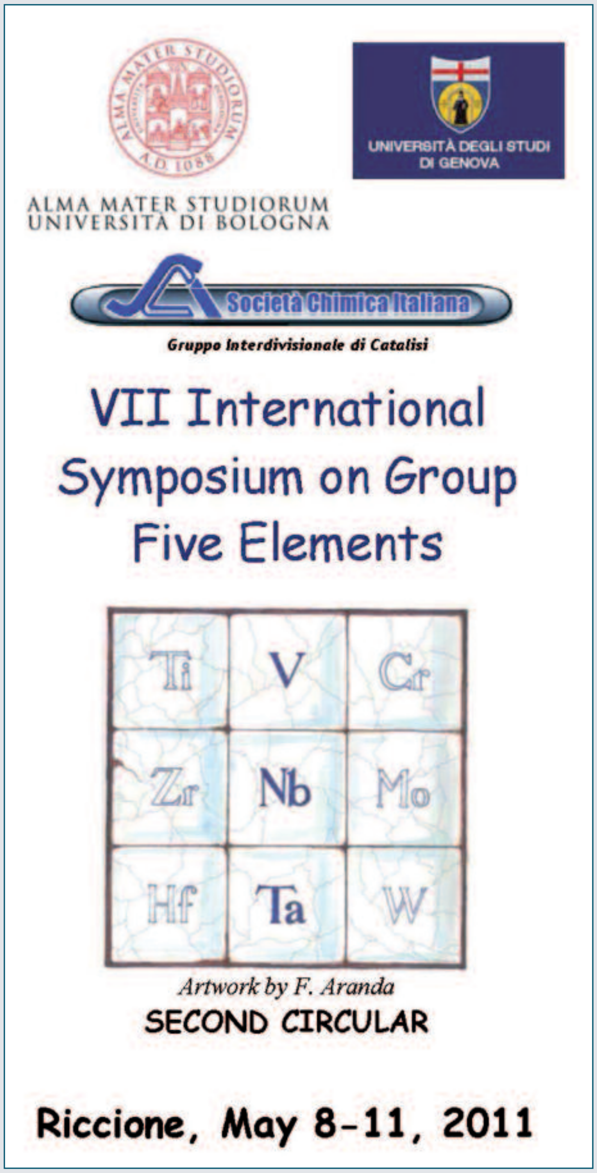

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VII International
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Artwork by F. Aranda
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7TH INTERNATIONAL SYMPOSIUM ON GROUP FIVE ELEMENTS

The last May, 2011, the 7th International Symposium on Group Five Elements was held in Riccione. The previous editions of this series were held in Hawaii (1989), Tokyo (1993 and 1995), Rio de Janeiro, (1999), Toledo (2002), Hancock, Massachusetts, USA (2005), and Poznan (2008), first devoted only to niobium chemistry, then to vanadium, niobium and tantalum (group 5 elements) chemistry. The program contained four invited lectures, 39 oral communications and 50 poster communications. Around hundred people attended to the congress from 25 different countries.

The 7th *International Symposium on Group Five Elements*, coorganized by the Interdivisional Group of Catalysis of the Italian Chemical Society (GIC) and the University of Bologna (Prof. Fabrizio Cavani and Prof. Guido Busca co-chairmen), was much focused, at least as the invited lectures are concerned, on theoretical and surface science aspects. In fact, two really exciting lectures have been done by Veronica Ganduglia-Pirovano from Instituto de Catalisis y Petroleoquimica (CSIC, Madrid) and Shamil Shaikhutdinov (Fritz Haber Institute of the Max Planck Society, Berlin), mainly focused on theoretical studies of supported vanadia catalysts. The third invited lecture of Cristophe Copéret (now at ETH, Zurich) approached experimental results on hydrocarbon conversion (in particular, alkane methathesis) together with theoretical studies on supported oxide catalysts. Definitely experimental was, instead, the fourth invited lecture given by Izabela Nowak (Poznan) who gave a deep analysis of data concerning porous materials containing niobium.

