In situ real time monitoring of Pt-VO_2 nanoparticle-nanowire assembly by GISAXS

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ABSTRACT

Methanol is a hydrogen carrier for fuel cells and its chemical transformations are of great current interest. Methanol oxidation by vanadium oxides is well studied, hence, serves as a good measure for catalytic activity. Arrays of VO_2 nanowires grown on r-cut sapphire prove to be unique for the *in situ* catalytic activity tests. Here, we present size and morphology dependent activity of Platinum coated single crystalline VO_2 nanowires in methanol oxidation reactions using Grazing Incidence Small Angle X-ray Scattering (GISAXS). Our findings show an unexpected sintering behavior of Pt at temperatures as low as 200 ^oC.

Keywords: catalysis, CVD, VO_2, nanowires, platinum, methanol oxidation, GISAXS

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1. INTRODUCTION

The performance of a heterogeneous catalyst is a highly sensitive, dynamic function of its surface chemistry since the shape, size and step edges determine the activity or selectivity.[1, 2] These "active" sites, particularly the structures that form the surface topography, are usually at the levels of several nanometers or smaller.[3]

Surface X-ray diffraction techniques stand out among the tools to monitor surface state crystal phases with nanoscale resolution *in situ* while a catalytic reaction is taking place.[4, 5] They are advantageous over in situ transmission electron microscopy (TEM) and low energy electron diffraction (LEED) since the X-ray transmission and penetration depth is greater so that they do not require low pressure environments, nor do they require conductive samples to deal with sample charging.[6] High resolution TEM (HRTEM) is another contender but is hard to apply to reactive gas mixtures since a significant fraction of the e-beam is deflected by the gaseous phase.[7]

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Environmental TEM (ETEM), on the other hand, has limitations due to the use of cell windows that create extra electron scattering and also can only be done in small volumes and at low temperatures.[7]

High intensity x-ray beams available at Synchrotron facilities (especially Grazing Incidence X-Ray Scattering – GISAXS) are highly precise and require a short (0.1 sec) exposure time to obtain data, enabling real time monitoring.[8-11] This, furthermore, minimizes the damage that comes from the x-ray beam since the contact time between the sample and the beam is limited.[12] GISAXS is also known to detect structural changes with < 1 nm sensitivity.[13]

There is an important dynamic synergy between catalyst and its support[14] that can be monitored using GISAXS. Platinum particles on VO_2 nanowires offer an ideal system to study catalyst and support changes since platinum is a highly active and robust catalyst. Our group has studied platinum clusters extensively. [5, 11, 13, 15] Platinum sintering is not observed below 320 ^oC for nanoclusters of 12 Å [15] and 500 ^oC for bulk [16] under oxidative gas mixtures. Platinum nanoparticles of <5 nm on a VO_2 nanowire surface of ~60 nm could be expected to present an excellent opportunity to detect subtle catalyst/support changes in the framework while gas catalysis is taking place. To the best of our knowledge, there are also few reports on single crystal VO_2 nanowires and none of those show direct synthesis under ambient conditions, or direct synthesis with a supported catalyst.[17, 18]

2. EXPERIMENTAL

2.1 Synthesis of VO_2 nanowires.

In a horizontal electrical furnace equipped with a quartz tube (Figure 1) substrates of SiO_2, Al_2O_3 are placed with a ranging distance to the quartz or alumina boats that contain the source powder. A constant flow of ultra pure grade 5.0 Helium was passed at a rate of 300 sccm. VO_2 nanowire arrays observed on the r-cut sapphire substrate in 2 hours at 650 ^oC (Figure 2).

