

## **Electronic supplementary information**

### **Highly dispersed Cu(II), Co(II) and Ni(II) catalysts covalently immobilized on imine modified silica for cyclohexane oxidation with hydrogen peroxide**

R. Antony<sup>a</sup>, S. Theodore David Manickam<sup>a,\*</sup>, Pratap Kollu<sup>b</sup>, P.V. Chandrasekar<sup>c</sup>,

K. Karuppasamy<sup>a</sup>, S. Balakumar<sup>a</sup>

<sup>1</sup>Centre for Scientific and Applied Research, PSN College of Engineering and Technology,  
Tirunelveli-627 152, Tamil Nadu, India.

<sup>2</sup>Department of Metallurgical Engineering and Materials Science, Indian Institute of  
Technology, Mumbai-400076, India.

<sup>3</sup>College of Physics and Information Engineering, Institute of Optoelectronic Display, Fuzhou  
University, Fuzhou-350002, PR China.

#### **Table of contents**

1. EDS spectrum of silica gel (Fig. S1)
2. EDS spectrum of amino modified silica gel, SiO<sub>2</sub>-NH<sub>2</sub> (Fig. S2)
3. EDS spectrum of imine modified silica gel, L (Fig. S3)
4. EDS spectrum of Cu(II) catalyst (1) (Fig. S4)
5. EDS spectrum of Co(II) catalyst (2) (Fig. S5)
6. EDS spectrum of Ni(II) catalyst (3) (Fig. S6)
7. UV-Vis. spectrum of silica gel (Fig. S7)
8. UV-Vis. spectrum of amino modified silica gel, SiO<sub>2</sub>-NH<sub>2</sub> (Fig. S8)
9. SEM image of silica gel (Fig. S9)
10. Thermal decomposition steps of silica gel, L and catalysts *viz* 1, 2 and 3 (Table S1)

### EDS analysis of Silica gel

#### Net Counts

<i>O</i>	<i>Si</i>
19873	98836

#### Weight %

<i>O</i>	<i>Si</i>
41.90	58.10

#### Atom %

<i>O</i>	<i>Si</i>
55.87	44.13

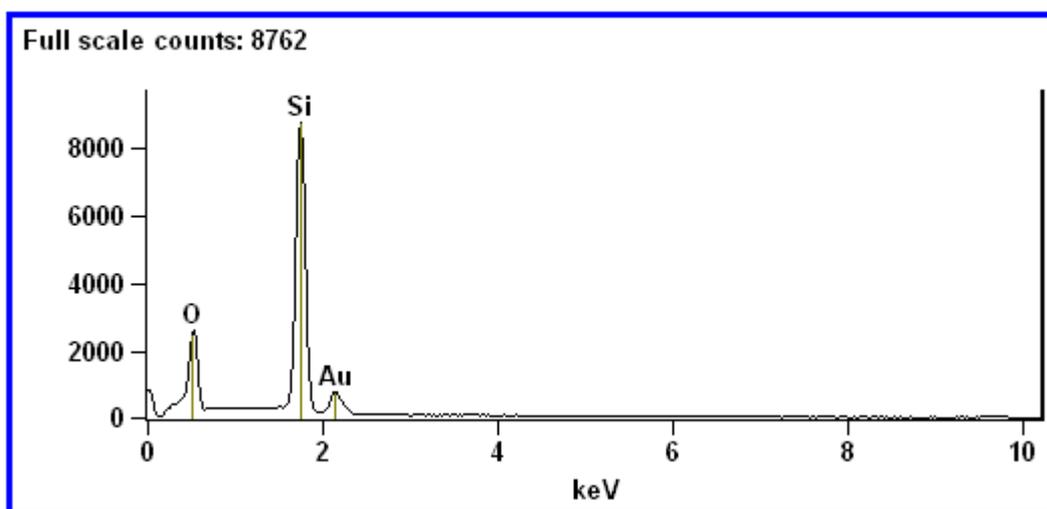
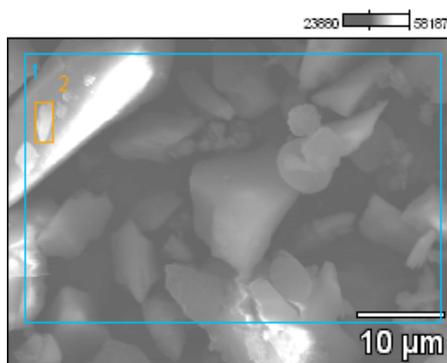


