTaO ₃	0.4	0.15	334.9	2.5	48.9	438.5	0.62
NaTaO ₃ :La	1.3	0.11	544.9	0.5	47.5	642.4	0.9
1Wt%Pd/NaTaO ₃ :La	1.1	2.2	1217.8	12.1	66.1	1423.0	2.0
0.15Wt%Pt/NaTaO ₃ :La	7.3	0.5	1007.7	3.1	21.3	1064.1	1.5
1Wt%CuO/NaTaO ₃ :La	0.16	0.28	940.1	7.1	270.5	1496.1	2.1
0.2Wt%NiO/NaTaO ₃ :La	0.4	0.2	1030.6	7.7	280.7	1608.2	2.3
0.15Pt/Ni/NaTaO ₃ :La	3.4	3.7	1117.2	0.13	53.5	1235.2	1.7
0.15Pt/Cu/NaTaO ₃ :La	0.53	1.8	1288.8	1.1	23.9	1343.1	1.9

Cumulative product profile after 20 hours of irradiation observed during the photo catalytic reduction of CO₂ on all the catalysts are compiled in Table.1, Among these co catalysts, NiO and CuO loaded on NaTaO₃:La displays maximum CO₂ conversion with methanol and ethanol as major products, Since the conduction band level of NiO and CuO is just below that of NaTaO₃, the photo generated electrons from NaTaO₃ can be easily be transferred to that NiO and CuO, which helps in the reduction process. Hydrocarbon (methane, ethane) products are somewhat increased in the case of Pt, Pd doped catalyst. In order to improve the hydrocarbon products in NiO and CuO loaded on NaTaO₃:La material, we have prepared bimetallic system ie,

Pt/NiO/NaTaO₃:La and Pt/CuO/NaTaO₃:La and investigated activity towards CO₂ reduction, which exhibit good hydrocarbon product yields.



Conclusions:

We have synthesised NaTaO₃:La by hydrothermal synthesis, various co-catalyst was introduced by wet impregnation method, UV-DRS shows that modified materials are visible light active compared to NaTaO₃:La. We have demonstrated the influence of bimetallic system i.e., Pt/CuO and Pt/NiO on NaTaO₃:La for the photocatalytic reduction of CO₂ with water, the observed results show that CuO and NiO facilitates the formation of methanol and ethanol, while loaded with Pt on those catalyst hydrocarbon (methane, ethane) selectivity have been increased. NaTaO₃ based catalysts could become viable alternatives to titania for this crucial application.

Acknowledgements

We gratefully acknowledge the Department of Science & Technology, Govt. of India for the grant towards establishing NCCR at IIT Madras and M/s Hindustan Petroleum Corporation Limited, Mumbai for funding the project on photocatalytic conversion of CO₂.

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Hydrogenolysis of Sorbitol over Fly ash and Hydroxyapatite Supported Metal Catalysts

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The depletion of fossil fuel reservoirs, together with the indispensable shift of the feedstock base towards a biorefinery approach, necessitates utilizing renewable resources on a large scale for the production of chemicals and fuel. Thus, the use of efficient and environmentally benign technologies has become an imperative. Hydrogenolysis, which results in the cleavage of C-C and C-O bonds by hydrogen, offers a promising possibility for future biorefinery concepts. This concept is currently intensively discussed in the context of the transformation of glycerol to ethylene and propylene glycol, and has great potential in regard to the conversion of further biomass-derived polyols, such as sugars or sugar alcohols. The biomolecules can be transformed into various compounds already integrated in today's fossil fuel based value chains; thus, hydrogenolysis bears the potential to bridge the available technologies and future refinery concepts.

Many studies on the transformation of sorbitol into Ethylene glycol (EG), propane diol (PDs) and glycerol (Gly) have been reported over the years. We had earlier reported studies on Ni, Pt and Ru supported on the basic support, NaY. A general observation is that the reaction proceeds better in a basic medium, typically, in the presence of $\text{Ca}(\text{OH})_2$. Among the many supported metal catalysts, Ni and Ru being the most preferred metals and SiO_2 and carbon (different forms) being the most used supports. In order to investigate the influences the performance of the supported metal catalyst we carried out the reaction over Fly ash and Hap catalysts.