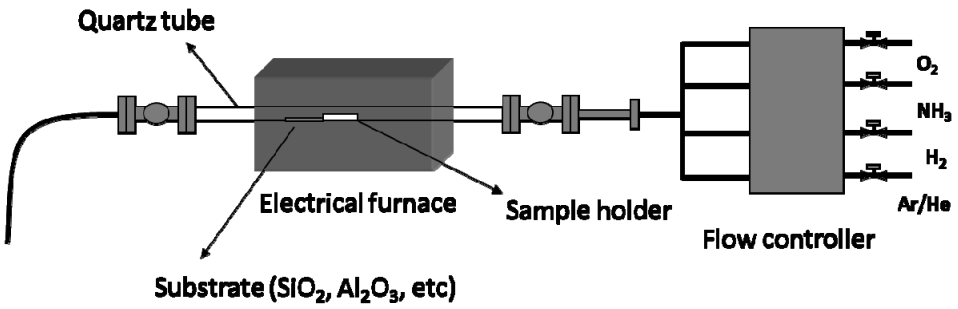

Figure 1. Electrical furnace with a quartz tube.

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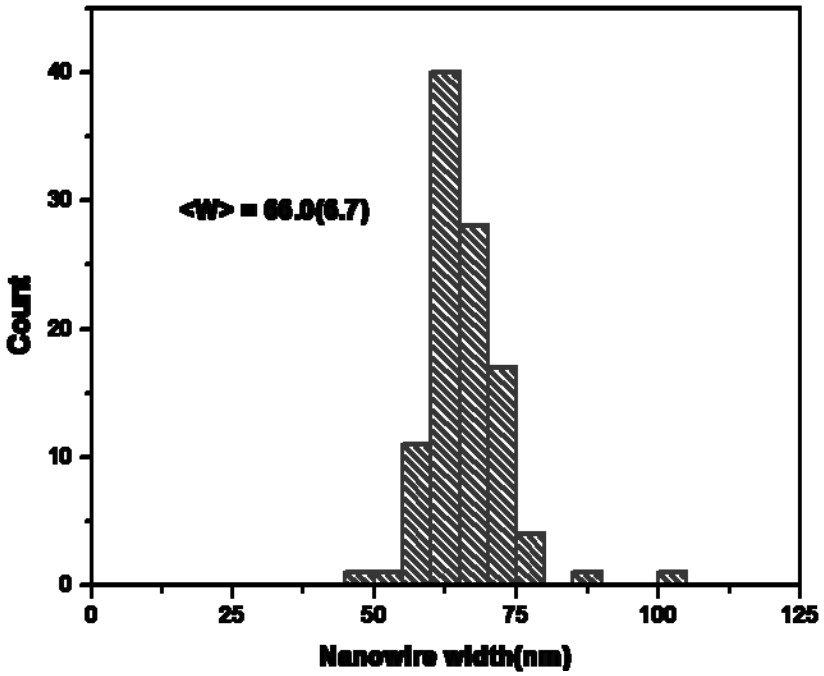

Figure 2. The average width of the as synthesized VO_2 nanowires.

2.2 Platinum deposition

5 nm platinum and gold films were deposited over the nanowire arrays using electron beam evaporation at a base pressure of 2.0×10^{-6} Torr.

2.3 Methanol oxidation

1% Methanol (50 sccm) and oxygen (50 sccm) were fed into a custom built reactor (Figure 3) which was located in front of the synchrotron beam of the 12-ID of Argonne National Laboratory's Advanced Photon Source. The exhaust gas was analyzed using a Quadrapole MS.

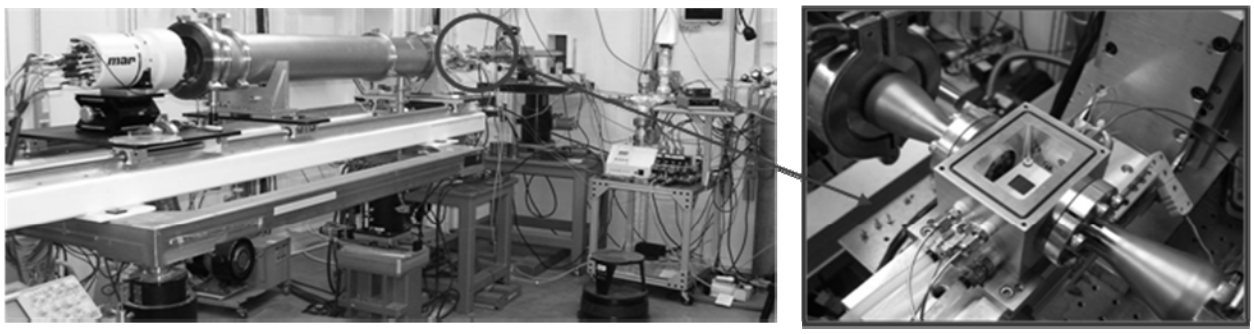

Figure 3. Our custom built reactor was placed in front of the beam source 12-ID at the APS of Argonne National Laboratory.

