

# Comparison of noble metal oxide/titanium monolith catalysts in wet oxidation of process wastewaters

Antal Tungler<sup>1\*</sup>, Arezoo M. Hosseini<sup>1</sup>, Zoltán Schay<sup>1</sup>, Sándor Szabó<sup>2</sup>, János Kristóf<sup>3</sup>, Éva Széles<sup>1</sup>

<sup>1</sup>Hungarian Academy of Sciences Institute of Isotopes, Budapest, 1121, Hungary

<sup>2</sup>Chemical Research Center of HAS Bp, 1025, <sup>3</sup>Pannon University, Veszprém, 8200

\*atungler@iki.kfki.hu

## Introduction

Catalytic Wet (Air)Oxidation has been applied to many different model effluents and some complex industrial wastes [1-6]. Three rather detailed reviews described wet oxidation and catalytic wet oxidation [7-9] of wastewaters, even that of some industrial process wastewaters. In the present work the activity of different monolith catalysts was compared in WO of phenolate solution and a real pharmaceutical process wastewater.

## Experimental

The samples were oxidized in a 850 ml stainless steel high pressure autoclave equipped with a magnetic stirrer (rpm 700), at 230°C and 50 bar total pressure (~22 bar oxygen partial pressure) at basic pH. The catalysts were titanium mesh (0.5x100x500 mm in size) with Ru and/or Ir, Ta oxide coating, a commercial one and four others prepared in our laboratory .

The water samples were characterized with their COD and TOC values. The catalysts were characterized by SEM, XPS and LA-ICPMS.

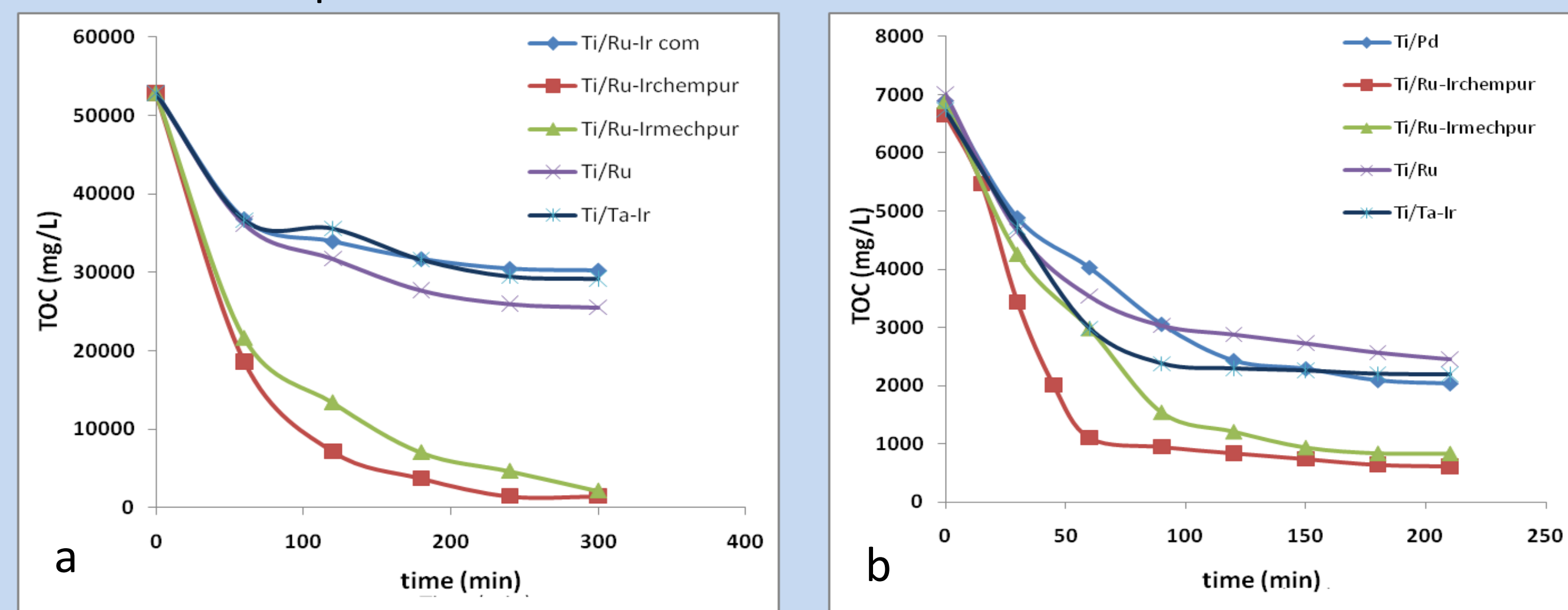


Figure 1. TOC decrease in a process wastewater (a) and phenolate solution oxidation (b) with different monolith catalysts.