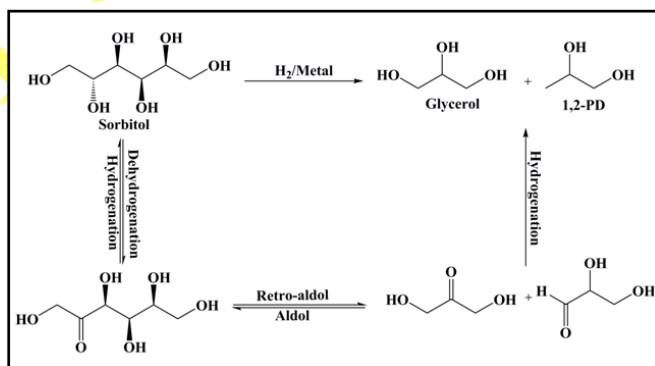


Fig. 1. Mechanism of the hydrogenolysis of sorbitol in the presence of a base.

Fly ash (FA) is the chief inorganic solid waste of coal combustion present in the flue gases of coal-based thermal power plants and is generally considered as a threat to health by air pollution. FA is a mixture of inorganic oxides, mainly SiO_2 , Al_2O_3 , Fe_2O_3 , CaO , MgO , K_2O , Na_2O and TiO_2 present in different amounts depending on the coal used. Various uses have been found for FA, which include soil beneficiation in agriculture, manufacture of bricks etc. The presence of large amounts of SiO_2 and Al_2O_3 has prompted the use of FA as a source for the synthesis of glass-ceramics, zeolites and mesoporous materials and as catalysts for various reactions, such as oxidation, benzylation, Knoevenagel condensation, SCR of NO and transesterification for bio-diesel synthesis. It has also been used as a support for catalytically active oxides and metals. The major inorganic constituent of bones and teeth is a calcium phosphate phase with a composition similar to that of synthetic hydroxyapatite (HAP; $\text{Ca}_5(\text{PO}_4)_3\text{OH}$). This similarity is on the basis of the excellent biological properties of HAP-based materials: bone bonding capability, osteoconductivity, and biocompatibility. Along with composition, the morphological characteristics of HAP particles, such as shape, size, and size distribution, play an important role in the mechanical, chemical, and biological properties of HAP-based materials. HAP is very stable and the least soluble among all the calcium orthophosphates at normal temperature and pH value range from 4 to 12. HAP has recently received much attention in view of its potential usefulness as adsorbent and most importantly as catalyst in solid/gas reactions. Taking into account environmental and economical considerations, the handling of hydroxyapatite used as a catalyst presents many advantages such as easier separation and recovery from the reaction mixture and thus, enhanced recycling possibilities, which are now well established in fine organic synthesis.

In the present work we have studied the use of FA-supported metals (Ni, Cu Ru and Pt) and HAP-supported metals as catalysts in the hydrogenolysis of sorbitol (15 % aqueous solution) into glycols. In the FA-supported metal catalyst the loading of the metals was: Ni, 6%; Cu, 6 %; Ru 1 %; and Pt, 1 %. Ni/FA was found to be the most active and selective (for glycols) amongst all the catalysts. The influences of temperature, catalyst loading and reusability on sorbitol conversion and selectivity were investigated with this catalyst.

The influence of the addition of the base $\text{Ca}(\text{OH})_2$ on conversion and product yields is also reported. Reactions over Ni, 6%; Ru, 1%; and Pt, 1 % HAP-supported metal catalyst were also studied.