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3. RESULTS AND DISCUSSION

In order to obtain the desired well defined nanowire array, we developed a catalyst free VO_2 growth starting from VO_2 powder under ambient conditions (Figure 4a). Our earlier mechanistic assessments suggest that super cooled droplets are responsible for the catalyst free synthesis of these single crystal VO_2 nanowires.

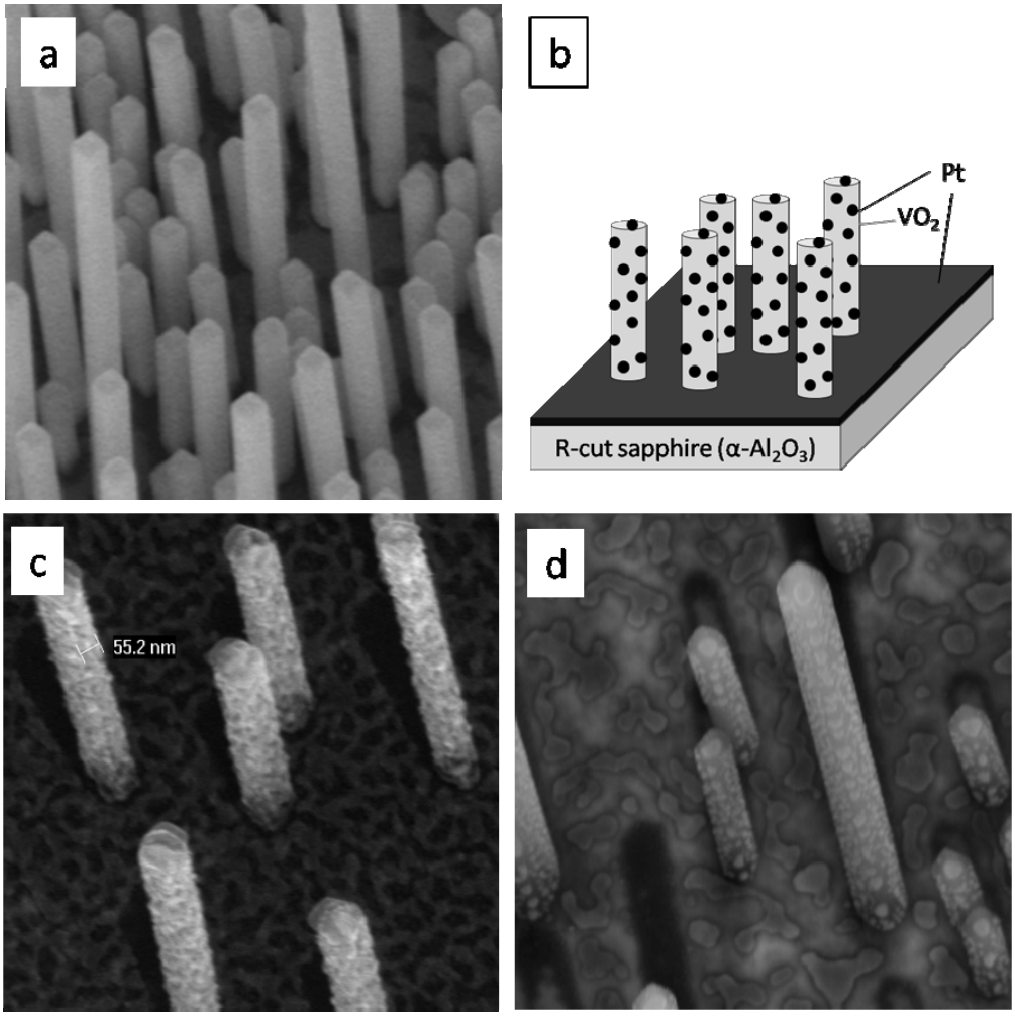

Figure 4. Scanning electron micrographs from (a) single crystal VO_2 nanowire arrays, (b) scheme of the intended platinum presence on the nanowires (c) VO_2 nanowire arrays with 5 nm platinum that is deposited via e-beam and are pictured after gas catalysis reaction, (d) control experiment with 5 nm gold deposits.