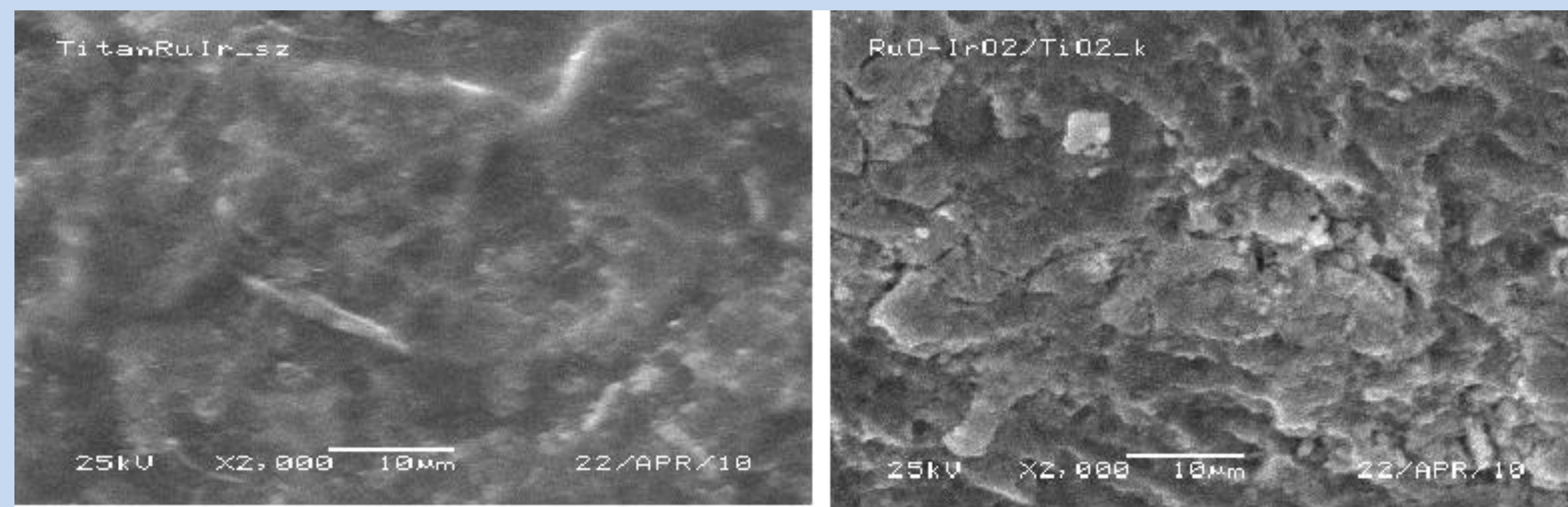


Figure 2 SEM picture of Ru-Ir oxide catalysts prepared on chemically purified (left) and mechanically purified (right) Ti mesh.