As expected indeed, the main protagonist in the congress was vanadium. Particularly relevant the contribution concerning heterogeneous catalytic oxidations based on vanadium catalysts. Among other, very interesting the results of the paper presented by Prof. Arne Andersson (Lund, Sweden) on the use of vanadia-based catalyst for methanol oxidation to formaldehyde to avoid the problems arising from loss of molybdenum oxides occurring with iron-molybdate based industrial catalysts. Prof. José Manuel Lopez Nieto (ITQ-UPV, Valencia, Spain) presented a study on oxidation of H_2S to sulphur over alkali-promoted vanadia catalysts. Prof. Israel Wachs (Lehigh University, USA) assessed the surface properties of vanadium-containing mixed oxides. Dr. Miguel Bañares (ICP-CSIC, Madrid) presented a theoretical study performed in collaboration with Prof. Monica Calatayud (Paris), where new aspects of the coordination surface chemistry of vanadium were presented. A session has been devoted to DeNOx catalysis by ammonia over vanadia catalyst, with contributions of W. Grünert (Bochum, Germany), I. Nova (Politecnico di Milano) and S.B. Rasmussen (ICP-CSIC, Madrid). Several were the contributions concerning ammoxidation reactions and alkane oxidative dehydrogenation, as well as chlorocarbon total oxidation. New catalytic materials containing vanadium were also described, such as vanadium-containing oxynitrides (C. Janke, Rostock, Germany) and V-containing mesoporous solids (M. Piumetti, Politecnico di Torino, and S. Dzwigaj, Paris). More extended than in the previous meeting were the sessions devoted to vanadium complexes and inorganic compounds. This allowed to propose a more close relation between the audience of this series of congresses with the ambient of inorganic vanadium complex chemistry. Prof. Valeria Conte (Università di Roma Tor Vergata) e Prof. Noritaka Mizuno (Tokyo) presented excellent contributions concerning oxidations using hydrogen peroxide catalyzed by V-containing systems. Prof. Marcello Crucianelli (L'Aquila) also reported experimental results as well as theoretical calculations in the same field. Prof. Giulia Licini (Padova) reported on the catalytic activity of V complexes in the oxidation of different substrates by alkylperoxides.

The intense development of the use of niobium species as the main component of catalysts for various processes (mainly oxidations, acid-catalyzed and photocatalytic reactions) has been underlined in many contributions. The most traditional application is related to the acidity of niobium oxide, used in bulk form as an acid catalyst or as support for metal or in mixed oxides. In this context, T. Onfroy (CNRS, Ivry sur Seine) has reported new insight on the acidity of Nb_2O_5 as a function of the calcination temperature, investigating the relationship between Brønsted acidity and the catalytic activity for the acid catalyzed reaction of propan-2-ol dehydration. On the other hand A. Takagaki (University of Tokyo) has shown that mesoporous Nb-W mixed oxides, after calcinations at high temperature, exhibited remarkable acid catalytic activity in Friedel-Crafts alkylation, surpassing conventional solid acids, due to their high surface area, relevant pore size, mesoporous structure and strong Brønsted acid sites. A novel approach to Nb-based acid catalysts has been also reported by K. Rohan (IFP, Solaize) who studied several Lindqvist niobium-tungsten heteropolyanions (HPA) to be used in catalytic reactions requiring acidic sites and thermal stability. Remarkably, for these systems the conservation of HPA structure after dissolution in water was ascertained.

Oxidation reactions are another very important field of application of niobium catalysts. M. Ziolek (University of Poznan) has discussed the diversity of niobium species effective in catalytic oxidation with oxygen and hydrogen peroxide in the liquid phase. Niobium oxides and niobiosilicates as active phases and supports for gold have been studied. The nature of the oxidant (oxygen vs H_2O_2) as well as the nature of the the solid containing niobium (amorphous vs crystalline) resulted determinant for the catalytic performances: amorphous Nb-containing catalysts revealed unique properties in the liquid phase oxidation of cyclohexene with H_2O_2 due to the formation of niobium peroxo radicals, whilst crystalline niobium systems do not exhibit these properties. On the contrary, when gas oxygen is used as oxi-

In the photograph, from left to right: Israel E. Wachs (USA), Guido Busca (Italy), Miguel A. Bañares (Spain), M. Olga Guerrero-Perez (Spain), Maria Ziolek (Poland), Goutam Deo (India), Fabrizio Cavani (Italy), Victor Teixeira da Silva (Brazil) dant in the glycerol oxidation, crystalline Nb_2O_5 is much more active and selective to glyceric acid than amorphous species. The modification of crystalline niobia with gold significantly enhances the activity in this reaction, due to the interaction of unsaturated Nb species with gold. The Au/Nb_2O_5 catalysts for glycerol oxidation were also discussed by I. Sobczak (University of Poznan) who evidenced the positive role on selectivity to glyceric acid of high gold dispersion and of Nb_2O_5 crystallinity. A smart application of Nb species incorporated into SBA-15 silica matrix was also reported: these systems resulted efficient oxidation catalysts in the presence of hydrogen peroxide in the liquid phase for the selective synthesis of vitamin K_3 (M. Selvaraj, University of Pusan).