For preparation of a model nanowires supported catalyst (Figure 4b), we deposited a 5 nm platinum film onto 60 nm wide VO_2 nanowires using electron beam evaporation at a base pressure of 2.0×10^{-6} Torr (Figure 4c). In a concurrent study, we deposited 5 nm gold on similar VO_2 nanowire arrays (Figure 4d). The catalyst activity and changes on the nanowires were monitored at the same time by our custom made reactor (Figure 5). The heating profile was defined so that we kept the reactive conditions for at least 5 minutes at each temperature. The

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temperatures were selected as 25, 50, 100, 150, 200, 230, 250 ^{o}C; with 230 ^{o}C being the optimum temperature for methanol oxidation.[19]

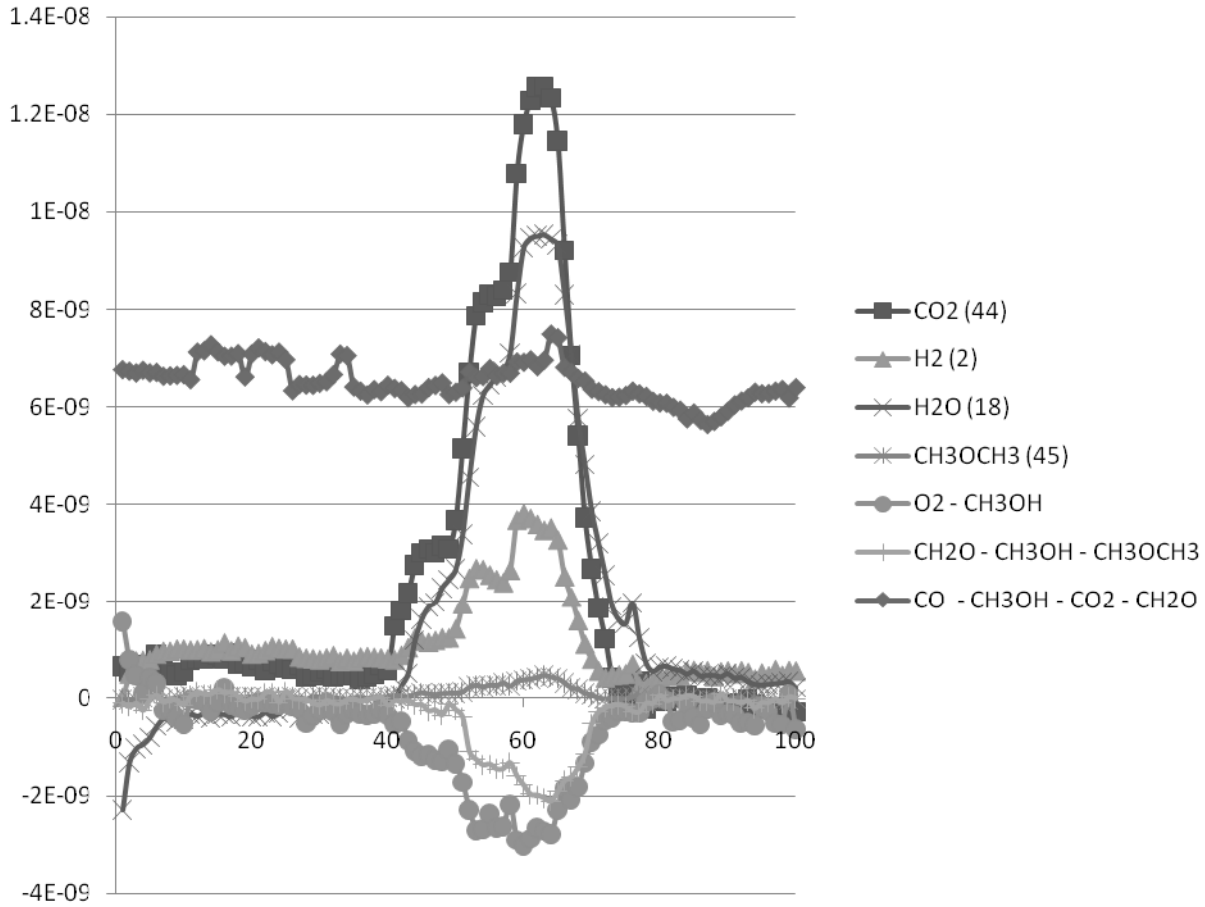

Figure 5. Comparison of the evolved and used gases with respect to time in the reactor.

In a typical run, platinum particles were observed to grow from 8 nm to 13 nm under reactive conditions at temperatures above 200 ^{o}C whereas shrinking to 5 nm was observed in an inert atmosphere (Figure 6). Figure 6 shows the intensity vs. q_{xy} collected via an angular line cut (Figure 6 inset) over the temperature range where size changes observed. 200 ^{o}C was noted when changes were first noticeable.

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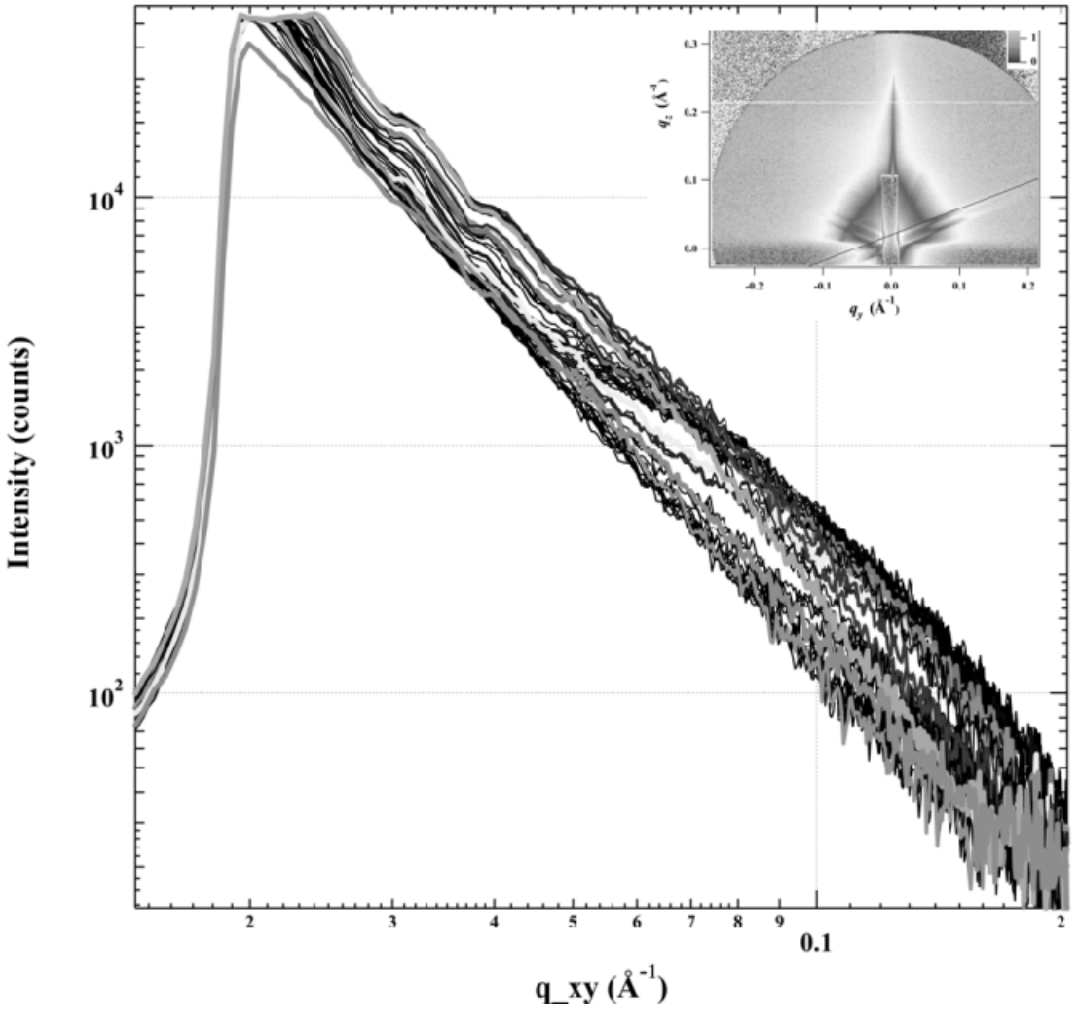