Fig. S1 EDS spectrum of silica gel

## EDS analysis of amino modified silica gel

### Net Counts

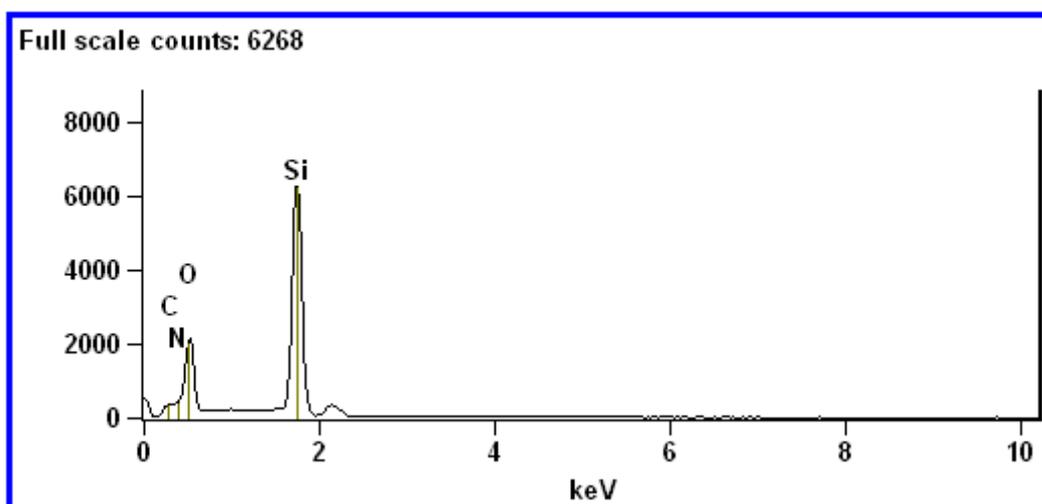
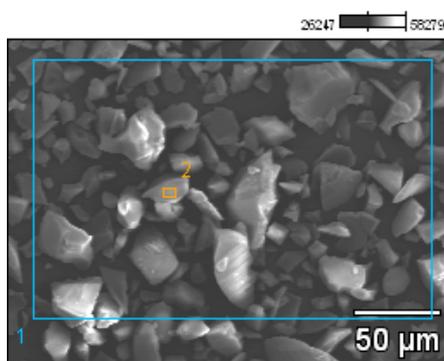
<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>
3040	3005	19453	72307