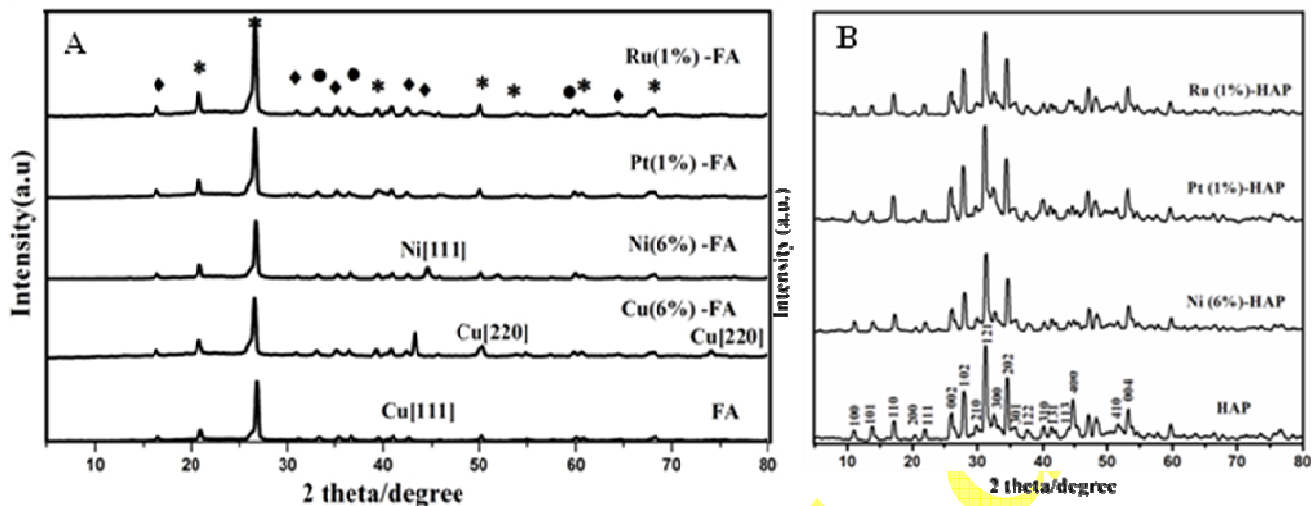


Fig.2. Powder XRD patterns of A) FA and the supported metal catalysts: (α -Quartz (*), mullite(◆) and hematite (●)); B) HAP and the supported metal catalysts.

References

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Alternate (to Pt) Electrode Materials for low Temperature Fuel Cells

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July 2013

The search for materials which can replace Pt especially in electrode applications has been on for many decades now [1-3]. Levy and Boudart [4] have postulated that carbides like WC or Mo₂C possess a similar electronic structure to that of Pt and thus exhibit Pt-like catalytic activity for a number of reactions [5]. It is essential that one examines the need for searching for alternate materials for Pt for electrode (especially anode applications) The conventionally accepted reasons are:// 1. Pt being a noble metal, the economics of using this material in fuel cells is not favourable for large scale adaptation.

2. Pt being noble metal, the available resources are limited and hence large scale usage may not be possible.

3. Pt metal is susceptible for deactivation by impurities normally present (especially CO) in the feed of the fuel inlet or formed during oxidation of the fuel.

4. Since the source of Pt is limited, it is essential that the dispersion(low loading and maximum active site formation) has to be effective and such synthetic strategy is not highly reproducible.

5. since the active metal has to be supported on a suitable conducting support (usually carbon) it is possible that potential induced aggregation may take place even if fine dispersion is obtained while synthesis of the electrode.

6. It has been estimated that if the all the vehicles on the road were to be powered by performing Hydrogen air fuel cells, then the requirement of Pt would still be about five times the total amount that has been mined to date[6]

It is also essential to note the characteristics of a material that can be potential electrode material. They are:

1. They must be capable of being employed in both acid and alkaline media.
2. The potential window that is available must be suitable for most of the electron transfer process and the electrode itself should not undergo any reaction within this potential window.
3. The charge transfer between the electrode and electrolyte should be a reversible process. This may mean that the Fermi level (free energy of the electrons) of the electrode should be such that the charge transfer process becomes feasible.
4. The electrode material employed must not be too expensive.
5. The material employed should be as inert as possible and should promote only electro-chemical reactions and should not undergo reaction with the depolarizer used for electron transfer.

It may be appropriate if we make few comments on the normal electrode materials that are employed. An ideal non-polarizable electrode is one in which the electro-chemical potential is unambiguously determined by the activities of the species involved and even if there were to be charge transfer the system reverts back to equilibrium state immediately. An ideal polarizable electrode is one that is capable of acquiring electrical potential difference with respect to reference electrode by the application of external voltage source and this potential difference persists even if the external source is disconnected. Among the three prominent options for the replacement of Pt in the anodes of the fuel cells, perovskites appear to have an important position. The reasons for this choice can be due to:

1. Since the composition of the perovskites (ABO_3 , A_2BO_4) are such that they are amenable for substitution in both A and B sites, a number of systems can be generated and they can be exploited. In the case of ABO_3 systems, it is possible one can have combinations of cations like I and V, II and IV or III and III charge states. This gives rise to a variety of systems. In this connection, it is essential to comprehend the type of ions that can be substituted in the perovskite type lattice. Generally A is a alkaline earth or rare earth metal ion like Sr, Ba, La, or Ce and B is a transition metal ion like Co, Fe, Ni, Cu or Ru. [7] The choice is governed by the ionic radius of the ions of choice and generally the A site ion is in a 12-fold coordination while B site ion is in six fold coordination. However, in the actual systems there can be variations in the coordination of A and B cations and also the structure can sustain certain amount of anion vacancy as well. All these contribute to some tolerance for the structure adopted and the tolerance factor is defined in terms of the radii of both the cations and anions by the following equation usually goes by the name Goldschmidt tolerance factor

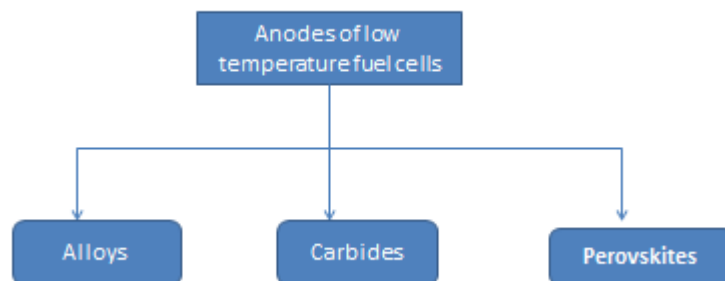


Figure 1: The three options as substitutes for Pt for anode electrode for fuel cells

$$\text{Goldschmidt Tolerance factor } (t) = r_A + r_O / \sqrt{2}[r_B + r_O]$$

where r_A , r_B and r_O stand for the radius of A, B cations and Oxide anion respectively. Usually tolerance factor can vary from 0.71 to nearly one. A pictorial representation of typical A and B ions possible in ABO_3 oxides is shown in Fig.2.

Carbides as Substitutes for Pt

As stated above, starting from the postulate of Levy and Boudart[4], in recent years, tungsten carbide has been examined as possible (also support or replacement) substitute for Pt in a variety of reactions like hydrogen or oxygen evolution reactions (HER and OER) and methanol oxidation[8-12]. It has also been shown that tungsten carbide shows HER activity and reactivity towards CO oxidation. Against this background, Venkatasubramanian et al [13] have carried out DFT calculations on WC system and compared it with that of Pt. In Figure 3 the Density of States (DOS) for Pt and WC are shown wherein it is seen that the DOS for Pt and WC are similar near the d-band center. Partial DOS of WC namely the p-d band overlap with the C p-PDOS and W d-PDOS have same shape and similar intensity between -2.5 eV and -8 eV with a split d-band into bonding and anti-bonding states. They have postulated the following (1) there is compatibility of the electronic structure of Pt and WC which may facilitate electron transfer steps as in metallic Pt on WC.