Figure 6. The evidence of size increase extracted from GISAXS scans. Inset: line cut position (straight angular line) is shown on one of the GISAXS images.

There are several pathways that might cause the observed size change: 1) platinum particles are sintering at temperatures as low as 200 ^{o}C, 2) oxides of platinum are forming, or 3) platinum and VO_2 are forming an alloy that preserves the integrity of the crystals but allows the expansion of the grain sizes. Carbon cannot be detected by GISAXS and thus is not seemingly a viable explanation for the size changes.

In order to distinguish these possibilities, we first examined EDX scans on the VO_2-Pt structures to assess possible compositional transformations. Aside from relatively large amounts of oxygen, the presence of carbon was significant (Figure 7, Table 1). Little or no carbon was observed on bare surfaces where there was not any VO_2, and only Pt on the sapphire (α-Al_2O_3) substrate. One explanation could be that under reactive conditions carbon species are likely to associate with platinum particles.[20]

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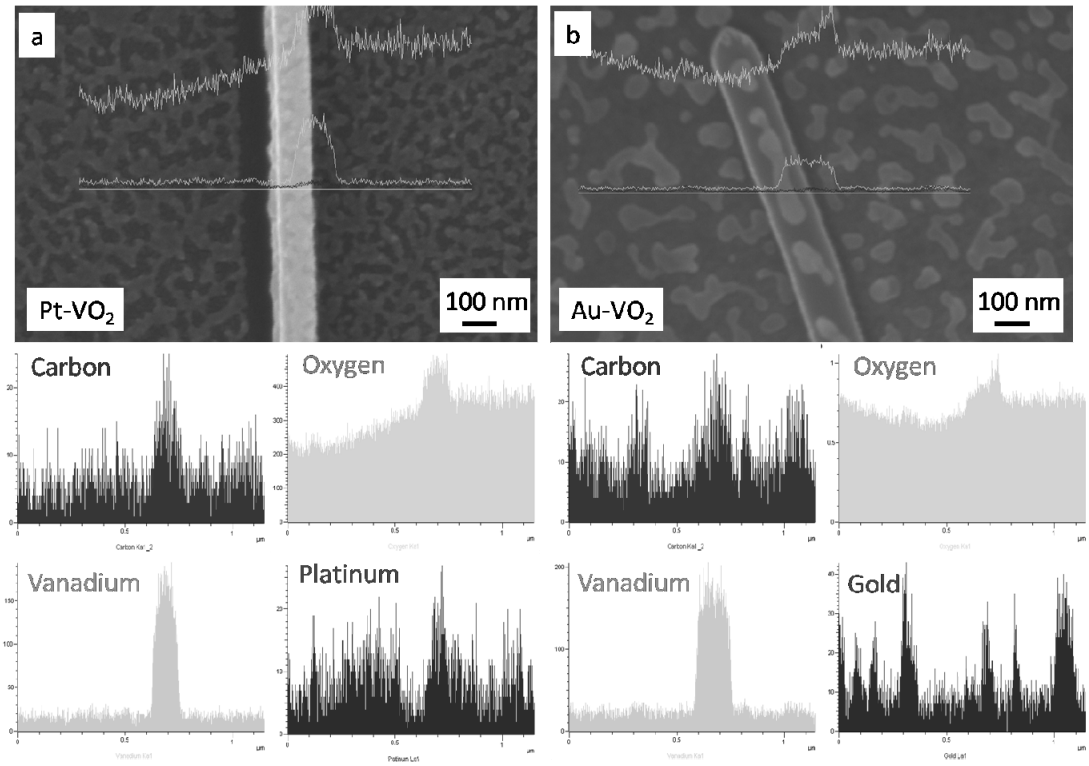