### Weight %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>
11.10	12.06	42.04	34.81

### Atom %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>
16.35	15.23	46.49	21.93



**Fig. S2** EDS spectrum of amino modified silica gel, SiO<sub>2</sub>-NH<sub>2</sub>

## EDS analysis of imine modified silica gel, L

### Net Counts

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>
3360	1770	13351	49000

### Weight %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>
15.92	10.74	40.93	32.41

### Atom %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>
22.83	13.21	44.07	19.88

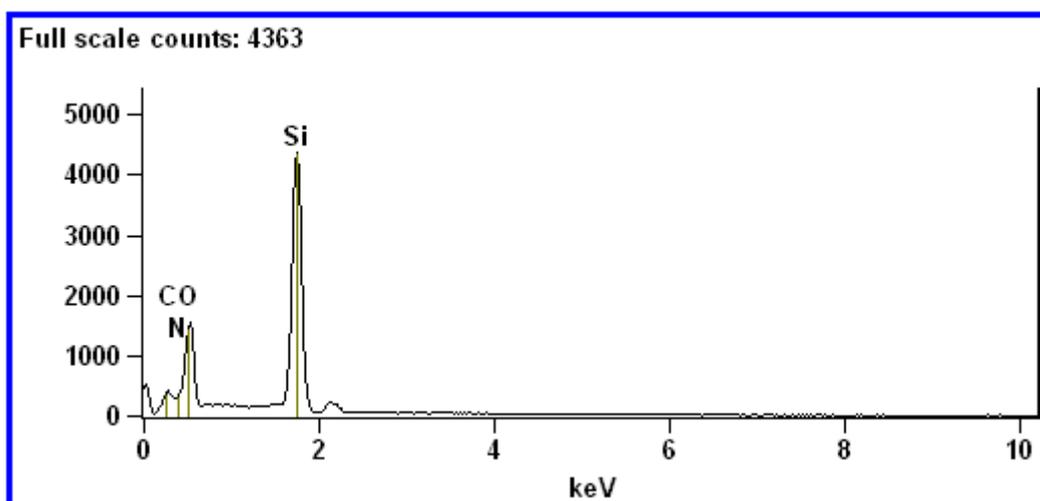
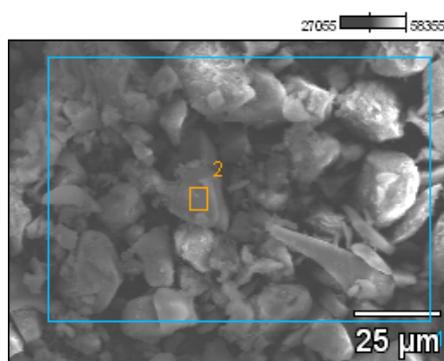


Fig. S3 EDS spectrum of imine modified silica gel, L

### EDS analysis of Cu(II) catalyst (catalyst 1)

#### Net Counts

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Cu</i>	<i>Cl</i>
3754	2082	14756	50505	292	271

#### Weight %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Cu</i>	<i>Cl</i>
15.60	11.11	39.51	29.63	2.21	1.94

#### Atom %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Cu</i>	<i>Cl</i>
22.60	13.81	43.75	18.68	0.60	0.55

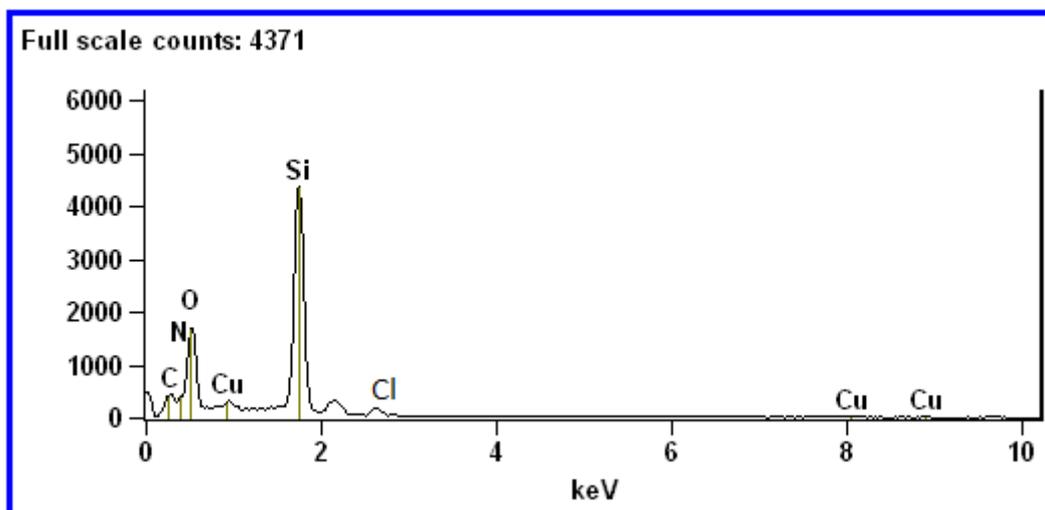
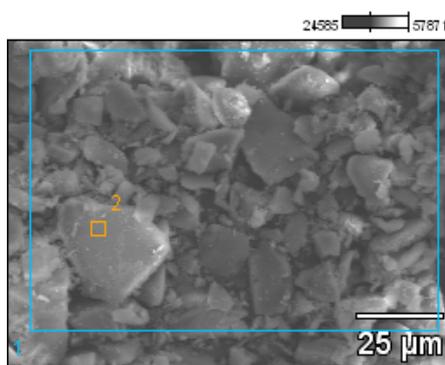


Fig. S4 EDS spectrum of Cu(II) catalyst (1)