MoVTeNbO catalysts resulted particularly promising for oxidation and ammoxidation of propane to acrylic acid and acrylonitrile respectively: in the absence of Nb these catalysts show poor activity and selectivity in both reactions. The positive effect of the addition of niobium was also ascertained for multimetal antimonates used for propane ammoxidation: acrylonitrile yield significantly increases when Nb-doped rutile systems are employed (A. Castelli, University of Bologna). Nb_2O_5-SiO_2 catalysts were reported to be also suitable for soybean oil epoxidation carried out in the presence of H_2O_2 to give valuable precursors for new lubricants synthesis (R. Turco, University of Napoli).

Finally, the novel applications of Nb derivatives in photocatalysis have been discussed. In particular photocatalytic aerobic oxidation of various alkanes was found to proceed over Nb_2O_5 and the selectivities to partial oxidation products resulted higher than that of TiO_2 (S. Furukawa, University of Kyoto). On the other hand $BiNbO_4$ was found to reveal interesting activity in the visible-light photodegradation of methyl violet thus resulting promising for energy and environmental applications (A.D. Li, University of Nanjing).

Some interesting applications of tantalum have been presented, mainly focusing on its ability to differently functionalize surfaces, on mixed oxides for oxidation reactions and photocatalysis. Though it is not the most used element in the catalysis based on group five elements, it can impart peculiar properties and lead to outstanding results. A first example was given by C. Copéret (ETH, Zurich) in his plenary lecture showing that the characterization of silica supported Ta surface species led to the discovery of alkanes metathesis *ca*. 15 years ago. A comparison was made with neighboring elements (Group IV and VI), which showed inactive for this reaction when supported on silica, though a different picture was drawn when using γ-Al_2O_3 as support, on which also Zr, W and Re were active. $(\equiv SiO)_2Ta(H)_x$ showed a promising catalyst for this application and a kinetic study allowed to define a possible mechanism for the reaction. Poisoning experiments with cyclopentane or oxygen also allowed to discriminate among the active sites. Only 50% of the exposed $Ta(H)_x$ sites were active for the metathesis of propane, likely corresponding to tris- or monohydride far from the silica oxygen (J. Thivolle Cazat, CNRS, Villeurbanne).

Ta_2O_5, as well as Nb_2O_5, may be used as acid catalyst and show Brønsted or Lewis acidity depending on the hydration degree and calcination temperature (T. Shishido, Kyoto University, Japan). Brønsted acidity may be retained by Ta_2O_5 at higher temperature than by Nb_2O_5, though the stability of the hydroxylated form depends on the oxide loading on alumina. Alumina is thought to stabilize a surface TaO_x amorphous layer, which reaches up to a monolayer of Ta_2O_5. The latter was constituted by a 2D structure of octahedrally coordinated TaO_6 units.

The surface acidic properties of NbY and TaY zeolites have been investigated by FTIR spectroscopy after adsorption of pyridine or NO (A. Wojtaszek, Poznan). In addition to the detection of Lewis acid sites and of more or less acidic Nb-OH and Ta-OH species, the use of NO as probe molecule allowed to evidence the presence of redox centers, showing that TaY was characterized by stronger redox sites than the Nb-substituted material.

The structure of the active sites has been also investigated in Ta-BEA zeolites by means of periodic DFT studies to assess their relative stability and compared with experimental results (F. Tielens *et al.*, Univ. Paris 06). The change of surface energy of different Ta sites as a function of the chemical potential of oxygen and water was considered. The presence of Ta-OH sites was evidenced at high O_2 and H_2O potential, whereas no Ta=O sites were found stable. Another possible form is the Lewis acid base pair Ta^+-TaO^-. The most favorable structure for Ta sites is pentahedral.