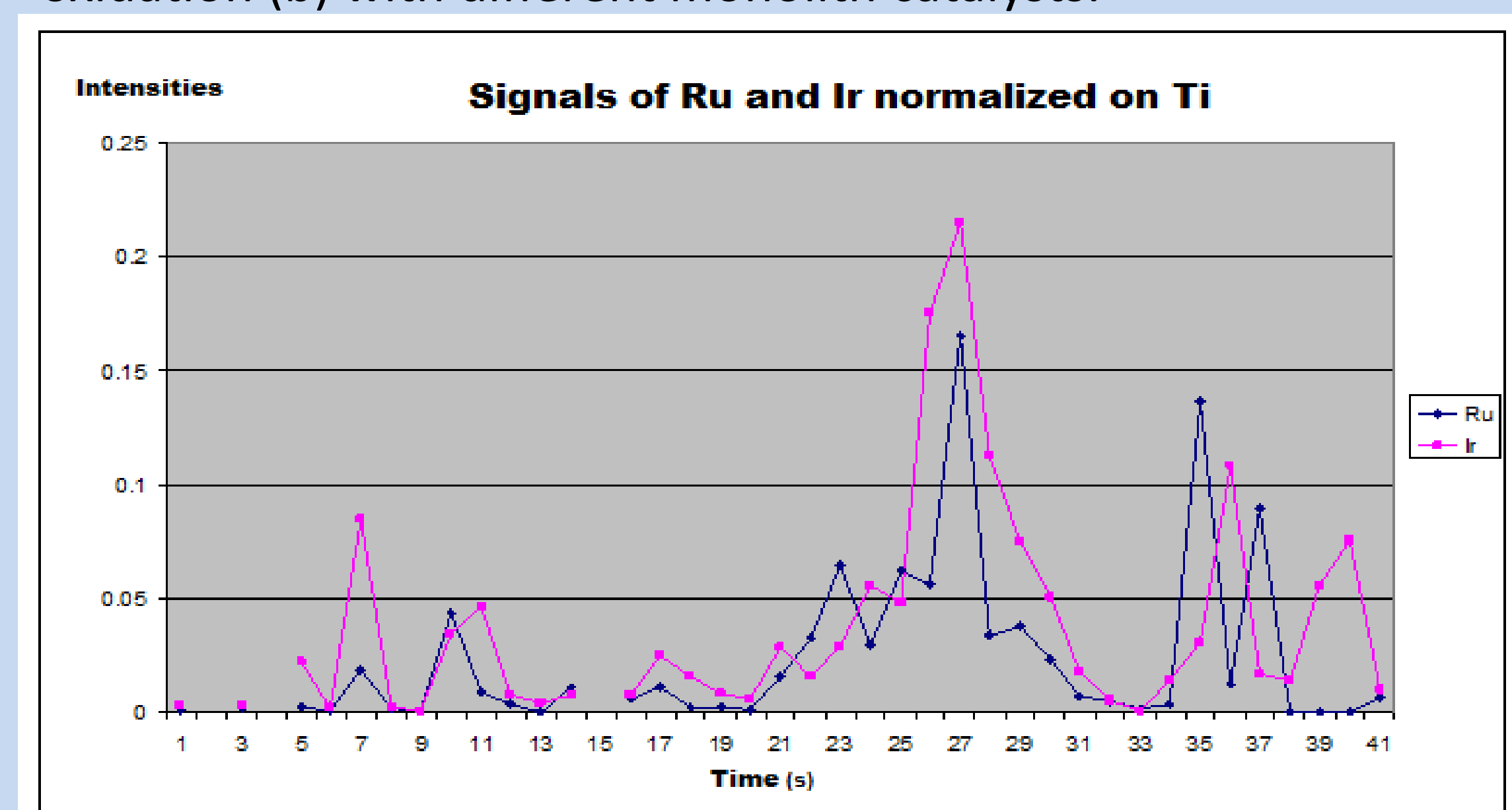


Figure 3 LA-ICPMS measurement of distribution of Ru and Ir on the surface of the commercial Ti catalyst mesh