### EDS analysis of Co(II) catalyst (catalyst 2)

#### Net Counts

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Co</i>	<i>Cl</i>
5818	3001	21999	69330	342	318

#### Weight %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Co</i>	<i>Cl</i>
16.30	11.19	41.80	28.68	1.06	0.97

#### Atom %

<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Co</i>	<i>Cl</i>
23.18	13.64	44.99	17.62	0.31	0.26

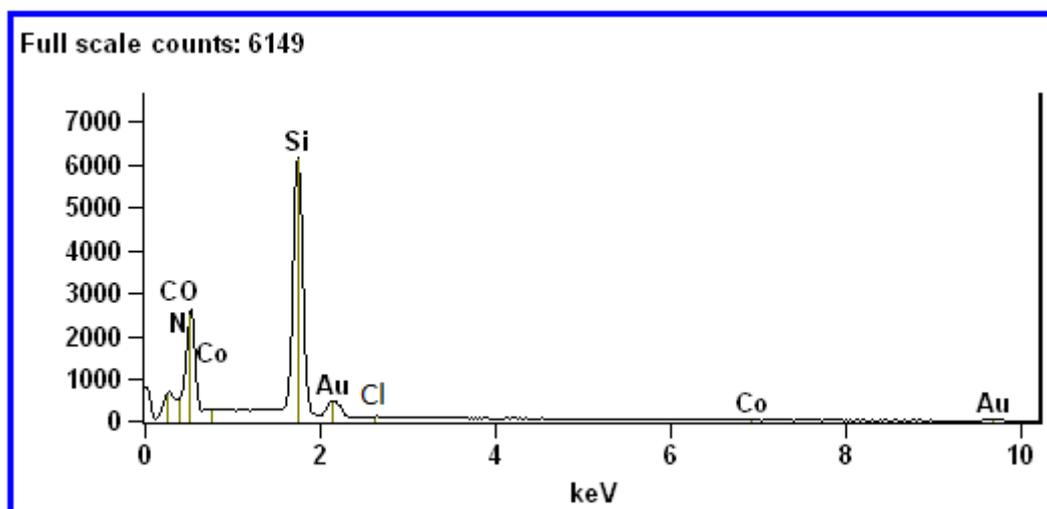
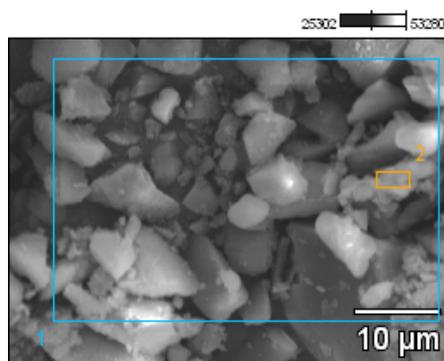


Fig. S5 EDS spectrum of Co(II) catalyst (2)

### EDS analysis of Ni catalyst (catalyst 3)

#### Net Counts

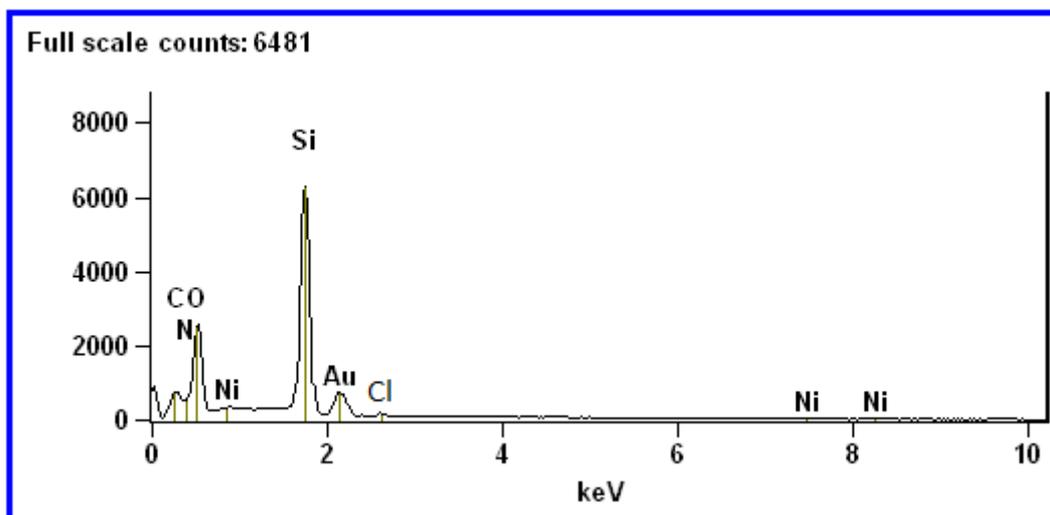
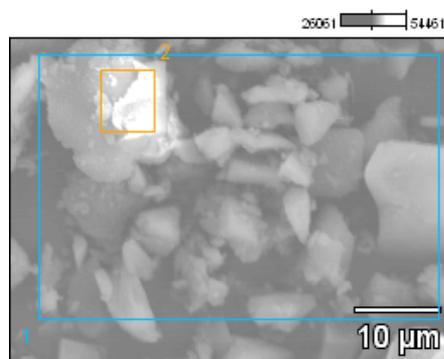
<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Ni</i>	<i>Cl</i>
6629	2813	21804	80450	230	208