NbF_5 and TaF_5 can be useful compounds to generate and stabilize radical cations, else difficult to isolate in solid form at room temperature (F. Marchetti *et al.,* Univ. di Pisa). Radical cations of monocyclic arenes were prepared by using MF_5 (M = Nb, Ta), which exhibited unexpected oxidizing properties. Similarly, salts of protonated 1,3-dimethoxybenzene were obtained. The key role of the anion in the stabilization of the products is due to its interaction with the π-density of the cation, which allowed the structural characterization in solid state by XRD and in solution by EPR.

Single and mixed oxides of Nb, Ta and Y were prepared with a relatively simple procedure by controlled hydrolysis of the respective ethoxides (X.-Y- Yang *et al.,* Univ. of Namur). The peculiarity of the approach is the formation of controlled micro- or meso-porosity embedded in a macro-porous system, so to avoid possible mass transfer limitations. The addition of 0.5 wt% Pd allowed activity testing for the oxidation of toluene, where Ta_2O_5 showed the highest activity. A dependence of activity on the textural and structural properties, in particular on pore wall thickness, was found in mesoporous Ta_2O_5 photocatalysts for water splitting. The oxide has been prepared in mesoporous or layered form on SBA-15, showing higher photocatalytic activity in the former case (A. Iguchi *et al.,* Tokyo Inst. of Technology). Ta, Nb and V mixed oxides, such as $InTaO_4$, $BiTaO_4$, $InNbO_4$, Ag_3NbO_4 and $AgVO_4$, were tested as photocatalysts (R. Ullah, Curtin Univ., Australia). Photocatalytic tests have been carried out for the degradation of methylene blue (liquid phase) and toluene decomposition (gas phase) under UV irradiation. Good results were achieved if compared with the reference P25 material, especially after doping with some cations, such as Ni^{2+} or Cu^{2+} for $InTaO_4$ or Ba^{2+} for $BiTaO_4$. The role of different active sites in Ta-based photocatalysts for water splitting has been investigated by means of various spectroscopic techniques (S.P. Phivilay, Lehigh Univ., USA). Independently from the structure of the oxide, β-Ta_2O_5 or distorted perovskite $NaTaO_3$ and $NaTaO_3$:La, a 4.1 eV band gap was found for all the materials. The photoluminescence spectra may be greatly enhanced by the addition of NiO, which intentionally would play the role of co-catalyst. However, the absence of La and Ni in the outermost layers of the surface suggests that NiO does not represent an active site for this reaction. Many attempts have been also carried out to improve visible light absorption by the photocatalysts. Some of them are reported in (H.F. Zhai, Nanjing Univ., China) by using $BiNbO_4$ and $BiTaO_4$ prepared by sol-gel and tested for the photochemical degradation of methyl violet. Interestingly, the properties of Ta(V) oxide as semiconductor with high band gap and dielectric constant may be used also to build up special optical devices (X.-Y. Yang, Univ. of Technology, Wuhan, China). Group V metal oxides were also tested as supports for gold in the oxidation of glycerol in liquid phase. Au particles were loaded on V_2O_5, Nb_2O_5 and Ta_2O_5 by different techniques. Gold particle size, and consequently catalytic activity, depended on the deposition procedure and the support oxide nature (I. Sobczak, Poznan). The oxidative dehydrogenation of different hydrocarbons and alcohols has been carried out over mixed oxide catalysts, containing V, Nb and Ta, prepared by a hydrotalcite-like precursor (I.P. Belomestnykh, Russian Academy of Science, Moscow). The textural properties of the final catalyst depended on the synthesis conditions and particularly on the particle size of the precursor. At 400 °C, 45% conversion and 95-97% selectivity to ethylene was achieved over VMoNbTa-O. The same sample showed also 80% styrene yield (97-98% selectivity) at 420 °C. Similar catalysts, including Mg and Al in their formulation, were found promising also for the oxidative dehydrogenation of alcohols.

In conclusion, though Ta-based catalysts are used in well defined reacting systems only, in such cases their peculiar properties usually allow to overperform competing materials. It has been decided that the 8th congress of this series will be held in Malaga (Spain) in 2014 (contact person Prof. Olga Guerrero-Pérez).