(2) The overlap of p-d bands can alter the free energy of adsorbed hydro-

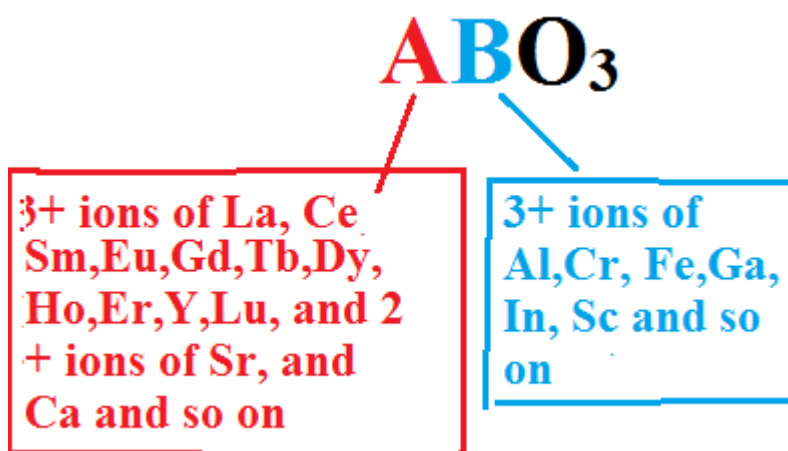


Figure 2: Typical ions that can take A or B positions in ABO₃ oxides

gen, thereby accounting for the increased reactivity for HER. Base electrocatalysts have always been suggested for methanol electro-oxidation. Electrocatalyst made from base materials must be able to resist corrosive action of the acid electrolytes. Base metallic materials are normally themselves thermodynamically unstable in acid medium. Requirement for any base electrocatalyst is that it is passive towards corrosion. As stated above tungsten carbide has been regarded as promising catalyst that can replace noble metals for the anodic oxidation of methanol [14]. The catalytic activity exhibited by the tungsten carbide is almost comparable to that of the noble metal platinum [15]. It was reported that such a catalytic activity results from closer similarity in the electronic structure between WC and platinum. The electro-catalytic activity of WC and tungsten based double carbides (W, M) C (where M = V, Cr, Mn, Ni and Mo) was investigated with the focus on methanol oxidation in sulphuric acid [16]. Only Mo containing carbide is found to be able to promote methanol oxidation activity. The magnitude of the over potential required to drive methanol oxidation reaction on the carbide surface is -0.3 V, which is almost comparable to that observed on platinum. However, carbide catalysts were prepared by chemical vapor deposition method (CVD) using tungsten and molybdenum carbonyls, which is rather expensive. Later, (W, Mo) carbide active powder have been made using lyophilized ammonium salt of tungstic and molybdic acid, which was turned into oxide powder by treatment at 973 K in air, followed by carburizing with CO gas. To activate the carbide further, alkaline activation treatment was given to (W, Mo) C. (W, Mo) C has been shown to exhibit some electrocatalytic activity for

methanol oxidation [17,18] in acidic medium. In order to develop a cheaper preparation method for the production of tungsten carbide powder catalysts, Burstein [19] synthesized the tungsten carbide by reducing the oxide powder in the flow of methane and hydrogen at 1096 K. But it shows no significant activity for the methanol oxidation. Moreover, the material exhibits significant passivity towards corrosion, suggesting the requirement for specific surface composition and geometry in order to achieve required electro-catalytic activity for methanol oxidation. The carburized Ni/W [20] prepared by mixing equimolar proportions of nickel nitrate and sodium tungstate; after drying, the tungstate was reduced in a methane/hydrogen atmosphere at 1096 K, was studied for electrochemical oxidation of methanol in sulphuric acid medium. This material showed very low corrosion rate in acid and exhibits significant activity for methanol oxidation upto a potential of -0.6 V vs SHE, after which the trans passivation of the state occurred and the corrosion current increased. The oxidation is enhanced in the transpassive region. Though, the methanol oxidation is taking place, but it takes place at higher potentials, which is of little interest in the fuel cells. The Co was also tried in place of Ni, but significant activity was not observed for the methanol oxidation in sulphuric acid. The carburized Ni/W and Ru/W were compared for the methanol oxidation, it was found that Ni based catalysts showed a minimal potential of 0.3 V (SHE) for methanol oxidation was observed at 2.5 mA/cm², whereas for the Ru based catalysts, the minimal potentials of 0.7 V (SHE) for methanol oxidation was observed at 2.5 mA/cm². These electrodes are found to exhibit irreproducibility and scatter from one electrode to another, the potential at which methanol oxidation occurs at a rate comparable between these two catalysts, is higher for Ru based electrode: it is an inferior catalyst. Though, the carbides exhibit measurable activity for methanol oxidation, comparable to that of platinum, the synthesis of the electrode material is expensive thus limiting immediate implementation.

Alloy Systems

Alternate alloy systems have been examined and this has been reviewed recently [20].

Methanol Oxidation on Pt Based Alloys - Pt-Ru system

The most successful binary catalyst for methanol oxidation in sulphuric acid is Pt-Ru. A proposed role for Ru in conjunction with Pt for methanol oxidation is its function in enabling desorption of catalyst poisons from Pt surface. For optimum activity, ruthenium should be in a solid solution with Pt [19]. The role of ruthenium in the mechanism of methanol oxidation is not straight

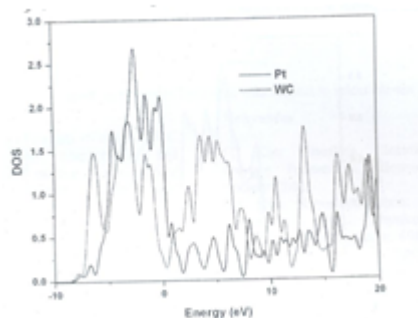


Figure 3: Density of States for Pt and WC below and above Fermi level, (Reproduced from Ref 13).