#### Weight %

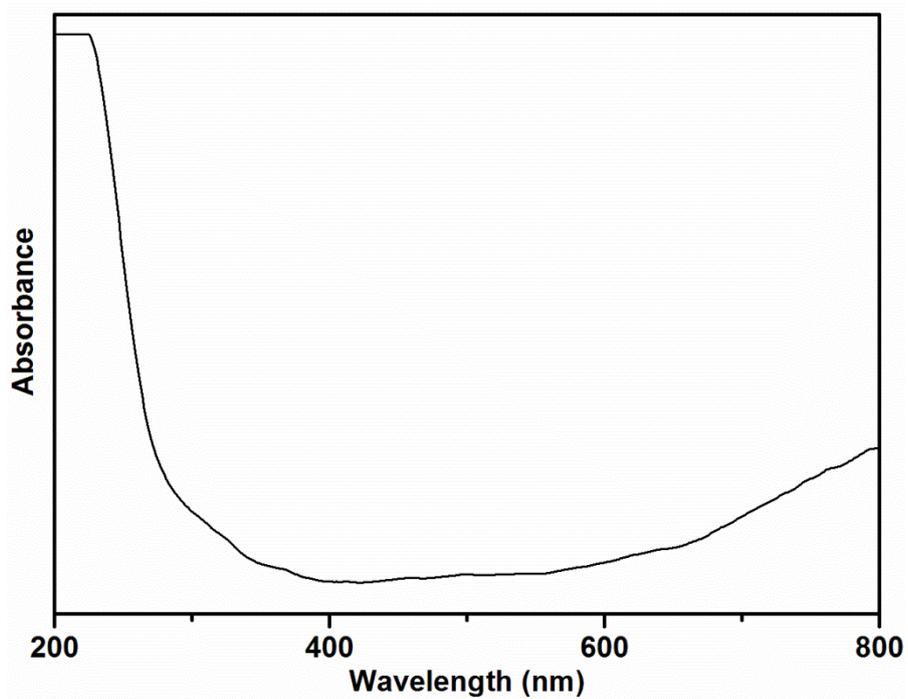
<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Ni</i>	<i>Cl</i>
17.92	10.40	39.47	30.64	0.81	0.76