Figure 7. Line Scan EDX data for (a) Pt-VO_2 and (b) Au-VO_2 systems after methanol oxidation reaction. Elements given underneath each SEM picture are from that system following the path given on the pictures.

Table 1. SEM-EDX values

	Atomic weight percent (%)				
Position	**Platinum**	**Vanadium**	**Carbon**	**Aluminum**	**Oxygen**
Single nanowire (60 nm)	0.39	1.08	7.16	24.07	67.30
Single nanowire	0.40	0.74	6.53	24.82	67.51
Array of nanowires	0.48	1.93	9.47	36.40	51.72
Surface far from nanowires	0.43	-	-	39.73	59.84

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The presence of oxygen in the EDX scan, raised doubts about the existence of VO_2 after the gas catalysis reaction since VO_2 tends to oxidize in oxidative environments.[19] In several thorough scans, however, Raman spectroscopy confirmed the retention of VO_2 structures (Figure 8).

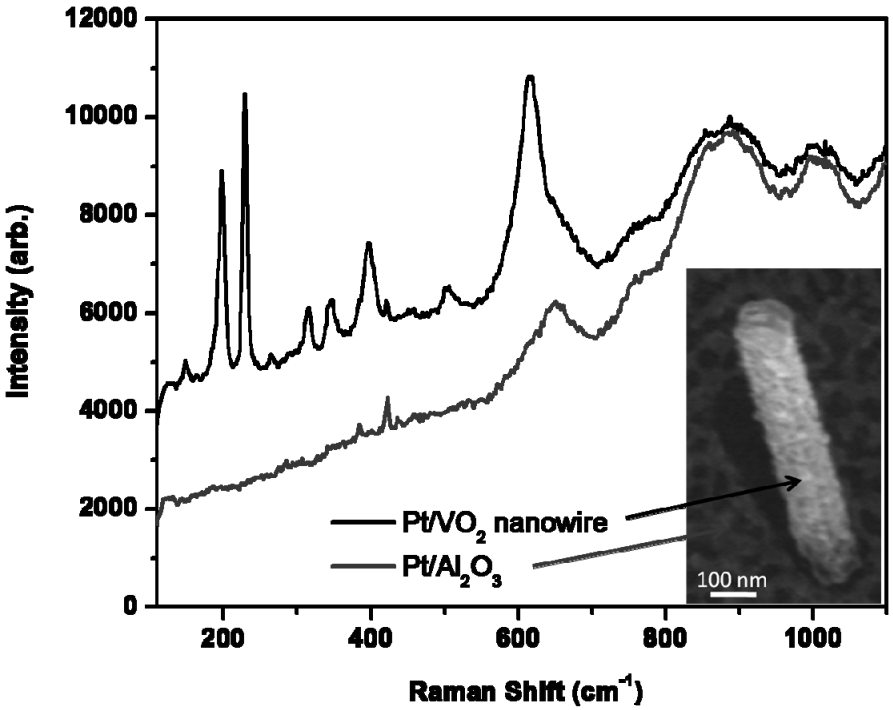

Figure 8. Raman data. VO_2 remains unchanged after reaction

Clearly, there is much that remains to be studied on this Pt-VO_2 nanoparticle-nanowire assembly. For example, one can get even greater crystal structure definition with high resolution TEM. An additional number of control reactions might also better resolve the nature of the changes observed. But it is evident that the promises of the approach used to study the model system are significant. This study showed us that coupling conventional spectroscopic techniques such as STXM and ETEM with in situ GISAXS monitoring on well defined nanostructured systems has the potential to answer outstanding questions of heterogeneous catalysis. These answers may, then, lead the way to the ultimate goal of catalysis by design.

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