forward, although the successive de-protonation of methanol through a series of adsorbed intermediates leading to intermediate (Ru) (Pt)₂COH, which is then oxidized to CO₂ is proposed. This suggests that the optimum ratio of Pt to Ru is 2:1, assuming a uniform distribution of Ru in Pt. However, the difficulty in achieving such ideal structures probably explains the various reported optimized Pt to Ru ratios between 9:1 to 1:1. The anodic oxidation of methanol on Pt-Ru has been studied by many groups and the results from these investigations are in good agreement. Pt-Ru catalyst form chemisorbed oxygen species at potentials (ca 0.25 V vs RHE). Thus typically there is an overpotential barrier between 0.25-3.0 V before significant oxidation currents are observed. Investigations on highly dispersed Pt-Ru catalyst by stripping voltammetry of CO suggest that the surface metal alloy domains of atomic ratio Ru: Pt catalysts are key for higher DMFC anode activity [21]. The catalytic activity of Pt-Ru depends not only on maximizing the surface area and providing a surface with maximum number alloy sites of atomic ratio 1:1 but also on the presence of Ru oxides. The presence of various oxides, primarily amorphous hydrous oxides of Ru, has an inhibiting effect on surface activity, although they can play a role in terms of enhancing proton conductivity. The above conclusions were substantiated by Arico et al., [22] in which they analyzed and compared the performance of commercial (E-TEK) catalyst with an in house catalyst prepared by a colloidal method. The E-TEK catalyst contained a substantial amount of RuO₂ whilst the in house catalyst did not. The role of hydrous ruthenium oxide as a catalyst promoter has been highlighted recently in terms of its mixed electronic and proton conductivity [23]. Commercial Pt-Ru black catalysts were shown to contain a high proportion of ruthenium oxide which was essential for their

high catalytic activity. The formation of anhydrous oxides of Ru has a deleterious effect on methanol oxidation. Pt-Ru catalysts are not subjected to temperatures higher than 423 K, to ensure high activity. In summary the authors conclude that a proton conducting, electrocatalytic, corrosion resistance RuO_xH_y component in Pt-Ru electrocatalysts expresses three key properties: (a) Electronically conducting (b) Proton conducting (c) Is an innate good water dissociater, which is one of the mechanisms for proton movement in the material.

Pt-Sn Catalysts

Controversy exists as to the activity of Pt-Sn alloys for methanol oxidation. Whereas some workers report poor activity[24], this is disputed by others [25]. This contradiction may well be due to the binary binary system not being an alloy but simply a mixture of the two metals. Additionally it is known that electrodeposited or electrosorbed Sn on Pt is a good catalysts for methanol oxidation. It has been suggested as a possible explanation as to why some apparent Pt-Sn alloys are active catalysts while others are not [26]. Furthermore, Sn may leach from the catalysts under acidic conditions and be re-adsorbed electrochemically at Pt sites producing a Sn modified Pt surface suitable for methanol oxidation. This is undesirable for DMFCs in long-term use due to inevitable variations in performance and possible migration of ionic tin into the electrolyte membrane and possibly to the cathode surface. Shukla et al.,[27] used X-ray photo-electron spectroscopy (XPS) to study the effect of Sn and Ru additions to platinised carbons in order to elucidate differences in mechanistic behaviour. They argued that, Sn produced a modification in the electronic environment around Pt-sites (through a charge transfer in the Pt-Sn alloy), Ru-sites in Pt-Ru alloys promoted the formation of lattice bonded oxygenated species in the vicinity of methanolic residues adsorbed on Pt-sites. XPS showed the presence of strongly bonded oxygen species on Sn sites in the Pt-Sn system, which would limit the oxidation of methanol to CO_2 in relation to labile-bonded oxygen. The work confirmed the observation that Pt-Sn catalyst is excellent for methanol oxidation at low potentials [28], but that at higher potentials Pt-Ru catalysts were more effective, when labile bonded oxygen would be present on the surface. Abdul-Rahim [29] prepared Pt-Sn catalysts by electrodepositing Sn onto Pt substrates and found that the surface concentration of Sn was a defining factor in the activity of the catalysts produced. In addition it was shown that repeated potential cycling from the potential for oxygen evolution to that for hydrogen evolution enhanced the activity. Such cycling was found to have