#### Atom %

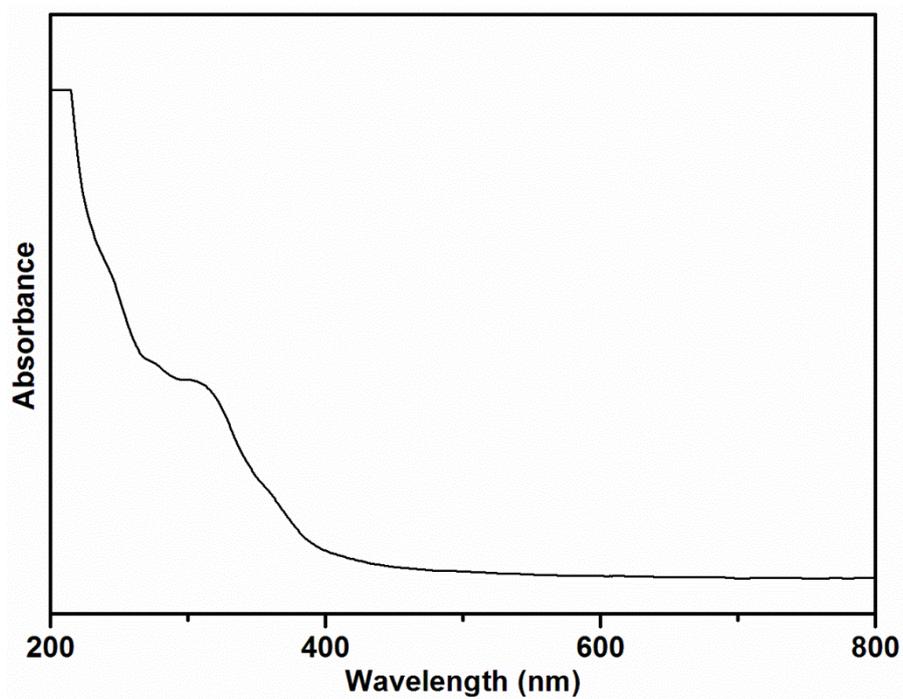
<i>C</i>	<i>N</i>	<i>O</i>	<i>Si</i>	<i>Ni</i>	<i>Cl</i>
25.53	12.70	42.54	18.79	0.24	0.20



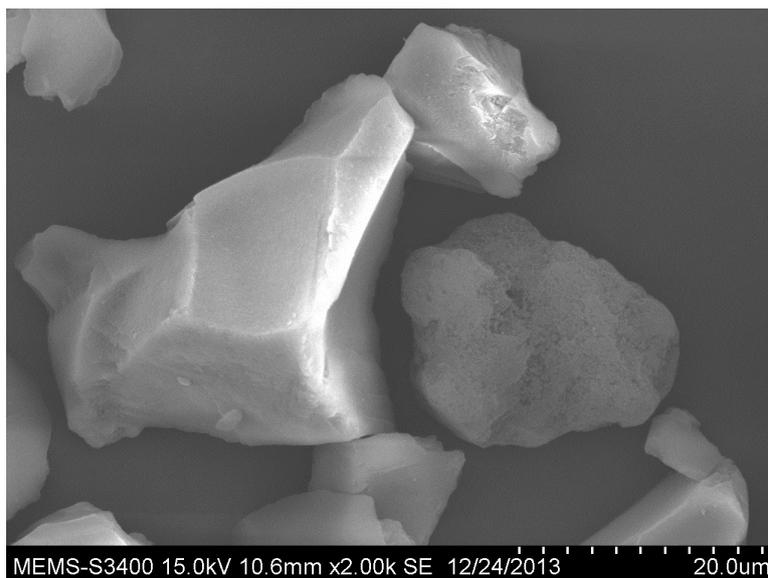
**Fig. S6** EDS spectrum of Ni(II) catalyst (3)



**Fig. S7** UV-Vis. spectrum of silica gel



**Fig. S8** UV-Vis. spectrum of amino modified silica gel, SiO<sub>2</sub>-NH<sub>2</sub>



**Fig. S9** SEM image of silica gel

**Table S1** Thermal decomposition steps of silica gel, L and catalysts *viz* 1, 2 and 3

Compound	1 <sup>st</sup> stage, °C (wt loss, %)	2 <sup>nd</sup> stage, °C (wt loss, %)	3 <sup>rd</sup> stage, °C (wt loss, %)	4 <sup>th</sup> stage, °C (wt gain, %)
L	0-110 (~3)	110-370 (~4)	370-800 (~10)	-
Catalyst 1	0-110 (~2)	110-360 (~3)	360-570 (~3)	570-800 (~8)
Catalyst 2	0-110 (~3)	110-340 (~4)	340-570 (~7)	570-800 (~4)
Catalyst 3	0-110 (~2)	110-370 (~4)	370-610 (~5)	610-800 (~3)

1<sup>st</sup> stage: desorption of physically adsorbed water

2<sup>nd</sup> stage: decay of organic moiety

3<sup>rd</sup> stage: dehydroxylation of surface silanol groups

4<sup>th</sup> stage: oxidation reactions