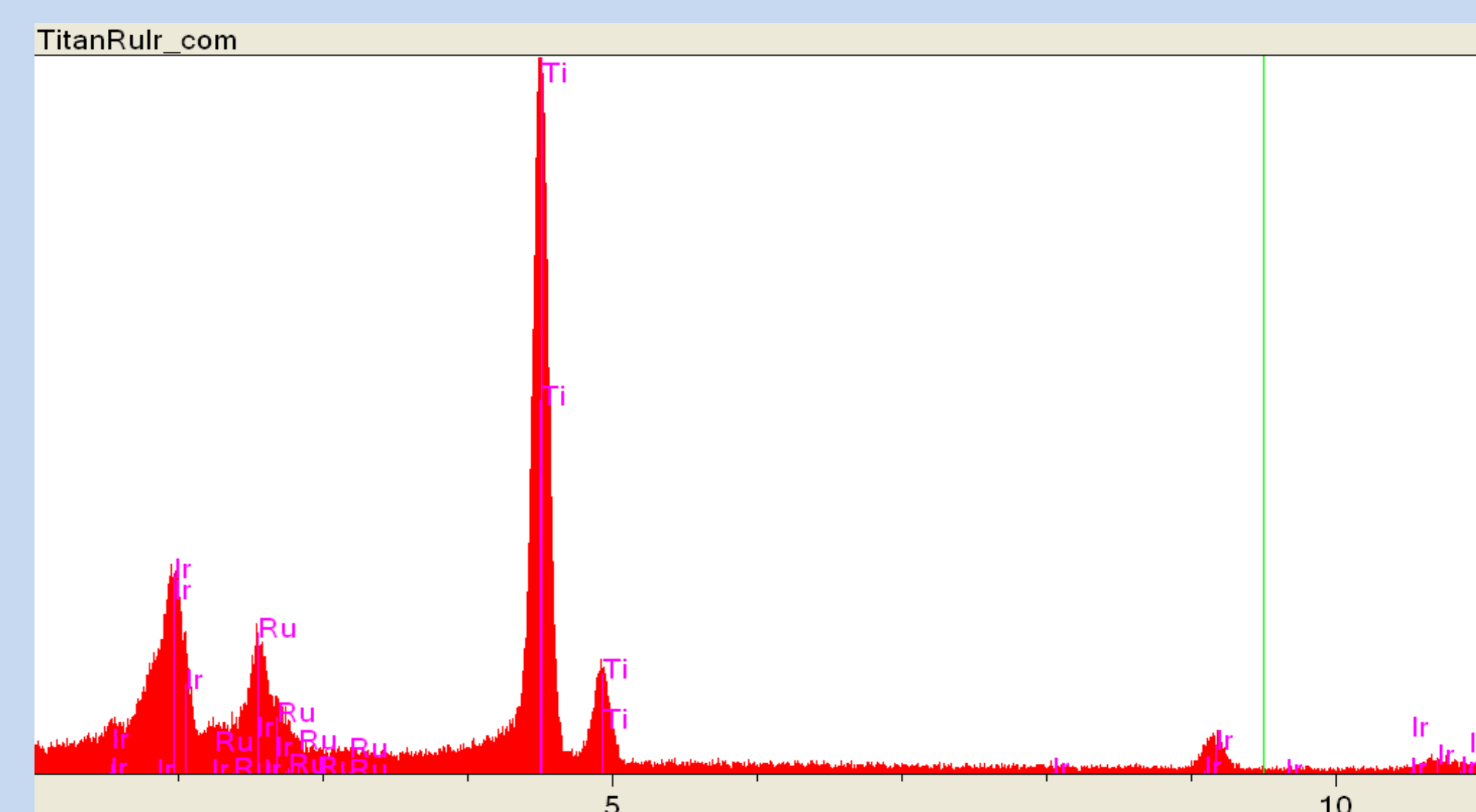