Table 1: Effect of Catalyst Promoter on Methanol Oxidation

Promotion by	Catalyst Promoter	Comment
Alloying and dissolution to produce highly reticulated surfaces	Cr,Fe,Sn	Typically less than 100 mV lower potential than Pt
Surface adatoms	Sn,Bi	
Alloys	Ru, Sn,Mo,Os,Ir,Ti,Re	Ru has the best effect. Sn, Mo, Os and Re are substantial promoters.
Metal oxides	Ru	Hydrous Ru oxide is the most active catalyst
Base metal oxides	W, Ti, Nb, Zr,Ta	W oxide is a notable promoter. Small effect for other metal oxides

only a minimal effect on the catalyst stability. In addition to binary Pt-Sn catalysts, ternary and quaternary, including Ru and W [30,31] catalysts have been prepared and appear promising.

Catalyst Promoters for Methanol Oxidation

The promotion of Pt by a range of metals (and oxides) to enhance methanol oxidation is well known. The species that have had a reported positive effect on methanol oxidation are summarized in Table 2. Of the catalyst promoters considered, significant recent activity was focused on the use of Ru, Sn and W with Pt. Though metals like Bi, Pb, Mo, Sb, In and their oxides or alloys enhance the activity of Pt for methanol oxidation, they dissolve in acid medium during the course of the reaction. table

Transition Metal Macrocycles

A number of insoluble metal chelates will also chemisorb oxygen, the most chemically stable are the metallo porphyrins, metal phthalocyanines and metal tetraazannulens. A summary of the available data are given in Table for oxygen reduction (ORR) and also methanol tolerance for fuel cell applications in Table. 4.

Table 2: Preparation methods, electrocatalytic activity for oxygen reduction, and selectivity towards oxygen reduction on transition metal oxides compared to Pt from ref.32, n.r. Not reported

catalyst	Preparation method	Electrolyte medium	No of electrons transferred	catalytic activity vs Pt
$\text{La}-2\text{NiO}-4 + \delta$ (Ln=La,Nd,Pr)	citrate method	Alkali	n.r	n.r
LaMnO_3/C	Chelating method	alkali	n.r	n.r
$\text{La}_{1-x}\text{Sr}_x\text{Mn}_{1-y}\text{Fe}_y\text{O}_{3+\delta}$ (x=0 to 0.4;y-0.to0.8)	reverse Micelle	acid/alkali	n.r	excellent
TiO_2	electro deposition	alkali	4/2	n.r
REMn_2O_3 (Re=Dy, Ho,Er Tm,Yb,andLu)	citrate	alkali	n.r	n.r
$\text{La}_{0.6}\text{Ca}_{0.4}\text{CoO}_3$	citrate	alkali	n.r	n.r
$\text{Ni}_x\text{Al}_{1-x}\text{Mn}_2\text{O}_4$	sol gel	alkali	n.r.	n.r.
$\text{La}_{1-x}\text{A}_x\text{MnO}_3$ (A=Na,K,Rb)	solid state	alkali	n.r	n.r
$\text{Co}_3\text{O}_4, \text{PbCo}_5\text{O}_x$	sol gel	alkai	4	n.r
MnCo_2O_4	citrate	alkali	4	n.r
$\text{Pb}_2(\text{Pb}_{0.58}\text{Ru}_{1.42})\text{O}_6\text{O}'_{0.5}$	precipitation	alkali	n.r	comparable

Table 3: Preparation method, electrocatalytic activity and selectivity towards oxygen reduction and methanol tolerance of transition chalcogenides compared to Pt(adopted from Ref 32) n.r. Not reported

Catalyst	preparation method	electrolyte medium	No of electrons electrons transferred	catalytic activity for O ₂ reduction	methanol tolerance
Mo _{6-x} Ru _x Se ₈ x=1.8	solid state reaction	acid	4	Low	Excellent
Mo _x Ru _y S _z Mo _x Os _y S _z W _x Ru _y S _z , Re _x Ru _y S _z	solid state reaction	Acid	n.r	Low	n.r
Mo _x Ru _y SeO _z	precipitation method	Acid	4	Low	excellent
Ru _x S _Y (CO) _n	Pyrolysis	Acid	4	Low	excellent
Ru _x Se	aqueous medium	Acid	4	comparable	Excellent
Ru _x Se _y	Impregnation	Acid	4	comparable	Excellent
Ru _x Se _y O _z	Colloidal	Acid	4	Comparable	Excellent
Ru _x Se _y ,Ru _x Te _y	solid state	Acid	4	low	n.r.
Ru _x Cr _y Se _z Ru _x Fe _y Se _z	precipitation	Acid	4	n.r.	n.r.
M _x Mo ₆ S ₈ (M=Ag,Ba,Cd,Zn Sn,Pb,In,Pd)	precipitation	Acid	4	n.r.	n.r.
M _x Mo _{6-x} Te ₈ (M=Pt,Ru,Os,Rh)	precipitation	Acid	4	n.r.	n.r