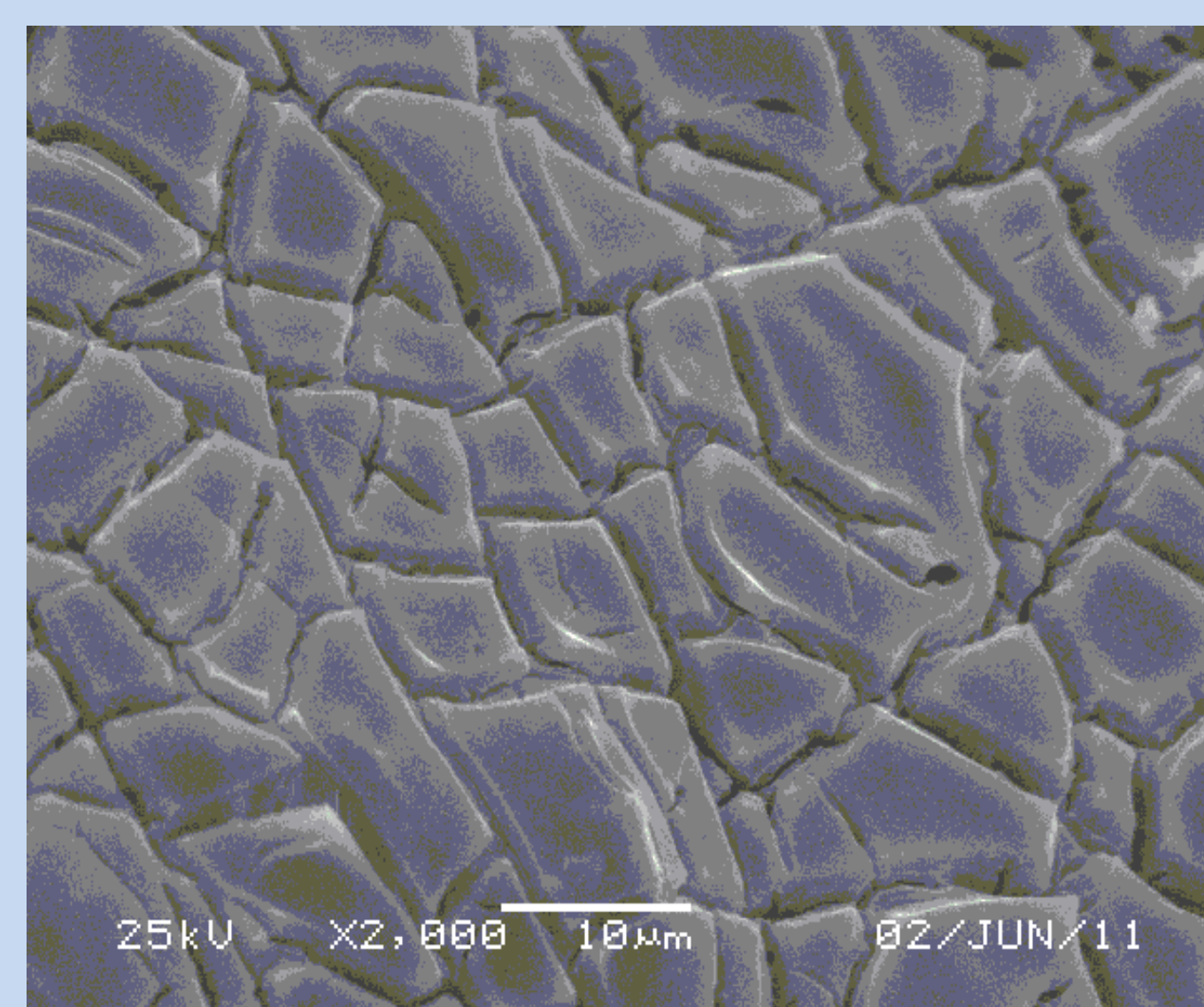


Figure 4-7 SEM pictures and surface analysis of the commercial Ti catalyst mesh, above before use, bottom after ~200 hours usage.

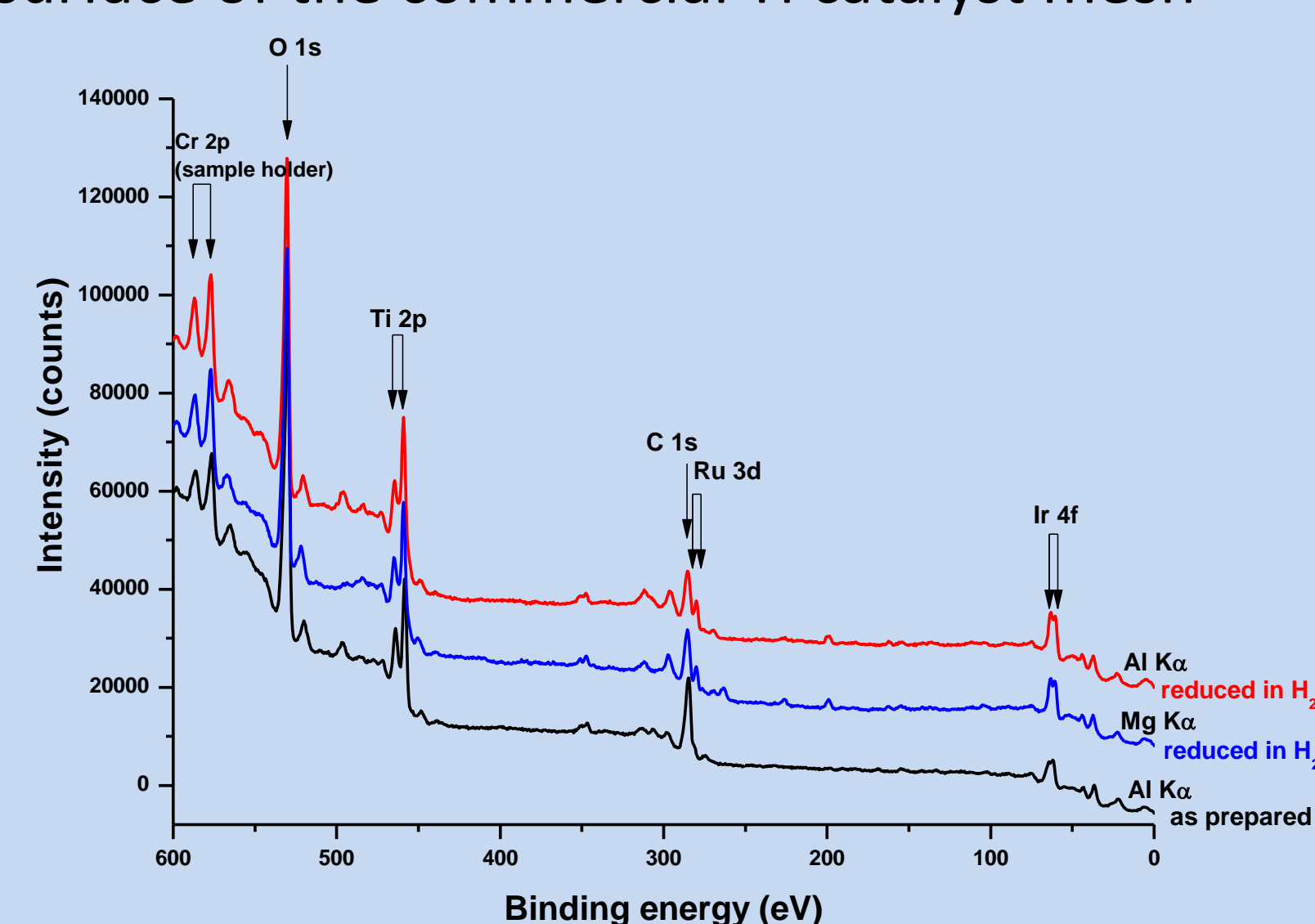
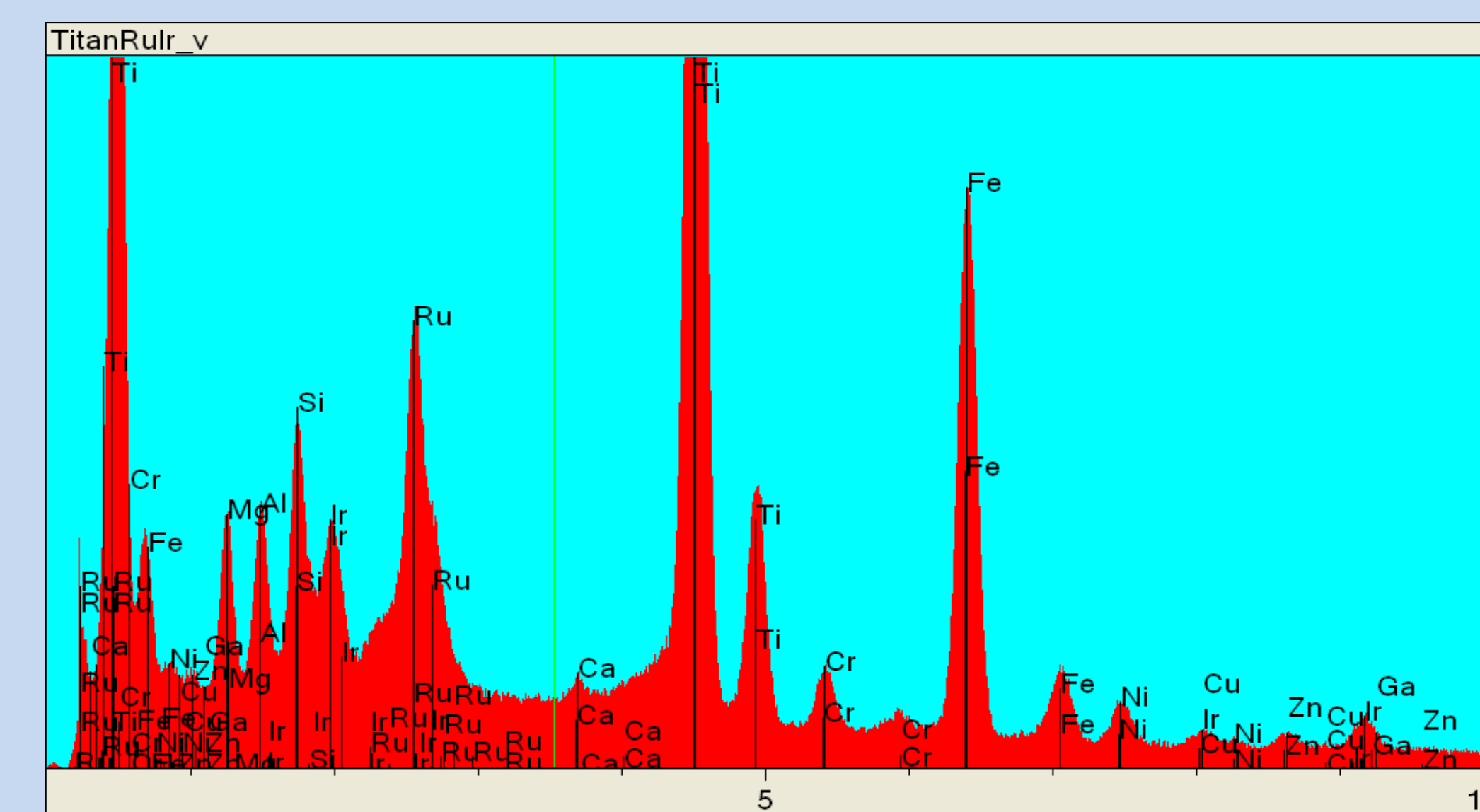
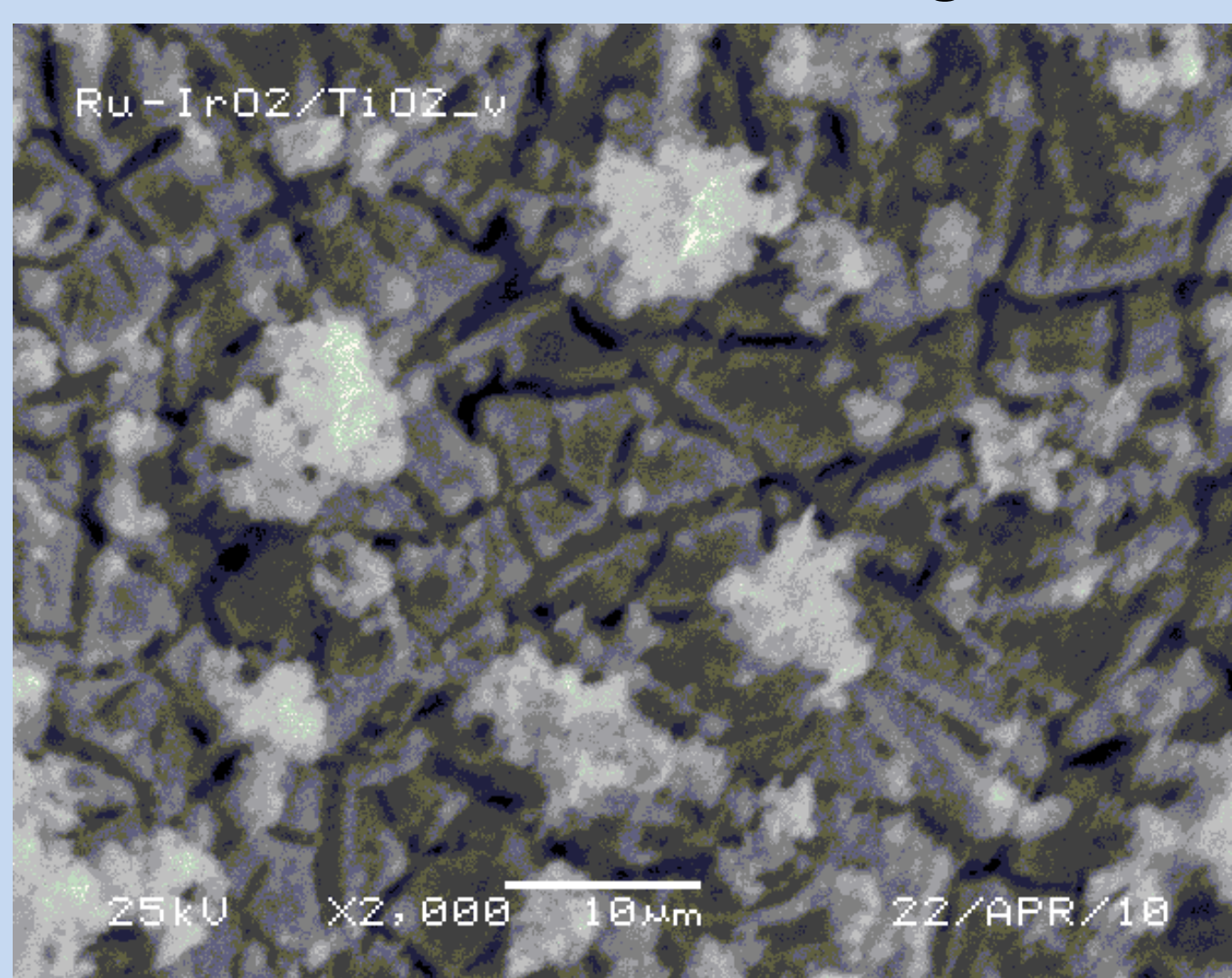