Table 4: Electrocatalytic activity and selectivity towards oxygen reduction on transition metal macrocycles compared to Pt; n.r. denotes not reported:

From Ref.32

Catalyst	Electrolyte medium	No of electrons transferred	catalytic activity for oxygen reduction	methanol tolerance
CoPc	Alkali/acid	2	n.r.	n.r
CoTSPc	Alkali/acid	2	n.r.	n.r
CoTPP	Acid	2	n.r.	n.r
pillared dicobalt porphyrins	Acid	4	n.r.	n.r.
planar dicobalt Porphyrins	Alkali	4	n.r.	n.r.
Poly-CoTAPc	acid/alkali	4	n.r.	n.r.
HT-CONPc	Acid	3.8	n.r.	n.r
Co porphyrins with Ru(NH ₃) ₅	Acid	3.5	n.r.	n.r.
FePc	Alkali	4	n.r.	n.r.
FeTSPc	Alkali	4	n.r.	n.r.
FeTPyPz	Alkali	4	N.r.	n.r.
HT-FeTPPCl	Acid	4	n.r.	n.r
FeAc/Pyrrole	Acid	3.9	N.R.	n.R.
FeTMPy/VulcanXC72R	acid	2.7	n.r.	n.r.
FeTPPS/vulcanXC72R	Acid	2.7	n.r	n.r.
FeNPc/PrintexXE2	Acid	3.5	N.R.	n.R.
Fe(Phen) ₃ /XC72R	Acid	3.7	n.r.	n.r.
Co-TPP/FeTPP	Acid	4	comparable	excellent
FeTMPP-Cl	acid	4	comparable	Excellent
CoTAA	Acid	2	comparable	Excellent
CoTcPc/XC72R	Acid	n.r.	comparable	n.r.
FePC/XC72R	Acid	4	comparable	n.r

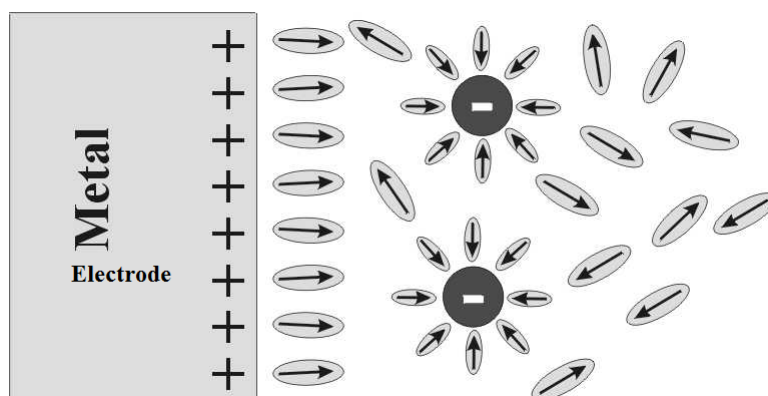


Figure 4: A simple model for the Electrode/Electrolyte Interface).

Perspective

Generally, when one looks for alternative material for electrode applications, it is natural to consider the stability under potential conditions. However when alternate electrode materials are sought for energy conversion devices, the electro-chemical potential of the electrons in the electrode is the main concern and thus electronic property of the material is also considered. However since the electrode functions in an interface the natural potential difference that exists can also contribute to the electron transfer process.

In this presentation, the conventional methodology of evaluating literature is alone resorted to but it is necessary to beyond this to evolve some governing principles. The available models of the structure electrode/electrolyte interface in terms of some diffuse double or multi-layer models are grossly insufficient since the specific sites in the electrode will promote specific adsorption and the information on the nature of the adsorbed species is truly in-sufficient since there can be solvation or the supporting electrolyte normally employed for electrochemical reasons can also affect the nature of the adsorbed species which could also alter the electronic structure of the electrode. This clarity on this aspect is still not complete [33]. A simple model is given in Fig.4.

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