Figure 8 XPS spectra of the commercial mesh catalyst



## Results/Discussion

SEM showed the different structures of the active layer. On the chemically purified Ti mesh the noble metal oxide layer is continual (Figure 2 left), on the mechanically purified Ti mesh (Figure 2 right) it is fragmented, similarly to the commercial mesh (Figure 4). The SEM pictures and surface analysis (Figures 4-7) indicate that after longer use the surface is covered with precipitates, mainly iron and silicium oxide. LA-ICPMS (Laser ablation- Inductively coupled plasma mass spectrometry) gave the surface concentration distribution of the noble metal oxide components. The two oxides (Ru, Ir) are in nearly the same concentration on the targeted sites. XPS (Figure 8) gave information about the chemical valencies of the catalitically active substances, they are definitely oxides of Ru and Ir on the oxidized Ti.

The activity of the different monolith catalysts depended on the noble metal type and on the preparation method. In the oxidation of both substrates, of the real process wastewater and of the phenolate solution the Ru-Ir oxide coated Ti catalysts were more active, in the case of the real process wastewater complete mineralization occurred. (Fig. 1, a, b. chempur-Ti mesh chemically, mechpur-mechanically purified, com-commercial). All reactions have two periods: in the first fast one the degradation of larger molecules, in the second slower one the oxidation of the resistant main intermediates, that of carboxylic acids with small molecular weight takes place.

## Acknowledgement

The Authors thank Bp Sewage Works Ltd. (FCSM), NSF (OTKA) No.80154, Swiss-Hungarian projects SH7/2/14 for their financial supports.

## References.

1. Eugenia Suarez-Ojeda M, Guisalsola A, Baeza J.A, Fabregat A, Stuber F, Fortuny A, Carrera J (2007) *Chemosphere* 66: 2096-2105.
2. Luck F (1999) *Catal. Today* 53: 81-91.
3. Pintara A, Gorazol B, Besson M, Gallezot P (2004) *Appl Catal B* 47(3): 143-152.
4. Lei Y J, Zhang S D, He J C, Wu J C, Yang Y (2005) *Platinum Metals Rev* 49 (2): 91-97.
5. Yang S X, Feng Y J, Wan F J, Lin Q Y, Zhu W P, Jiang Z P (2005) *J of Environmental Sciences* 17 (4): 623-626.
6. Heponiemi A, Rahikka L, Lassi U, Kuokkanen T, *Chemical Engineering Transactions*, 17( 2009)
7. Bhargava S K, Tardio J, Prasad J, Föger K, Akolekar D B, Grocott S C (2006) *Ind Eng Chem Res* 45:1221-1258.
8. Cybulski A (2007) *Ind Eng Chem Res* 46: 4007-4033.
9. Janez Levec, Albin Pintar (2007) *Catalysis Today*, 124, 3-4,172-184